Development of Durable Textile-Conductive Polymer Composites.

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Abstract.

The research described in this thesis investigated a range of techniques for the *in situ* polymerisation of thiophene-based intrinsically conductive polymers (ICPs) on textile substrates. Following a review of the literature, three potentially useful techniques were identified; a simple aqueous technique; a vapour phase technique; and a two-stage impregnation technique. The literature also indicated that thiophene-based ICPs were likely to be more durable than those prepared from other precursors.

The aqueous technique proved unsuccessful, but both the vapour and two-stage impregnation techniques were used to prepare textile-ICP composites using 2,2'-bithiophene and 3,4-ethylenedioxythiophene (EDOT). Polymerisation was effected by chemical oxidation of the precursor, with iron (III) salts being the best oxidants. The main drawbacks of the vapour system were the long vapour exposure times (e.g. several days) and/or elevated temperatures required to polymerise these relatively unreactive precursors. Two-stage impregnation was somewhat messy and inefficient, so a novel refinement of the technique (referred to as 'single dip') was developed. With this system, the specimen was impregnated with both precursor and oxidant from a single solution, then removed from the solution and the solvent allowed to evaporate. It was only at this stage that polymerisation occurred, and when more reactive ICP precursors (such as pyrrole) were used, polymerisation tended to occur in solution, and was less effective.

The influence of various treatment parameters was established, while tests confirmed that the deposited ICP layer had no detrimental effect on the desirable fabric properties of flexibility and strength. Composites with surface resistance as low as 65 Ω/square were prepared with less than 6% ICP load on the textile (perchlorate-doped poly(EDOT)). The durability of poly(EDOT) composites was far better than polypyrrole under ageing in ambient conditions, accelerated ageing at elevated temperatures, and when given a treatment that simulated laundering. Finally, a scheme for continuously depositing ICPs onto textiles by this approach was designed, as a way of demonstrating the potential for scale-up of the system.

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Chapter 1 Introduction.

1.1 Electrically Conductive Textiles.

Electrically conductive textiles are of growing interest for many applications; from relatively mundane uses in static electricity dissipation and electromagnetic interference shielding, to sophisticated uses in sensing and 'wearable electronics'. They are of particular interest because they combine one of the great technological advancements in history with materials that humans interact with almost continuously in day-to-day existence. Textiles are an attractive platform to integrate advanced technologies with, especially when human interaction with the technology is encouraged. But the same properties that make textiles appealing for human interaction (lightness, breathability, extensibility and flexibility) are generally incompatible with the properties (rigidity and impermeability) of electronic materials like wires and films.

This comparison is something of a generalisation. Certainly textiles can be (and often are) made in a rigid form, while flexible electronics are starting to emerge. However, even in these cases, the levels of durability are very different. Textiles must survive not only their conditions of use (which can be severe, with abrasion, repeated flexing, exposure to ultraviolet radiation and so on), but also garment care procedures, such as washing, dry-cleaning and pressing. Overcoming the incompatibility between textile and electronic material properties is crucial to the successful development of useful electronic textile technologies.

One approach to preparing electronic textile systems is to incorporate the electronic functionality into the textile material itself, rather than as subsequent attachment to the textile. The level of integration can be at the fabric level (perhaps by applying a conductive coating or print to the fabric), the yarn level (by preparing a conductive yarn using metallic fibres, for example), or down to the fibre level (by depositing an electro-active material onto the fibre surface, or even creating the fibres directly from the electro-active material). One type of electro-active material is the 'intrinsically conductive polymer' (ICP). ICPs are conjugated structures (i.e. they have alternating single and double bonds along the macromolecular chain), and it is this structure than provides the underlying mechanism by which conduction can occur. In a manner similar to conventional semi-conductors such as silicon and germanium, impurities (dopants) are added to ICPs to modify conductivity. This is described in more detail in Chapter 2. In theory, ICPs can achieve metal-like conductivity levels, and are sometimes referred to as 'synthetic metals' or 'organic metals'.

There are more conventional approaches to making conductive textiles. Metal (and metal-coated polymer) fibres and yarns have existed for some time, and are very useful in simple applications. Metal fibres (stainless steel fibre is one widely available example) have very good conductivity but often relatively poor mechanical properties, being strong but inextensible. They are, essentially, very fine metal wires, so are malleable but also prone to metal fatigue. A compromise is metal-coated polymer fibres (silver-clad nylon is one example that is commercially available), which have lower conductivity but are more 'textile-compatible' in processing and use. Metal and metallised fibres have fixed and relatively stable electronic properties.

The conductivity of carbon can also be used in textile systems. Carbon fibres are widely used for their mechanical properties, but conductive versions are also available. They are generally stable materials, with conductivity usually lower than metal fibres. Carbon black powders can be combined with polymers to make conductive fibres for anti-static applications, but there is a limit to the loading (and therefore the conductivity) that can be achieved before the fibre properties begin to deteriorate. Electro-active systems based on carbon can be prepared by using carbon nano-particles, such as single or multi-wall nano-tubes but these are beyond the scope of this work.

An 'all-polymer' conductive textile system is appealing, and ICPs are the obvious way to achieve this. Textile-ICP composites should retain the best properties of both components. ICPs have a wide range of electronic functionalities (some of which are described in Chapter 2), but generally poor mechanical properties. The very good mechanical properties of the textile substrate help to overcome these deficiencies. ICPs are also relatively easily modified during synthesis, and these modifications give rise to materials that have different electro-active properties. This means that they can respond to different environmental stimuli in different ways. Sophisticated sensing applications can be based on this behaviour, and are discussed in more detail in Section 2.3.

While an electro-active system (i.e. with dynamic electrical properties) has many applications, it is also essential to be able to prepare stable and durable textile-ICP composites. An underlying stability means that the electro-active behaviour of such a system is more likely to be reproducible. Stability also allows the use of textile-ICP composites in applications where fixed conductivity is essential, such as signal transmission yarns (replacements for wires in wearable electronics) and textile heating elements. It also means that a mechanism to isolate sensitivity to only the targeted stimuli may be available. Durability is essential, so that a system created today will still have the same functionality a month or a year later. A chemical sensing garment (for example) that loses its functionality after washing would not be commercially viable. Therefore, techniques for preparing durable textile-ICP composites are required. This thesis reports on investigations into the use of a variety of techniques and materials to achieve this end.

1.2 Definitions and Conventions Used in this Work.

Many textile-related terms are used without explanation in this thesis. A brief textile glossary is provided in Appendix 1, with those terms defined.

It is a convention in this thesis that the term 'ICP precursor' is used most of the time as an alternative to 'monomer'. While most ICP precursors can be considered monomers, one that is used extensively in this work is 2,2'-bithiophene, which can be considered to be a dimer. Therefore, the convention used is to refer to all molecules that are polymerised into ICPs as 'precursors'.

The term 'textile-ICP composite' or 'textile-conductive polymer composite' is used to refer to a textile structure (yarn or fabric) that has had an ICP applied to it. Sometimes they are referred to as 'conductive polymer-coated fabrics/yarns'.

1.3 Thesis Overview.

A review of the literature relevant to the deposition of ICPs onto textile substrates is presented in Chapter 2. In Chapter 3, the aims of this research are described, and Chapter 4 details the basic experimental techniques used in this work, alongside information about the materials (substrates and chemicals) used.

Four different techniques for the deposition of ICPs onto textiles are investigated in Chapters 5, 6, 7 and 8. The first three are concerned with techniques from the literature, while the fourth describes an alternative technique developed in this research. The latter is investigated in the greatest depth, with a wide range of process parameters examined and the resulting textile-ICP composites extensively analysed.

Finally, the techniques are summarised and compared in Chapter 9, with conclusions and areas of potential future study discussed in Chapter 10. References are provided in the final section of this thesis. Appendices are provided on CD-ROM, and include a glossary of textile terms, background information on textile fibre polymers, images of the specimens prepared in this work, and various additional data and analyses not required in the principal text.

Chapter 2 Literature Review.

In this chapter, the research most relevant to the preparation of textile-conductive polymer composites is reviewed. The main focus is on techniques for *in situ* polymerisation of intrinsically conductive polymer (ICP) precursors onto fabrics, as this has been the favoured approach. The techniques fall into four general categories:

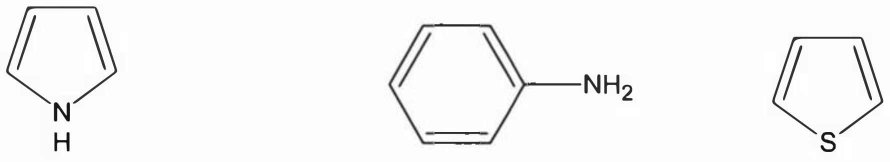
- Chemical polymerisation in a single step at low reagent concentration, in an aqueous system.
- Chemical polymerisation by successive impregnation of high concentration reagents in two steps.
- Chemical polymerisation by exposure to reagents in vapour form.
- Electrochemical polymerisation onto a non-conductive substrate.

As the focus of this research is on techniques for deposition of ICPs onto textile substrates, it is logical to review the features of each technique in turn, with reference to the literature. In addition, the less commonly employed use of soluble variants of ICPs is reviewed, as an alternative approach to *in situ* polymerisation. The preparation of fibres (that might be suitable for conversion into textile materials) from ICPs is reviewed, while a brief review of conductive polymer precursors and their polymerisation is provided as background (a wider evaluation of this outside the textile field is beyond the scope of this review). Applications that have been developed for textile-ICP composites are appraised.

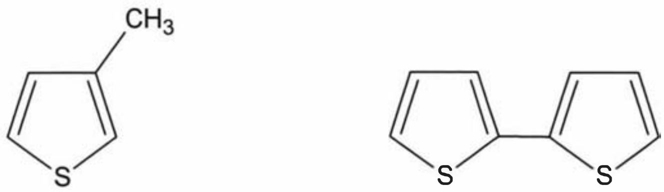
2.1 Intrinsically Conductive Polymers and their Polymerisation.

2.1.1 General Principles.

The first electrically conductive polymer synthesised was polyacetylene (reported in 1977 by Shirakawa *et al.* [1]), which is a silvery material, unstable in air. Since then, interest in conductive polymers has grown, as has the range of precursors from which they can be synthesised. ICP precursors based on heterocyclic molecules are of particular interest because of their relatively good environmental stability. Pyrrole and aniline (Figure 2.1; a and b) have been extensively researched, and polymers with good conductivity can be synthesised from them by chemical or electrochemical polymerisation. Thiophene is less reactive, but it, and derivatives of it (Figure 2.1; c, d, and e), have been polymerised electrochemically and chemically. Uniform films can be produced in electrochemical cells, while chemical polymerisation tends to produce polymer powders, as the polymer precipitates out of solution with increasing molecular weight.



a. Pyrrole (C_4H_5N) b. Aniline (C_6H_7N) c. Thiophene (C_4H_4S)



d. 3-Methylthiophene (C_5H_6S) e. 2,2'-Bithiophene ($C_8H_6S_2$)

Figure 2.1. Some intrinsically conductive polymer (ICP) precursors.

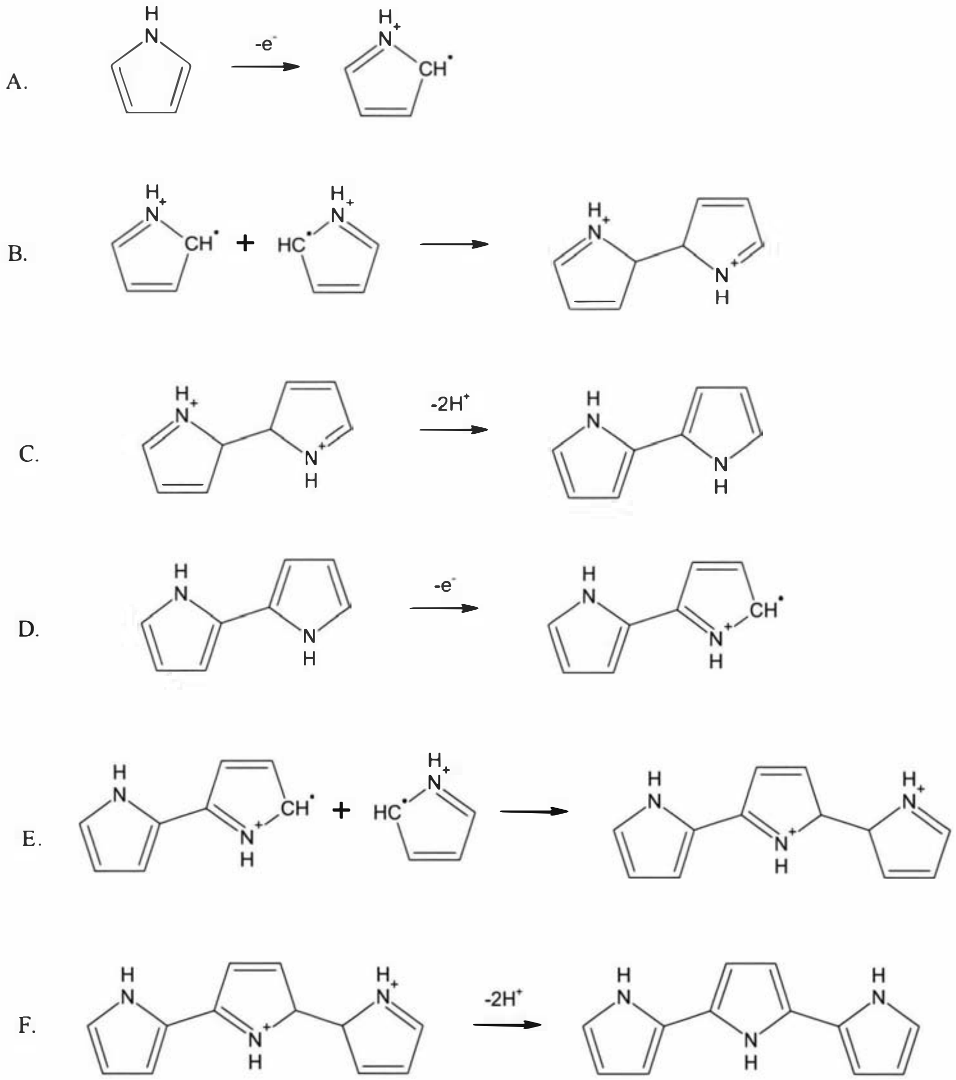


Figure 2.2. Polymerisation scheme for pyrrole → polypyrrole (from Kaynak *et al.* [2]).

The polymerisation of ICPs is an oxidation process, as presented for pyrrole in Figure 2.2 [2]. The pyrrole molecule is oxidised to yield a radical cation (A). Radical cations can combine to form di-cations (B), which are then de-protonated to yield a dimer (C). The process continues with oxidation of the dimer to form a radical cation of the dimer (D), which can react with other radical cations (monomers, dimers, and so on) to form trimers, tetramers and polymers (E and F). Polymer growth through the 2- and 5-positions (as shown in Figure 2.2) is an idealised case, and branching/non-linear chain formation occurs through the 3- and 4-positions. For a precursor such as 3-methylthiophene, the 3-position is blocked and the 4-position sterically hindered by the methyl group, meaning that, in principle, polymerisation at the 2- and 5-positions should be more likely to occur in 3-methylthiophene than in thiophene.

ICPs are conductive when fully oxidised and 'doped' with an anion, and only semi-conducting in their undoped (reduced) state. This is shown (for pyrrole) in Figure 2.3, where oxidation causes both polymerisation and the incorporation of a dopant anion (A^-). Doping (by oxidation) and de-doping (by reduction) are reversible processes.

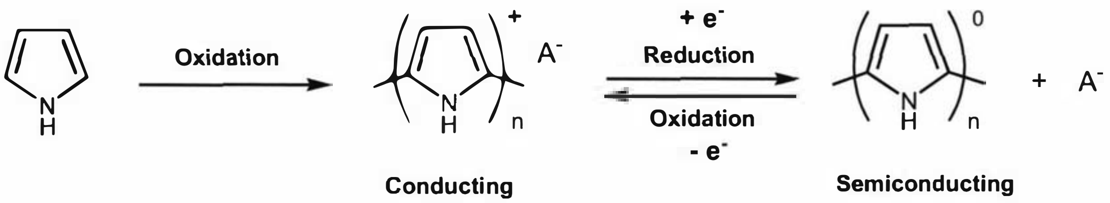


Figure 2.3. Scheme for chemical polymerisation and doping of polypyrrole.

An important early paper on the chemical polymerisation of polypyrrole was that by Armes in 1987 [3]. The work he described was an investigation into the optimum reaction conditions for polymerising pyrrole in an aqueous system with anhydrous iron (III) chloride as the oxidant. The polymer was prepared by simply mixing pyrrole with aqueous iron (III) chloride solutions in a range of concentrations, thereby providing a range of oxidant-to-precursor ratios. The polymerisation was allowed to occur in solution, and the conductivity (measured using a four-probe technique) of the resultant pelletised precipitate (polypyrrole) varied between 3 and 28 S/cm, but followed no discernible trend with respect to reagent ratio. Less polymer was formed at lower oxidant concentrations, but the polypyrrole formed was no less conductive. At higher concentrations (ratio ≥ 2.00), elemental analysis revealed an 'ash%' of 1-2% (i.e. a component other than C, N, H, Cl or O), which was assumed to be iron present in the polymer. This was concluded to be iron incorporated into an iron-based dopant anion, $FeCl_4^-$, which competes with Cl^- to be incorporated into the polymer. It is therefore likely that when oxidative synthesis of conductive polymers is carried out with an excess of Fe^{3+}, the polymer contains significant quantities of iron (III) based anions. The research also confirmed the importance of the solvent: when diethyl ether was used in place of water, polymerisation only occurred above a reagent ratio of 2.00, suggesting that the activity of the oxidant may be reduced in non-aqueous solvents. Polypyrrole powders were also observed to absorb carbon dioxide from the atmosphere, to a maximum of approximately 6% by mass in 10-15 minutes. All of the above observations were confirmed for iron (III) chloride hexahydrate, as well as for the anhydrous form.

While the environmental stability of polypyrrole is good by comparison with polyacetylene, it is nevertheless sensitive to moisture and tends to degrade (become less conductive) fairly rapidly. The conductivity degradation of polypyrrole was investigated by researchers at Macquarie University [4]. They described the conductivity mechanism in conductive polymers as a 'variable range hopping process', whereby electrons (although associated with specific monomer rings) are capable of transport to adjacent sites. A non-idealised, one-dimensional chain structure (i.e. the presence of short and variable length polymer chains, bond misfits and dopant-induced acceptor states) brings about a higher number of these available sites. Oxygen has an inhibiting role, apparently reducing the local potential so that electrons are confined to monomer units and are unable to contribute to conduction. This is thought to be a reason why the conductivity of polypyrrole degrades gradually in air; a process that can be accelerated by heating. The researchers' experimental work supported this hypothesis. Durability aspects of textile-ICP composite conductivity are reviewed in more detail elsewhere, but polythiophenes are reported to have greater stability than polypyrroles [5,6]; hence they are of particular interest in making durable textile-ICP composites.

One relatively new thiophene-derived precursor is poly(3,4-ethylenedioxythiophene), investigated by Pei *et al.* in 1994 [7]. The precursor, 3,4-ethylenedioxythiophene (EDOT) (shown in Figure 2.4), was synthesised by the researchers, and initially polymerised by chemical means using iron (III) chloride. A black insoluble material (poly(EDOT)) resulted. Further experimentation focused on electrochemical polymerisation, and it was observed that the process could be carried out at a lower potential than thiophene, implying that the polymerisation reaction is easier to instigate with EDOT. They also noted that the structure of EDOT blocks competing polymerisation through the 3- and 4-positions, which should result in the formation of unbranched polymer chains. Also of significance is the high environmental stability they observed for poly(EDOT) films when exposed to heat, having largely unchanged resistance even after exposure to 110°C for over 60 hours.

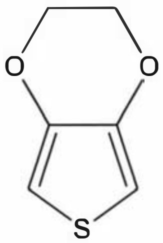


Figure 2.4. 3,4-ethylenedioxythiophene (EDOT), $C_6H_6O_2S$.

Conductive polymers are generally considered to have poor mechanical properties, tending to be weak and brittle. There is, therefore, much interest in incorporating them into other materials to overcome these limitations. Conductivity may be lower in a composite than in the pure polymer, but materials of this type are far more robust and suitable for technological applications. Incorporating ICPs into textiles is one field of investigation that has received recent attention.

Malinauskas provides a very useful review paper [8] of the various techniques that can be employed for the deposition of electrically conductive polymers onto various substrates (including textiles), as a means of overcoming their inherently poor mechanical properties. Four general techniques were identified:

- Application of a solution of the ICP, then removal of the solvent (use of this approach being limited by the lack of soluble ICPs). This approach is not a focus of this thesis, but is briefly discussed in Section 2.2.5.
- Electrochemical polymerisation of the ICP onto a substrate used as an electrode (limited by the need for a conductive substrate – most substrates of interest are insulating). Variations on this approach are discussed in Section 2.2.4.
- Chemical polymerisation in solution using strong oxidants, where the reaction conditions were adjusted to achieve spontaneous polymer deposition onto the surface of a substrate immersed in the solution, rather than precipitating as amorphous ICP. The well-known Milliken-developed technique [9] is the best example of this approach for textile substrates, and is discussed in detail in Section 2.2.1.
- Surface-located chemical polymerisation, where the substrate is impregnated with either precursor or oxidant, then exposed to the other component to initiate polymerisation. The two-stage impregnation method [10] and vapour deposition [11] are examples of this approach used on textiles, and are discussed in detail in Sections 2.2.2 and 2.2.3 respectively.

Malinauskas went on to review the important literature relating to each of these techniques from 1995 to 2001.

Of historical interest are two early attempts to produce electrically conductive textiles using so-called conductive polymers. One of these [12], described "textiles coated with a new flexible electrically conducing polymer", and an electrode system to carry and distribute current to the system that was resistant to flexing. The fabrics were available from Ioco Ltd, and seem to have had remarkable properties (for example, surface resistance on a polyester substrate of approximately 400 Ω/square), given that the report predates the development of intrinsically conductive polymer by several years. No details were provided, but an examination of the patent database of the time indicates that the technology involved a coating of electrically conductive silicone (ICI EP567) applied to Terylene® (polyester) fabric [13].

The second paper made less significant claims, but nevertheless illustrates that the need for conductive textiles was recognised quite some time ago, and that a variety of approaches have been employed to create them. The researchers were attempting to prepare anti-static nylon and polyester fabrics [14] with the goal of achieving surface resistance levels similar to those of natural fibre fabrics (wool and cotton). Synthetic fibres typically have resistance in the peta-ohm range (10^{15} Ω), while wool and cotton are in the tera-ohm range (10^{12} Ω). They achieved their aims by applying hydrophilic cross-linked polymers to the synthetic fibres by a variety of methods. These polymers increased the amount of water absorbed on the surface of the fibres, and thus reduced static build-up.

2.1.2 Deposition of ICPs onto Non-Textile Substrates.

There are several pieces of research of particular relevance to the *in situ* polymerisation of conductive polymers onto textiles. These relate to the deposition of polymers onto non-textile substrates (often glass) or electrochemically onto metal surfaces. A full examination of the electrochemical polymerisation of conductive polymers is outside the scope of this work, so only research papers with specific relevance have been reviewed.

A novel vapour deposition apparatus was used by Mohammadi *et al.* to create polypyrrole films on metal and metal-coated glass substrates [15], although it appears that any substrate material could have been used. It is likely (although not stated) that conductive substrates were used so that electrochemical manipulations of the films could be subsequently carried out. The apparatus consisted of a vacuum chamber with separate sub-chambers from which pyrrole vapour, hot iron (III) chloride vapour (250°C) and water vapour could be introduced in the vicinity of a cooled (0°C) substrate. The exact progression of polypyrrole formation was not clearly described, but presumably the reagents (or reaction intermediates) condensed onto the substrate and polypyrrole formed *in situ*. The researchers found that the substrate they used had no influence on film properties (although this was a very narrow range of quite similar substrate materials). They also found that the polymerisation would not occur unless some water vapour was present, suggesting that H_2O molecules were necessary to provide H^+ ions to initiate polymerisation. The films (which had conductivities from 10^{-2} to 1 S/cm), had elemental ratios of (N:C:Cl:O) 1:3.9:0.26:0.41. The ratio of N:C is consistent with that of pyrrole (1:4), and the Cl:N ratio indicates a doping ratio of one chloride ion for every four pyrrole units. Various analyses (XPS, FTIR) indicated strong similarity between polypyrrole films prepared by this technique and those prepared electrochemically.

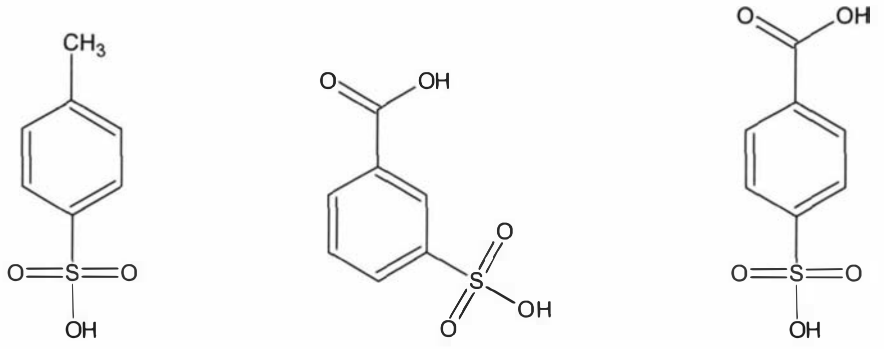
Plasma polymerisation of ICP precursors was an approach described by Cherian and Radhakrishnan [16]. They used the technique to deposit thin films onto glass slides, but it would perhaps be possible to use a similar approach to deposit ICPs onto textile substrates. A glass deposition chamber was loaded with glass slides and evacuated, then pyrrole vapour admitted. Aluminium electrodes wrapped around the chamber generated the RF plasma within it, and the polymer was deposited on the slides. The polypyrrole films so-formed were then doped by exposure to iodine vapour for 10-15 minutes. Conductivity measurements were not provided, but their other analyses indicated the formation of conductive polypyrrole films. The mechanism of deposition was not fully explained, but presumably substrates other than glass slides could be used.

An appealing approach to forming conductive polymer films on solid substrates was described by Wu and Chen [17]. A polyaniline film was grown as a "self-assembling monolayer" on silicon wafer and glass that had been treated with H_2SO_4 and H_2O_2. A pendant aniline with a silicon group (called a 'silane'), was attached to the substrate via the silicon. The substrate was then dipped in a mixture of aniline, an oxidising agent and HCl. This resulted in the formation of polyaniline film, which was said to have good adhesion. For comparative purposes, polyaniline films were also cast from polyaniline dissolved in 1-methyl-2-pyrrolidone. These had poor adhesion to the substrates, so the researchers concluded that their self-assembled monolayer polyaniline film was chemically bonded to the surface.

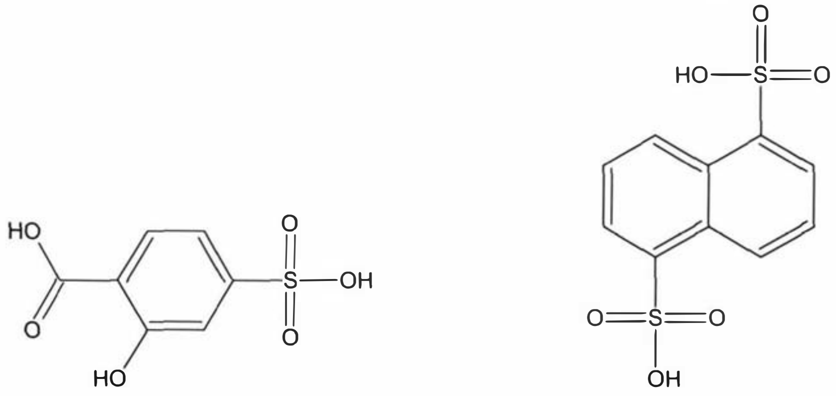
The stability of conductivity over time and with exposure to heat and moisture was studied by Österholm *et al.* [18]. They prepared films electrochemically from thiophene, with $LiBF_4$ as the electrolyte. The resultant polythiophene films (doped with BF_4^-) were reduced by electrochemical and chemical processes, and then re-doped by immersion in a $FeCl_3$/nitromethane solution. The resultant films were described as "$FeCl_4^-$-doped polythiophene". Exposure to ambient laboratory conditions resulted in film conductivity loss of only 30% over 15 months, although comparisons with other heterocyclic conductive polymers were not provided (only polyacetylene – known to have poor stability – was discussed). The BF_4^--doped polymer and another doped with ClO_4^- were also tested, and found to be inferior. Heating and cooling cycles in an argon atmosphere (to give heat effects only, not air exposure) showed good stability, with only slight loss in conductivity after 10 cycles between 20 and 140°C. Exposure to an unspecified high humidity O_2 environment for 24 hours resulted in a 20% loss in conductivity. The stability of conductivity described is excellent, and highlights both the potential advantages of thiophene-based ICPs, and the influence of dopants on durability.

The stability of conductivity was investigated using aromatic sulphonic acids as dopants in electrochemically prepared films [19]. The conductivity was measured by a four-point probe method, before and after accelerated ageing for eight hours at 150°C. One aliphatic sulphonate ($HOOC\text{-}CH_2\text{-}SO_3H$) was included, and this specimen was non-conductive after the ageing treatment. Aromatic dopants with only one sulphonate (A in Figure 2.5, for example) provided poor stability, unless they also possessed an acid group (B in Figure 2.5, for example). The position of sulphonate groups also had some influence, with B being more stable than C. The best stability was from D; the ratio between conductivity before and after ageing treatment was 0.95 (i.e. a reduction of only 5%). E is a common dopant used in the preparation of conductive polymers, and also performed well, with a ratio of 0.88 between conductivity tested before and after ageing. The authors suggested that the acid groups act as antioxidants, preventing oxidation of the polymer, while the sulphonate group plays "an important role in the electrostatic fixation of the additives to the polymer matrix". The mechanism of oxidation and protection was still under further study at the time of publication.

Kaynak reported further investigations into the ageing of polypyrrole films, including tensile behaviour and microwave shielding properties [20]. Two types of films were prepared: a highly-doped film, electro-polymerised with 0.05 mol/L *p*-toluenesulphonate and 0.2 mol/L pyrrole in the electrolyte; and a lightly-doped film with 0.005 mol/L *p*-toluenesulphonate and 0.2 mol/L pyrrole. Conductivities (measured by a four-point probe method) were approximately 50 and 0.02 S/cm respectively. A reduction in breaking strain (extension) was found with ageing, levelling off after approximately two months at room temperature. Breaking stress (strength) and Young's modulus both increased with ageing, again plateauing after two months. This 'brittlisation' was attributed to the gradual loss of solvent from the films. The plasticising effect of both water and acetonitrile on polypyrrole films was also noted. The conductivity of the highly-doped film decreased by 20%, while the lightly-doped film decreased by 80%. In the former case, analysis indicated that loss of conductivity was due simply to oxidative degradation of the polymer backbone, while for the latter it appeared that more than one mechanism (including oxidative degradation) was operating. The microwave shielding efficiency followed the same pattern (as would be expected), decreasing by a much larger degree for the lightly-doped film than the highly-doped film.



A. *p*-toluenesulphonic acid   B. *m*-sulphobenzoic acid.   C. *p*-sulphobenzoic acid



D. 5-sulphosalicylic acid   E. 1,5-naphthalenedisulphonic acid

Figure 2.5. Aromatic sulphonic acid dopants.

2.2 Techniques for Preparing Textile-ICP Composites.

2.2.1 *In Situ* Polymerisation in an Aqueous System.

A technique for the deposition of polypyrrole on textile substrates in an aqueous system (also suitable for polyaniline, although rarely used) was pioneered by researchers at Milliken Research Corporation, and was first described in US Patent 4,803,096 [9] (with a continuation in part being US Patent 4,975,317 [21]). The basic technique was also widely reported in the scientific literature [22,23], and later in a trade journal [24]. In principle it is a very straightforward approach: the reagents (ICP precursor, oxidant and additional dopant) and the textile to be polymer-coated are placed in a vessel and agitated for a period of several hours. The process is carried out in an aqueous system, and the reagent concentrations are relatively low. One typical example provided in US4,975,317 consists of a 1.5 L volume containing 50 g of fabric with 16.7 g iron (III) chloride (0.04 mol/L), 2 g pyrrole (0.02 mol/L) and 1.5 g 37% HCl, resulting in a fabric with electrical resistance of about 3 kΩ/square. The relatively low reagent concentrations are typical of adsorption reactions, and the set-up is reminiscent of conventional textile dyeing procedures (which are also adsorption reactions). Dyeing apparatus is actually used in some examples, illustrating the relatively easy commercial scale-up that is possible with the system. Boutrois *et al.* [25] later reported a full-scale industrial process for coating entire rolls of fabric with polypyrrole by the technique. A special fabric rolling technique was used, to ensure good circulation of the reaction liquor and provide separation of the fabric layers. The reaction was carried out at <10°C for six hours.

A number of researchers have investigated features of this deposition technique, and these are discussed in the remainder of this section. However, three findings made by the Milliken researchers [9,21,22,23], that were not the focus of subsequent research, are the following:

- If the reaction is carried out in solvents other than water, the polymerisation occurs almost entirely in the solvent, with little deposition on the surface of the substrate.
- Water and reagent purity has no discernible effect, with the result in distilled water indistinguishable from that in tap water, and no benefit observed when precursor is distilled before use.
- Other oxidants (such as ammonium peroxidisulphate) can also be used, but are not as effective as iron (III) chloride. In a later paper [26], Hans Kuhn (one of the original Milliken developers) noted that iron (III) perchlorate was superior (although no data is provided), but that safety and economic reasons preclude its use.

2.2.1.1 Influence of Substrate Properties.

Milliken researchers consistently reported that fibre type (for example, whether the fabric used was made from polyester or cotton) had little effect [9,23]. This is somewhat surprising, as in an adsorption reaction, it is logical that the chemical and physical properties onto which reagents are being adsorbed will be relevant (the somewhat analogous process of dyeing is highly fibre type-dependent). Other researchers have examined the influence of the substrate surface properties in more detail, for example Avlyanov *et al*., who established that the hydrophobicity of the substrate influenced the conductivity and durability of the textile-ICP composite produced [27]. For hydrophobic surfaces the conductivity was higher, while adhesion of the polymer was better on hydrophilic substrates.

In another study that focused more on the polymerisation reaction kinetics (discussed in more detail below), Ferrero *et al.* used a range of synthetic fibre types (polyester, nylon 6, polypropylene and acrylic) [28]. They found that generally the lowest resistance resulted with nylon 6, and highest with polypropylene. An HPLC analysis of monomer and dopant adsorption by the fabrics indicated that nylon had high adsorption of monomer (presumably due to the presence of amide groups to which the slightly polar pyrrole molecule may have an affinity) and moderate adsorption of dopant, while polypropylene had particularly low adsorption of the dopant. These results are presented in Table 2.1, alongside surface resistance data. The adsorption is presented in terms of the amount per unit area of fabric – this is because the resistance measurement is surface resistance, rather than resistance of the bulk material. Thus it is polymerisation on the fabric surface that is most relevant.

Table 2.1. Reagent adsorption and surface resistance for deposition of polypyrrole onto synthetic fibre fabrics (data from Ferrero *et al.* [28]).

Fibre type*	Pyrrole (monomer) adsorption (mmol/m^2)	Dopant (Na_2NDS) adsorption (mmol/m^2)	Surface resistance (kΩ/square)
Polyester (A)	0.393	0.132	1.3
Polyester (B)	0.590	0.098	4.3
Nylon 6	0.717	0.081	0.5
Polypropylene	0.432	0.014	30.9
Acrylic	0.616	0.043	3.6

* Note that two polyester fabrics were used (A and B). Type B was the most comparable in specification to the other fabric types. More information on the properties of different fibre types is provided in Appendix 2.

The influence of fibre surface properties has also been investigated in the context of fibre surface modification. This was carried out on wool fabrics subsequently coated with polypyrrole by the Milliken technique [9], in unpublished data from the Wool Research Organisation of New Zealand [29]. With a standard polymerisation system using iron (III) chloride and NDSA as oxidant and dopant respectively, polypyrrole was deposited onto wool fabrics that had been pre-treated by chlorination, or with dobanic/sulphuric acid. Generally the surface treatments reduced fabric surface resistance, probably because they made the fibre surface more hydrophilic (and therefore easier to 'wet-out' with the polymerisation solution, but also increasing its affinity for the pyrrole). The interaction between the wool fibre and the polymerisation environment was discussed by Kaynak *et al.* [30], with the polymer-dopant system thought to attach to molecular groups on the wool fibre by ionic and hydrogen bonds. For this reason, they concluded that wool is an ideal substrate to use for the preparation of textile-conductive polymer composites. This is consistent with the findings already discussed for synthetic fibres [28].

Also investigating the influence of fibre modification, other researchers found that grafting acrylic acid (AAc) or N,N'-dimethylacrylamide (DMAA) on the surface of low density polyethylene fibres before ICP coating was carried out, enhanced the growth of electroactive films (AAc only), and improved adhesion of the ICP [31]. In this case, the AAc or DMAA probably had the effect of improving the adsorption of the polyethylene fibres, which have low adsorption in their pristine state.

In a subsequent patented enhancement to their technique, Milliken researchers described a method for producing patterned conductive textiles that exploits the variability in polymer deposition that occurs on different substrate surfaces [32]. This was done by applying a finish to the substrate that inhibits polypyrrole deposition in the treated areas. The inhibitor was a fluorocarbon or silicon (with fluorocarbons favoured), and could be printed onto the textile, with the resultant pattern being a negative image of the deposited polymer. Clearly the lack of sensitivity to substrate type Milliken researchers initially reported applies only to a narrow range of substrates.

In summary, it seems likely that the adsorption of polymerisation reagents onto the surface of the fibre does influence both the formation of the ICP and the properties of the composite. The higher the affinity of the surface for the monomer in particular, the lower the surface resistance seems to be. Unfortunately almost no researchers report the quantity of ICP deposited (for example as the percentage mass increase of the specimen), so it is difficult to say if the influence of fibre type is due to the deposition of a more conductive ICP structure, or if it is simply an outcome of deposition of a greater quantity of ICP.

2.2.1.2 Reaction Parameters.

The dopant species incorporated into the polymer during polymer deposition has been the focus of a number of research papers. The Milliken researchers [9,22,23] concluded that dopants such as 1,5-naphthalenedisulfonic acid (NDSA) and *p*-toluenesulphonic acid (*p*-TSA) provided better conductivity than simple acids like HCl. In a transcript of his Olney Medal Address to the American Association of Textile Chemists and Colorists [26], Hans Kuhn, who had worked on this at Milliken, stated that the planar structure of dopants such as naphthalene- or anthraquinone-2-sulphonic acid allowed stacking in the polymer structure, facilitating inter-chain electron hopping. Avlyanov *et al.* [27] examined the effect of various dopant ions, and also concluded that planar dopant ions led to formation of a more planar polypyrrole conformation, giving higher conductivity. They favoured *p*TSA, NDSA and anthraquinone-2-sulphonic acid (AQSA). Clearly these type of dopants are the most suitable, a finding that is consistent with work already reviewed [19] that examined electrochemically prepared polypyrrole films.

Both Milliken [9,21,22,23] and other researchers [33] have determined that polymerisation reactions at low temperature produce textiles with lower resistance than those carried out at room temperature. This indicates that a slow reaction (resulting from low temperature and low reagent concentration) produces the most conductive textile-ICP composites. In perhaps the most comprehensive experimental evaluation of the technique carried out by researchers other than from Milliken [33], the duration and temperature of the reaction was examined, comparing a system using agitation to one without, at both room temperature and 4°C. Without agitation, electrical resistance reached a minimum after approximately six hours for both temperatures, and increased time had no further effect. With agitation, however, the higher temperature polymerisation needed to be stopped after four hours, as it had the effect of abrading away the polymer deposited. The same effect was not observed for the low temperature polymerisation. At higher temperatures the polymer coating was thicker (hence the greater susceptibility to surface abrasion), but no more conductive. The optimum concentrations for dopant (AQSA in this case), oxidant (iron (III) chloride) and monomer (pyrrole) were also determined, above and below which the electrical resistance increased. They were about 0.018, 0.10 and 0.04 mol/L respectively.

Hirase *et al.* [34] examined reaction parameters for deposition of polyaniline (also identified by Milliken as suitable for polymerisation by their technique) onto wool and other fibre types. In particular they compared the performance of three oxidants (potassium iodate, ammonium peroxidisulphate and potassium dichromate) and two polymerisation durations (four and eight hours). The fabric samples were placed into 0.5N HCl after treatment (which presumably resulted in them being chloride-doped). Most of the composite fabrics produced had too low a conductivity to be able to draw any clear conclusion about the effect of fibre type, but one result stood out: the only conductive composite that could be formed with potassium iodate was on wool (shown in Figure 2.6 for the full set of fabrics). FTIR showed the formation of cysteic acid (presumably from cystine in wool) when potassium iodate was used, but not with the other two oxidants. The researchers postulated that aniline interacted with this species, resulting in deeper penetration into the fibre and a heavier ICP loading. Microscopic examination of the fibre cross-section supported this finding, but no data regarding the mass increase after polymer deposition was provided.

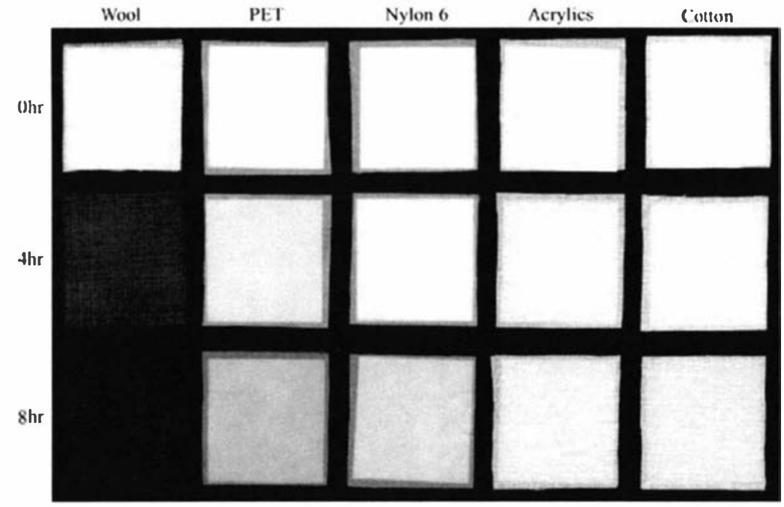


Figure 2.6. Textile-polyaniline composites prepared with KIO_3 as the oxidant (from Hirase *et al.* [34]). The dark samples were described as "deep green", indicating the conductive form of polyaniline.

The potential for the oxidant to alter the substrate properties, as well as bringing about polymerisation, is clear from this work. Aside from the wool/potassium iodate result, there was little difference in the efficacy of the other two oxidants.

The reaction kinetics of polymer deposition were investigated by Ferrero *et al.* [28], by examining the pyrrole polymerisation yield (based on HPLC determination of residual monomer). They found that the reaction (using APS as the oxidant) proceeded by pseudo first-order kinetics with or without the textile in the polymerisation solution; that is, the presence of the textile did not alter the reaction kinetics. Using a higher oxidant concentration gave a different kinetic curve and a higher yield, as shown in Figure 2.7. Depletion of the monomer stopped after 60 minutes, although other researchers have preferred polymerisation times of four hours [33] or more [34]. After 60 minutes the polymerisation reaction probably involves oligomers rather than monomer. They also observed that temperature had only slight effect on the reaction kinetics (increasing the rate, as would be expected), and did not change the final yield.

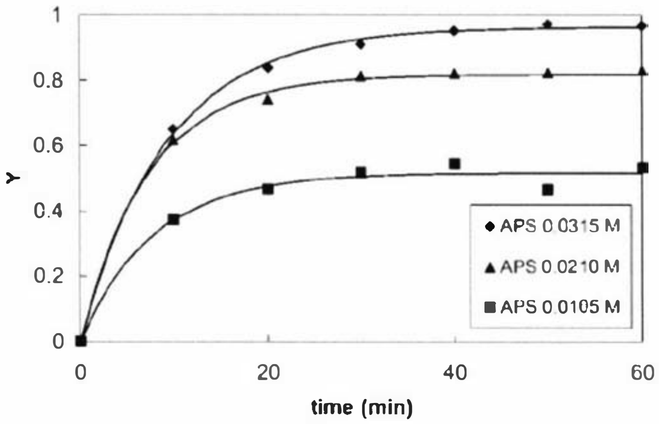


Figure 2.7. Pyrrole polymerisation yield (Y) as a function of time for different oxidant (APS) concentrations (from Ferrero *et al.* [28]).

It should be noted that Gregory *et al.* also examined the reaction kinetics with iron (III) chloride as the oxidant and observed a difference between the textile present/absent situations [22]. They observed that that when the textile was absent the reaction was slower. The disparity between these two conclusions may be due to the different oxidants used.

In summary, it is clear that aromatic disulphonic acids are the most effective dopants, and that low temperature polymerisation results in textile-ICP composites with the lowest resistance. Different oxidants certainly have an influence on the polymerisation process, with iron (III) chloride probably being best. Both pyrrole and aniline can be deposited onto textiles as conductive polymers, and although there is also a mention in the abstract of Kuhn's paper [26] of the possible use of thiophene in this polymerisation system, no reports of successful polymerisation of thiophene or thiophene-based ICP precursors by the Milliken aqueous polymerisation system have been found in the literature.

2.2.1.3 ICP Morphology and Molecular Structure.

The morphology of the ICP coating on the fibres has been examined by a number of researchers, typically by SEM. The images included in the first Milliken patent [9] showed a smooth uniform film, approximately 1 μm in thickness. Armes *et al.* [35] examined Milliken-supplied textile-ICP composites under higher SEM magnification than had been used previously, and discovered areas of globular deposits amongst the otherwise homogenous polypyrrole coating (see Figure 2.8, left). Energy-dispersive analytical x-ray techniques were used to establish that these were bulk polypyrrole deposits. Therefore, polymerisation by this method occurs predominantly, but not exclusively, on the fibre surfaces. Dall'Acqua *et al.*'s images of polypyrrole-coated viscose [36] confirmed this morphology (see Figure 2.8, right), as did numerous others [37-41].

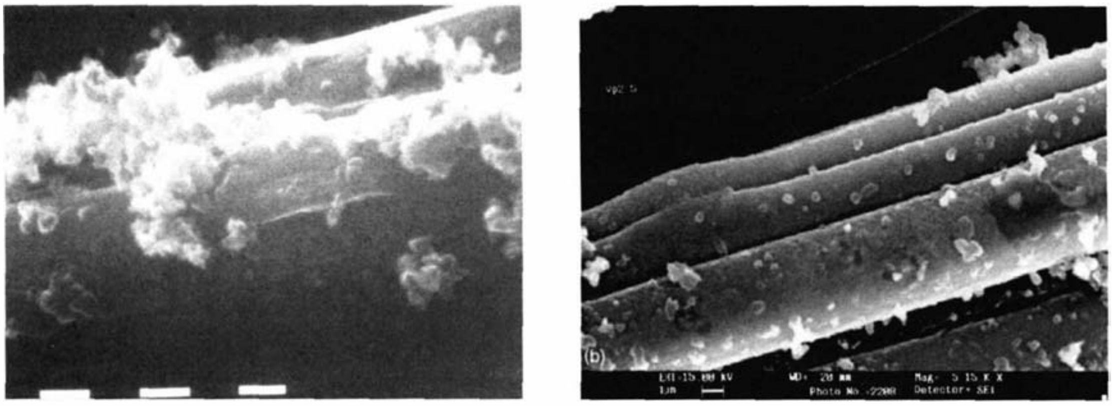


Figure 2.8. SEM images of polypyrrole-coated fibres.
Left: Polyester (not gold-sputtered, bars are 1 μm, from Armes *et al.* [35]).
Right: Viscose (from Dall'Acqua *et al.* [36]).

The molecular structure of the deposited polymer is probably quite difficult to analyse independently of the substrate (which is the majority component of the composite structure). Nevertheless, Kuhn [26] believed there was a higher degree of order in polymer layers deposited onto a substrate than in polymers precipitated as powders from solution, with about 70% of the desirable 2,5-coupling (in other words, relatively linear chain formation). Powders have about 45% 2,5-coupling. The presence of the substrate provides a degree of ordering of the polymer deposition.

2.2.1.4 Textile Properties and Ageing Behaviour.

How the textile properties are altered by the ICP deposition process is critical to how they might be used. Ideally the treatment process should leave most of the inherent features of the textile (such as flexibility and extensibility) unchanged. Relatively little investigation into this has been done. In one of the few, wool yarns (as opposed to fabrics) were used as a substrate for polypyrrole deposition by Kaynak *et al.* [30]. They do not actually discuss why this would be a useful approach, but there are potentially two reasons:

a. By treating yarn and then converting it into fabric it is possible to ensure that there is no inter-yarn polymer bridging, meaning that fabric flexibility and extensibility will be better. The yarns will not be 'glued together', and therefore can behave mechanically as they would in an untreated fabric.
b. It would be possible to combine treated and untreated yarns in patterned structures, to create electronically active and non-active regions in the same fabric. With the exception of the patterning technique reported above [32], this is the only way to achieve this effect.

Generally, treatment of the fabric would be preferable, as the conversion process from yarn to fabric (knitting or weaving, followed by fabric finishing) places tensile and abrasive strain on the yarn, which may cause damage to, or even removal of, the polymer coating. The research found that treated yarns showed increased tenacity, due to the reinforcing effect of the polypyrrole coating. The initial modulus was reduced; this was attributed to the reduction in surface friction between fibres, causing more inter-fibre slippage during extension. Dall'Acqua *et al.* [36] found that their polypyrrole-coated viscose fabrics had no significant change in tensile properties after deposition; although the chemically aggressive nature of the polymerisation conditions (oxidant, low pH) may have caused degradation of the cellulose that constitutes viscose, the reinforcing effect of the polypyrrole coating compensated.

Dall'Acqua *et al.* also examined the fastness to washing, light exposure and rubbing of their viscose fabrics [36]; one a conventional viscose rayon, the other a modern variant called lyocell. Both are regenerated cellulose fibres, typically manufactured from wood pulp. The results are presented in Table 2.2. The colour change was assessed against standard fabric samples. For washing and rubbing fastness, a value of 5 indicates no change in colour, while 1 is a drastic change. For light fastness, the top value of the scale is 7. Where two values are given (for example 4-5) the grade is between the two numbers.

Table 2.2. Fastness properties of polypyrrole-coated regenerated cellulose fabrics (from Dall'Acqua *et al.* [36]).

Fabric	Washing	Light	Rubbing
Viscose	4-5	6-7	3-4 (dry) / 1 (moist)
Lyocell	4-5	6-7	1-2 (dry) / 1 (moist)

These results indicate that, in most circumstances, the polymer coating had good adhesion to the fibres. The exception was rubbing, particularly with moisture present, which indicates that the ICP was not permanently bound to the fibres. Despite the generally good adhesion, the coating's electrical properties decreased by 70-80% (the property in question was not stated – it is assumed to be surface conductivity). In other words, although the coating remained intact, the conductivity of it was being degraded, probably by the mechanisms described below [42,43]. The application of a "siliconic oil" improved durability, with this specimen taking two months until a loss of 70-80% was reached, after which there was no further degradation.

Deterioration in electrical properties of a conductive textile material is an important aspect of its behaviour, and several researchers have examined this for textile-ICP composites prepared by the Milliken technique. Kuhn *et al.* [42] investigated it for Milliken fabrics that were commercially available at the time. They were found to have a conductivity loss that proceeded by two sequential steps: oxygen diffusion into the polymer, and its subsequent reaction with the polymer backbone. The authors suggest that the improved performance with aromatic sulphonic acid dopants (AQSA was the example given) was due in part to the coating morphology they induced, being smooth and (presumably) compact in structure, which limits oxygen diffusion. It seems likely that an additional direct benefit from using a large dopant anion (such as anthraquinone-2-sulphonate) would be a reduced tendency for it to migrate out of the polymer, although this was not highlighted in the paper.

In the previous year, Thiéblemont *et al.* had identified essentially the same mechanism for degradation of conductivity in aromatic sulphonate-doped polypyrrole-coated fabrics [43]. They investigated the ageing behaviour of polypyrrole-textile composites, using specimens prepared themselves as well as those obtained from Milliken. The specimens (which had been prepared with aromatic sulphonate dopants) were aged in ambient conditions at temperatures up to a maximum of 140°C, and their resistivity measured by a four-point technique. The work confirmed the superiority of 2-naphthalenesulphonate as a dopant species, and established a mechanism of degradation of conductivity in aromatic sulphonate-doped polypyrrole. The mechanism is based on a model of the diffusion of oxygen into the polymer.

Milliken researchers have more recently developed techniques for improving the stability of conductive textile-polypyrrole composites prepared by their one-step process [44,45]. This was done by adding 2,4-dihydroxybenzophenone (DHBP) to the polymerisation liquor in a ratio of between 1:1 and 1:4 (pyrrole-to-DHBP). The researchers did not offer an explanation of the mechanism whereby stability of conductivity was improved by this technique. In Kuhn's review paper [26], he speculated that it may have been because DHBP reduces the chlorine doping of the polymer, in favour of the aromatic sulphonic acid. Chlorine-doped ICPs are likely to be more vulnerable to de-doping, due to the relatively small size of the dopant anion.

Lian *et al*. made a study of the electrical properties of polypyrrole-coated fabrics prepared by the same method [46], with a particular focus on durability properties. Because the researchers had an interest in the potential of these composites as biomaterials, they carried out measurements of electrical properties after vacuum drying and gamma-radiation sterilisation. They found that vacuum drying slightly increased the volume and surface resistance of the composites, presumably because of the removal of some water from the conductive polymer. Generally the sterilisation process had no major deleterious effect on resistance. The researchers also noted that when the polypyrrole coating on the substrate exceeded approximately 1 μm, no further reduction in composite resistance was observed.

To summarise, textile-ICP composites prepared with polypyrrole by the Milliken technique retain many of the inherent textile properties of the substrate, with any degradation tending to be compensated for by the contribution of the polymer coating. Deterioration of electrical properties over time in ambient conditions is an ongoing concern.

2.2.2 *In Situ* Polymerisation by Two-Stage Impregnation.

In its simplest form, there are two fundamental components of any ICP polymerisation system: precursor and oxidant. Thus one approach to forming an ICP on the surface of a substrate is to impregnate it first with one of these two components, and then the other. The polymerisation techniques reviewed in this section all have this same basic feature: impregnation with each of the two components in sequence. This is in contrast with the one-step technique described in the previous section, where all reagents are introduced to the substrate at the same time.

One of the earliest attempts to create composites of ICPs and porous substrates was a two-stage impregnation carried out by Bjorklund and Lundström [10] using pyrrole with paper. The paper was dipped into a metal salt solution (oxidant), then placed into pure pyrrole, which polymerised immediately into black polypyrrole in and on the paper. They found that the oxidant and the solvent in which the oxidant was dissolved had a significant influence on polymer formation, and on the conductivity of that polymer. Best results were obtained using iron (III) chloride hexahydrate dissolved in 0.01 mol/L HCl, with decreasing resistivity following the increase in oxidant concentration up to a maximum of about 100 Ω·cm (see Section 4.3 regarding units of resistance/resistivity/conductivity), at oxidant concentrations above approximately 12 g/100 mL (0.44 mol/L). A significant feature of this technique (in almost all cases reviewed in this section) is that the reagent concentrations were much higher than those used in the one-step aqueous technique (Section 2.2.1).

Shortly after the publication of Bjorklund and Lundström's research, US Patent 4,617,228 described a very similar process [47], but with the impregnations carried out in the reverse order. The patented process involved impregnation with pyrrole (sometimes in combination with a substituted pyrrole such as 3-methylpyrrole) followed by impregnation with an oxidant associated with a dopant anion. Oxidants/dopants used included iron (III) and copper (II) salts, incorporating chloride, perchlorate and fluoroborate. Substrates used included foams and fibrous structures (that is, textiles). It was stated that the other properties of the substrate were largely unaffected by the treatment, and multiple applications were suggested as a means of increasing the conductivity of specimens. The patent made no reference to ICP precursors other than pyrrole and pyrrole variants, but Ruckenstein and Park [48-50] reported that 2,2'-bithiophene could also be polymerised *in situ* on porous substrates by a two-step impregnation method. The substrate was first impregnated with the precursor (in an acetonitrile solution), then partially dried before being impregnated with an oxidant solution. When they used pyrrole, the polymerisation reaction appeared to take place in the solution, but when bithiophene was used it did not begin until after removal from the solution, when solvent evaporation could occur. Morsli *et al.* [51] also studied poly(2,2'-bithiophene)-coated porous substrates (polystyrene in their case), but as their focus was on conduction mechanisms in ICPs they did not report anything that is of particular relevance to the research in this thesis.

Richardson *et al.* [52] demonstrated the versatility of the two-stage polymer impregnation technique for porous substrates, using it to deposit polypyrrole, polymethoxysulphonic acid and polyaniline onto specimens of wood (common pine and balsa). Iron (III) chloride, ammonium persulphate (APS) and hydrogen peroxide were used as oxidants, with additional potassium chloride added as a dopant for the latter two cases. Overall conductivity levels were not high, with a typical maximum value of 4.3 mS/cm for polypyrrole polymerised with iron (III) chloride. The same research group subsequently reported the deposition of polypyrrole by two-stage impregnation (using iron (III) chloride) onto cellulose fibres from *Pinus radiata*, and onto wool fibres [53]. Conductivity for cellulose varied widely between fibres, ranging from about 2 to 200 mS/cm. For wool it was also variable, and of the order of 0.1 mS/cm.

A number of researchers have used a high-reagent-concentration impregnation system for the preparation of textile-polyaniline composites. In some situations this has been as two separate impregnations; more commonly it has used successive additions of precursor and oxidant to a single vessel (or 'bath') in which the specimen is placed (this latter case is still closer in principle to the two-stage impregnation technique than to the one-step Milliken method). An early example of the technique used wool and glass-fibre fabrics [54] immersed in a solution of aniline and an acid (either an aromatic sulphonic acid or sulphuric acid), which was then chilled, and APS added as an oxidant. After two hours the specimens were removed and rinsed in a solution of the same acid used earlier. The composites prepared in this way had resistivity in the range 400-1000 Ω/cm; much lower than the composites prepared by applying a solution of polyaniline in N-methylpyrrolidone (NMP) to the fabrics and then driving off the NMP. The latter approach (that is, the use of solutions of polyaniline to coat textiles) is reviewed in more detail in Section 2.2.5.

Varesano *et al.* [55] also used a single bath with high reagent concentrations to deposit an ICP onto fibres; in this case polypyrrole onto wool. The exact technique was not described (reference is made to an Italian patent application that does not appear to have subsequently been published as a full patent), but of particular interest is that the coated fibres were subsequently spun into yarns, then knitted into fabric. The SEM images in Figure 2.9 show the coating morphology and the effect that subsequent processing had on the deposited polypyrrole.

The coating appears to be basically smooth with a large number granular deposits present, which were largely removed by the mechanical processes that the fibre was subjected to as it was processed into a fabric. This suggests that the granular deposits were not well bound to the fibres, so were probably polypyrrole that formed in the solution and then accumulated on the fibre surface. The frictional forces of fibres rubbing against each other and against surfaces of the processing machinery then dislodged the particles, with the result that the processed fibre surface was relatively clean. The coating is obviously quite thin, as the familiar overlapping scale structure of the wool fibre surface is not obscured by the coating.

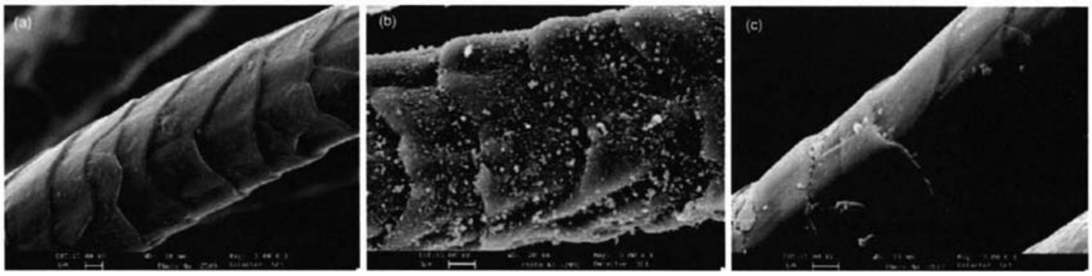


Figure 2.9. Polypyrrole-coated wool fibres: untreated (left), after coating (centre), after further processing (right) (from Varesano *et al.* [55]).

Another variant on the basic two-stage impregnation technique was employed by Lekpittaya *et al.* [56], and is described as 'admicellar polymerisation'. It is effectively a two-stage process in one vessel, but with a surfactant (dodecylbenzenesulphonic acid – DBSA) added alongside the monomer. This was vigorously agitated to form admicelles on the fibre surfaces, into which the monomer is adsorbed. This places the monomer preferentially on the fibre surface, and when oxidant addition occurs in the second step, polymerisation occurs on the fibre surface. Pyrrole, aniline and thiophene monomers were polymerised onto cotton and polyester fabrics by this technique. An important parameter in this work is the system's critical micelle concentration (CMC), which was 1.2 mmol/L. The relatively hydrophobic monomer 'partitioned' into the micelles, placing it on the fibre surface for subsequent polymerisation. Above the CMC it was suggested that "emulsion polymerisation may occur in the aqueous phase", that is, not restricted to the fibre surfaces. Common salt (NaCl) was used with the surfactant at the CMC to increase surfactant packing on the fibre surfaces, and thus increase the amount of monomer held in micelles.

The coating was reportedly very thin (although the actual amount deposited was not given), and surface resistivity values were high, as shown in Table 2.3. This may be inherent to the admicellar technique, but the oxidant used was APS, which would not have provided a dopant counter-ion (no subsequent doping was employed). However, both Huang and Liu [57], and Oh *et al.* [58] reported the use of DBSA as a dopant in their work, and it could have played the same role here (as well as acting as a surfactant). Also the monomer concentration was very low at only 5 to 15 mmol/L. At the higher monomer concentrations the resistivity did drop from the values given in Table 2.3; at 15 mmol/L it was lower by approximately one order of magnitude for aniline and thiophene on cotton, and four orders of magnitude on polyester. On polyester the drop in resistivity was larger: about five orders of magnitude for aniline and thiophene, and ten for pyrrole.

A final variant of the technique was described by Chan *et al.* [59]. They used an interfacial polymerisation technique based on that reported by Morita *et al.* [60] to prepare composites of polyaniline and poly(methyl methacrylate) on polystyrene. The technique involved introducing a layer of the substrate polymer and aniline dissolved in trichloromethane onto a layer of sodium persulphate in 5 M HCl. The latter was the oxidant/dopant solution. As the two layers are immiscible, they only interact at their interface, which is where oxidative polymerisation of the aniline occurred. After two hours at 27°C the composite material was removed, rinsed in 5 M HCl, and air-dried. The inside layer of the resultant material was emerald green, indicating the formation of conductive polyaniline. Elemental analyses of the bulk composite reflected the polymer substrate composition, suggesting that polyaniline was present as a very thin film. Other analyses indicated that the outer surface was pristine substrate polymer, while the inner surface was a uniform layer of HCl-doped polyaniline, ~50Å in thickness. The two layers appeared to be quite discrete, with conductivity of the outer surface < 1×10^{-12} S/cm (insulating), and the inner surface 20-30 S/cm. Exposure of the composite to ammonia solution converted the polyaniline surface into the non-conductive emeraldine base form (purple); a process which could be reversed by subsequent re-immersion in HCl. It may be possible to use an approach such as this to create one-sided conductive composites, using solid polymer substrates (such as textiles) into which ICP monomers had been absorbed.

Table 2.3. Surface resistivity for admicellar polymerised ICPs on cotton and polyester (from Lekpittaya *et al.* [56]).

Surfactant concentration (mmol/L)	Surface resistivity (Ω)					
	Pyrrole		Aniline		Thiophene	
	Cotton	Polyester	Cotton	Polyester	Cotton	Polyester
1.0 (<CMC)	2.3×10^{12}	2.9×10^{12}	3.4×10^{12}	6.9×10^{13}	3.4×10^{12}	7.4×10^{13}
1.2 (at CMC)	2.1×10^{12}	8.0×10^{11}	3.1×10^{12}	6.0×10^{13}	3.3. x 10^{12}	6.5×10^{13}
1.2 + 0.5 mol/L NaCl	1.4×10^{12}	3.0×10^{10}	2.4×10^{12}	5.9×10^{13}	2.6×10^{12}	8.5×10^{12}

2.2.2.1 Influence of Substrate Properties.

Substrate effects have been only occasionally examined in the literature. As already discussed, Lekpittaya *et al.* [56] demonstrated admicellar polymerisation by onto both cotton and polyester fabrics, with only slight differences between the two substrates (shown in Figure 2.10). With polypyrrole, polyester had lower resistivity, but for polyaniline and polythiophene, cotton had lower resistivity. Overall the resistivity values for polythiophene and polyaniline were quite high, so it could be that the substrate's electrical properties were tending to be reflected in the composite properties for these two ICPs (untreated polyester having a higher resistivity than cotton). Polypyrrole composites were much more conductive, so the resistivity of underlying substrate becomes much less relevant.

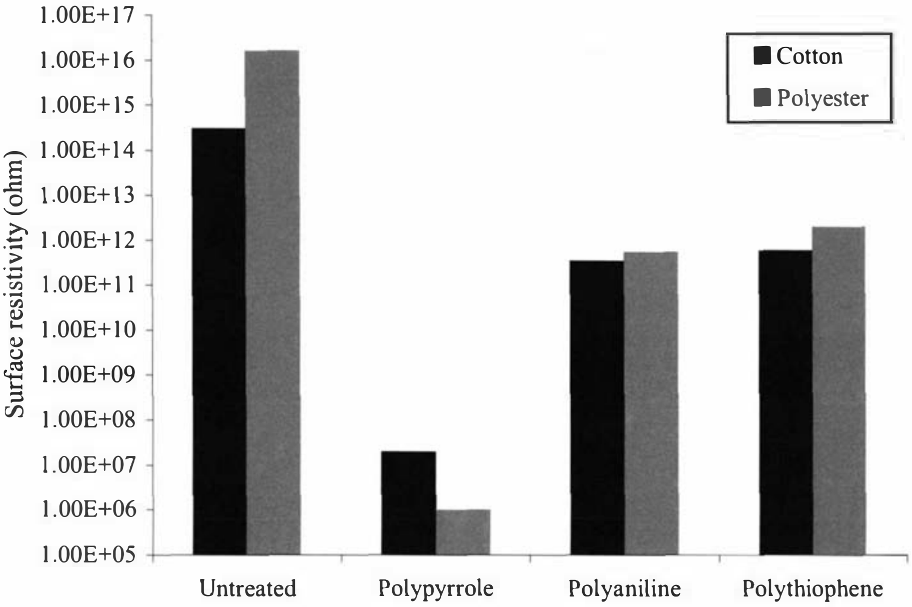


Figure 2.10. Effect of substrate fibre for admicellar polymerisation of ICPs onto cotton and polyester (from Lekpittaya *et al.* [56]).

A non-textile investigation into the preparation of polypyrrole-porous substrate composites was reported by Son *et al.* [61]. They prepared porous and non-porous particles from poly(methyl methacrylate), and used a simple two-step impregnation technique to deposit polypyrrole in/onto them. The particles were impregnated with iron (III) chloride from methanol or water; dried; impregnated with pyrrole from ethyl ether, chloroform or water for two hours; then dried again. No subsequent rinsing (before measuring conductivity) was mentioned in the paper, so it is possible that there was residual iron chloride (and water, because of iron chloride's hygroscopicity) present in the composite. The particles were pressed into pellets, before conductivity was measured by a four-probe method. They found that porous particles were far more conductive (13.1×10^{-3} S/cm compared with 0.37×10^{-3} S/cm for non-porous), presumably because of a higher loading of polypyrrole, although this was not stated. The specific surface area (SSA, in m^2/g) of the particles was determined, and it was found that particles with higher SSA created composites with higher conductivities. In a textile context, a higher SSA would result from using finer fibres, or fibres with an irregular cross-sectional shape.

Substrate properties were investigated in the context of fibre surface modification by Oh *et al.* [58,62]. They carried out plasma pre-treatments on nylon fabrics, and were able to prepare substrates with microscopically smoother surfaces than untreated substrates, both of which were then used for polyaniline deposition. Fabric specimens were plasma treated in a vacuum with oxygen, ammonia and argon gases for 10 minutes, with radio frequency power of 60 W. The different gases created different surfaces on the molecular level (assessed by XPS), and this was reflected in different conductivity values for the resulting polymer-coated specimens [62]. Oxygen provided the highest conductivity, with argon and ammonia resulting in a lower conductivity than the control (no plasma treatment). It was posited that acidic functional groups produced by oxygen plasma treatment (such as C-OH, C=O and C-O) enhanced the degree of polymerisation of polyaniline on the fibre surface. Certainly a better adhesion of the polymer to the fibre surface was apparent, as demonstrated by the superior durability of conductivity after several washing and abrasion cycles. This result, along with the findings of other researchers [29,31,63], shows that modification of the fibre surface before polymer deposition is a valuable technique.

2.2.2.2 Reaction Parameters.

Numerous researchers have examined the range of reaction parameters – such as reagents and their concentrations, solvents, and treatment times – that can be varied for ICP deposition by two-stage impregnation.

Monomer Concentration.

Monomer concentration was evaluated by Son *et al.* in their work on porous substrate particles [61]. They found that the conductivity increased with increasing concentration of pyrrole from 2 g/10 mL to 8 g/10 mL, but levelled out above this (shown in Figure 2.11, left). Essentially the same relationship was found by Lekpittaya *et al.* [56] (shown for polypyrrole on two fabric substrates in Figure 2.11, right). In both cases there was an initial rapid increase in conductivity (or decrease in resistivity), then a levelling out.

French researchers found a slightly different result in their work with the deposition of polyaniline onto glass-fibre fabrics [64]. The polymer was deposited by a simple two-stage impregnation technique: the fabric specimen was immersed in aqueous aniline hydrochloride, dried, then immersed in potassium dichromate in 2M HCl as an oxidant. Polymerisations were carried out at a range of oxidant concentrations, and they found that the conductivity of the composite did not always increase with monomer concentration (although indications were that the amount of polymer did increase). There was an optimum level at which conductivity was maximised, and the correlation between amount of deposited ICP and conductivity was not strong. Differences in the deposition techniques could explain why these results are not in complete agreement with those of other researchers [56,61], but one thing it does make clear is that conductivity is not only influenced by the amount of ICP deposited, but also by the 'quality' of it.

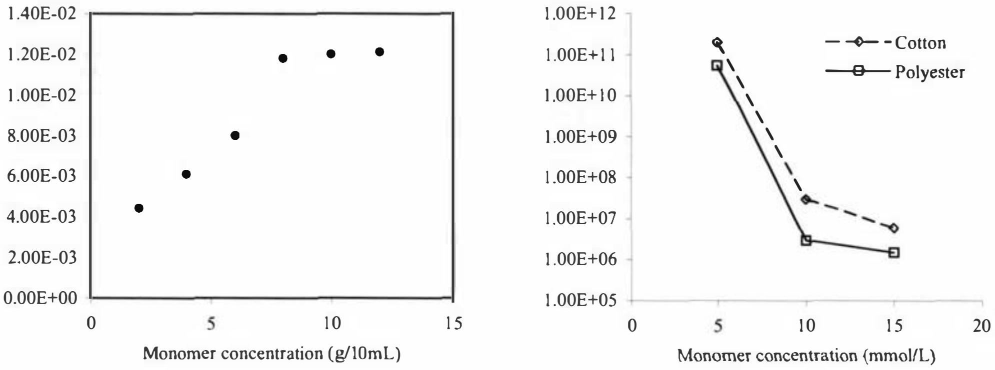


Figure 2.11. Effect of monomer concentration on electrical properties.
Left: Conductivity for polypyrrole on porous particles (from Son *et al.* [61]).
Right: Surface resistivity for polypyrrole on cotton and polyester by admicellar polymerisation (from Lekpittaya *et al.* [56]).

Oxidant Concentration.

Anbarasan *et al.* [65] found that higher concentrations of oxidant led to more efficient conversion of the monomer to fibre surface-located polymer. They believed that conductivity is closely correlated to amount of ICP deposited, so higher oxidant concentration results in a more conductive composite.

Solvents.

The solvents used are obviously important in the way they interact not only with reagents, but also with the surface substrate. A variety have been used in the literature, but controlled comparisons of different solvents are rare. Son *et al.* [61] found that the solvent used for monomer impregnation had some influence on composite conductance, with diethyl ether being superior to either chloroform or water. The concluded that this was because pyrrole is well dispersed in this solvent (although the 'wettability' of the substrate by each solvent will also be significant). Typically, oxidant solvents have been either water or methanol; presumably these relatively polar solvents are used to ensure a good dispersion of the oxidant (most commonly iron (III) chloride) at the high concentrations used. Harlin *et al.* used an aqueous oxidant solution of iron (III) chloride or APS/*p*-TSA in their work [66], but a very different monomer solvent: supercritical CO_2. They used this patented technique [67] to deposit polypyrrole and polyaniline onto polyester and nylon fibre. Industrially, supercritical CO_2 is of interest because it provides an alternative to organic solvents, thus reducing emissions of volatile organic compounds.

Dopant.

The choice of dopant has been of interest to a number of researchers. Thiéblemont *et al.* [68] found that conductivities were higher when aromatic sulphonates were used (*p*-TSA and 2-naphthalenesulphonate), compared to chloride alone (from the oxidant: iron (III) chloride). This is a result consistent with findings for the Milliken technique. The secondary dopant was impregnated onto the fabric at the same time as the monomer, and their textile-polypyrrole composites had remarkably low resistance (from 40 Ω/square for chloride alone to 10 Ω/square when 2-naphthalenesulphonate was also used). It must be noted, however, that multiple coatings were used to achieve these results, and the total mass of polymer added was not reported. Excessive mass add-on of polymer would render the fabric unusable in many applications because of the detrimental effect on fabric properties such as flexibility and elasticity.

Jin and Gong [69] found a different dopant effect. They used a process they describe as 'diffusion-deposition'; prior to impregnation with precursor (aniline) and then oxidant (APS), the substrate (polyester fibre or nylon fabric) was immersed in neat aniline for 16 hours, then rinsed. The composites were prepared in the presence of HCl (to provide a counter-ion for doping), and polymerisation was carried out in an aqueous system at 0-5°C for two hours. They found that using organic sulphonic acids such as *p*-TSA gave a reduced conductivity by comparison with HCl (see Table 2.4). They concluded that the larger counter-ions contributed by these acids actually hindered inter-chain transfer of electrons. This seems plausible, but other researchers have consistently found better results with large aromatic sulphonic acids [9,27,68], and attributed this to a more planar, compact (and therefore conductive) molecular structure.

This disagreement in dopant effect may be attributable to the fact that the other researchers worked with polypyrrole (whereas Jin and Gong [69] used polyaniline), but at least one other research group used polyaniline, and concluded that *p*-TSA was superior to HCl. This was the work of Anbarasan *et al.* [65], who reported a series of investigations into what they call the 'graft copolymerisation' of polyaniline onto nylon 6.6. This was carried out by a one-bath technique. The textile specimen placed in an aqueous solution of either HCl or *p*-TSA, then aniline was added, followed by the oxidant (APS). After 30 minutes at 45°C (during which time polymerisation occurs on and around the fibre), the specimen was rinsed in an HCl or *p*-TSA solution, then treated with aqueous ammonia for several hours. It was then dried and weighed. It was found that fibres prepared in *p*-TSA had more efficient grafting of polymer (that is, more polyaniline on the fibre, less in solution) than those prepared in HCl. The *p*-TSA specimens were also more conductive, with a resistance of 14-20 kΩ/cm compared with 8-10 MΩ/cm for HCl.

Table 2.4. Conductivity of textile-polyaniline composites prepared with different dopants (from Jin and Gong [69]).

Dopant (acid)	Conductivity (S/cm)	
	Polyester-polyaniline	Nylon-polyaniline
HCl	4.2×10^{-1}	4.6×10^{-1}
p-TSA	2.6×10^{-2}	4.2×10^{-2}
DBSA	3.2×10^{-3}	5.6×10^{-3}
SSA (sulphosalicylic acid)	7.6×10^{-3}	8.2×10^{-3}

Impregnation Time.

The duration of the various steps in the process might also have an effect on the polymer deposition and composite properties. Richardson *et al.* [52] found (with their two-stage polypyrrole deposition onto wood specimens) that the conductivity increased with longer impregnations; but at times beyond one minute they attributed this to residual oxidant (iron (III) chloride) trapped in the substrate. Overall conductivity levels were not high, with a typical maximum value of 4.3 mS/cm.

Lin *et al.* [70] also looked at immersion time, but for monomer impregnation. They prepared polyester-polypyrrole composite fabrics, and found no clear relationship between impregnation time and conductivity of the composite. (This was probably because the monomer was in an aqueous solution, and polyester fabric absorbs almost no water into its structure. Hence longer immersion times did not have the effect of increasing the monomer diffusion into the fibres, as it might with a more absorbent substrate such as cotton). They also experimented with the order of impregnations – monomer then oxidant or vice versa, and also found that it made no difference to the conductivity of the resultant composite fabrics.

2.2.2.3 ICP Morphology, Composition and Structure.

Park and Ruckenstein [50] examined the morphology of the ICP coating on cotton and polypropylene fibres for polypyrrole and polythiophene. SEM images of the specimens showed similar morphology for both ICPs on both fibre types: quite large quantities of loose polymer lodged in between fibres, as well as irregular growths on the fibre surface rather than smooth coatings. (Unfortunately the images are of too poor a quality to be reproduced here). Polymer loading data for the fibrous substrates was not provided, but for a polystyrene specimen prepared similarly to the textiles it was high: approximately a 1:1 mass ratio (ICP-to-substrate). This very high loading could be the reason that the fibre surfaces were much more irregularly coated than those observed by Varesano *et al.* [55].

More recently Johnston *et al.* [53] also used SEM to examine the coating morphology of polypyrrole deposited by two-stage impregnation on cellulose and wool fibres. They found (on both substrates) that the coating appeared to be smooth at low magnifications, but higher magnification revealed that it was made up of 'fused spheres', approximately 200 nm in diameter. This can be seen in Figure 2.12, particularly for the cellulose fibre. Beneventi *et al.* [71] also found that the polypyrrole coating 'film' on cellulose fibres was actually made up of fused spherical particles, but of larger diameter (~640 nm). This difference in size may be attributable to differences in the application method (for example, Beneventi *et al.* used oxidant impregnation followed by monomer, while Johnston *et al.* impregnated with monomer, then oxidant). At lower magnifications, the morphology of the polypyrrole-coated wool fibre was similar to that observed by Varesano *et al.* [55] (shown in Figure 2.9). The formation of 'fused spheres' of ICP suggests that polymer formation tends to initially occur at nucleation sites on the fibre, from which deposition grows three-dimensionally until the spheres become joined together in a continuous coating.

Thiéblemont *et al.* [68] investigated the composition of polypyrrole-textile composites and chemically prepared polypyrrole powders. The latter were prepared by mixing precursor, oxidant (iron (III) chloride) and dopant (*p*-toluenesulphonate or 2-naphthalenesulphonate) in water, then collecting the precipitate. For textile deposition, a two-step deposition method was used, whereby the textile was first impregnated with precursor and dopant, then immersed in the oxidant solution (using the same reagents as for the powder). Textiles had multiple coatings applied, presumably in order to increase the ratio of ICP to substrate and assist with elemental analysis of the ICP. Elemental analysis (neutronic activation) was used to determine the composition of the polymer, and revealed that chloride was displaced by the other dopants used, and that the ratio of pyrrole units to dopant species was ~1:0.32. (This is not substantially different to the findings of Mohammadi *et al.* [15], who found a doping ratio of ~1:0.26 for polypyrrole vapour-deposited onto non-textile substrates). When 2-naphthalenesulphonate was used, chloride was almost completely displaced as dopant, while when *p*-toluenesulphonate was used more than half the dopant was chloride.

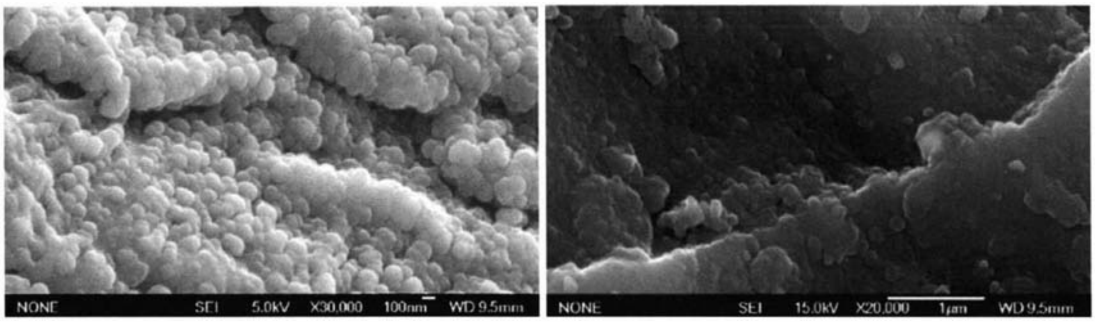


Figure 2.12. High-magnification SEM images of polypyrrole-coated cellulose (left) and wool (right) fibres (from Johnston *et al.* [53]).

2.2.2.4 Textile Properties and Ageing Behaviour.

Mechanical Properties.

The influence of the coating of ICP on a textile's mechanical properties has not been examined in any detail. Aydinli *et al.* [72] examined the mechanical properties of ultrahigh molecular-weight polyethylene foam-polypyrrole composites, prepared by two-step impregnation. Repeated impregnations of pyrrole and oxidant were used to build up the polypyrrole coating. Loadings of up to 50% ICP by mass were generated, and while the mechanical properties of the foam were not adversely affected by this loading, it is likely that textiles would be. Forveille and Olmedo [64] made a brief examination of the mechanical properties of their polyaniline-coated glass-fibre fabric's mechanical properties when used in a rigid composite structure with epoxy resin, and concluded that they were largely unchanged by polyaniline deposition (shown in Table 2.5). It must be emphasised that these results are for 13 layers of the fabric impregnated with an epoxy resin, so this is not really an assessment of 'textile' properties, rather those of a textile-reinforced rigid composite.

Table 2.5. Mechanical properties of a textile-reinforced composite prepared with polyaniline-coated glass-fibre fabric (from Forveille and Olmedo [64]).

	Flexural modulus (MPa)	Flexural stress (MPa)	Bending strain at break (mm)
Untreated	7560 (± 20%)	22 (± 8%)	5 (± 10%)
Polyaniline-coated	7710 (± 12%)	19 (± 20%)	4 (± 16%)

Although the addition of an ICP coating to a textile may cause it to become stiffer and less extensible, it is also important to consider the potentially degrading effect that reagents (particularly the oxidant) might have on the substrate. Beneventi *et al.* [71] observed a serious degradation of their cellulose fibres after polypyrrole deposition using iron (III) chloride: so much so that they could not form 'hand sheets' (of paper) from them. This would be particularly problematic for cellulose fibres, as they are vulnerable to acid hydrolysis in the low-pH, strongly-oxidative conditions that exist in the concentrated oxidant solutions typically used for the two-sage impregnation technique. Many other fibre types would be much less adversely effected.

ICP coating thickness could have a major influence on textile properties, in that thick coatings would tend to reduce the space in the fabric for fibres and yarns to move independently. Deposition of very thick coatings may even cause fibres to be 'glued together'. Forveille and Olmedo [64] found that ICP coating thickness increased linearly with successive coatings; the thickness of a single coating being approximately 150 nm, compared with the fibre diameter of 9 μm (9000 nm). A single coating of 150 nm is unlikely to have a large detrimental effect on the mechanical properties of the textile, and the same is true for the thin coatings produced by the admicellar polymerisation process [56]. Although coating thicknesses were not provided for the materials Lekpittaya *et al.* prepared, they did comment that an admicellar deposition of polystyrene onto a fabric had almost no effect on its air permeability. This implies that the pore size in the fabric was unchanged by polymer deposition, so fibre and yarn dimensions have probably not changed. Lin *et al.* [70] deposited polypyrrole coatings from approximately 0.1 to 0.6 μm by varying pyrrole concentration, but did not relate this to the mechanical properties of the textile.

Ageing and Durability.

Thiéblemont *et al.* [68] investigated the ageing behaviour of polypyrrole-textile composites prepared using iron (III) chloride, with and without 2-naphthalenesulphonate added for additional doping. GC/MS was used during ageing to measure the amounts of HCl (resulting from chloride loss) or naphthalene (resulting from 2-naphthalenesulphonate loss) given off by the composite over time. The composites prepared using 2-naphthalenesulphonate were much more stable to ageing in an inert nitrogen atmosphere across a range of temperatures, although the difference was more marked at high temperatures. GC/MS revealed that composites prepared with only chloride$^-$ present lost substantial amounts of HCl, while only minute amounts of naphthalene were detected when 2-naphthalenesulphonate was the dopant. They concluded that the greater conductivity decrease in polypyrrole doped with mineral anions is due to reaction of the anion with the polymer backbone and/or volatilisation of the anion. Aromatic sulphonate anions are less reactive and less volatile, so the gradual loss of conductivity when these were used may have been due to oxidation of the polymer backbone by oxygen or water. These results agree with the findings of other researchers who carried out ageing experiments on textile-polypyrrole composites prepared by the one-step technique (discussed in Section 2.2.1), which were all prepared with sulphonic acids [42,43]. In that case only the oxygen diffusion mechanism was identified, possibly because relatively non-volatile dopants were used.

Oh and Hong [58] also investigated the influence of various doping routes on the durability of conductivity, but assessed in terms of thermal stability. A version of two-stage impregnation was used, with initial impregnation in an aniline solution, followed by immersion in a solution of APS with HCl and various protonic acid dopants, including benzenesulphonic acid (BSA), DBSA and *p*-TSA. The nature of the sulphonic acid dopant influenced both conductivity and the thermal stability of conductivity, with BSA (lowest molecular weight) providing the highest conductivity, although DBSA (highest molecular weight) gave better thermal stability of conductivity. All specimens, however, degraded substantially. The mechanism of this was taken to be partly due to dopant loss, but also degradation of the conductive polymer network, as re-doping with the appropriate dopant did not give full recovery of conductivity. As all sulphonic acid dopants performed better than HCl on its own, it was concluded that high molecular weight dopants are less readily liberated from the polymer during ageing.

Durability of the electrical properties of a textile-ICP composite to washing, to exposure to light and to abrasion are all important to the usefulness in industrial/commercial applications. Jin and Gong [69] showed that their pre-polymerisation monomer diffusion step had a beneficial effect on durability: a simple wash test decreased the conductivity of non-diffused specimens by approximately 95%, while diffused specimens decreased in conductivity by approximately 50%. They concluded that the diffusion step resulted in the formation of polymer inside the fibre, which interacted with polymer deposited onto the fibre surface, resulting in better adhesion and a higher loading of polyaniline.

Nylon-polyaniline composite fabrics prepared by Oh *et al.* [73] using APS and HCl for oxidant and dopant respectively, were subjected to a range of durability tests, including abrasion, laundering, and exposure to radiation from a carbon-arc lamp for 100 hours. Detergents used in laundering caused a substantial loss (several orders of magnitude) in conductivity, whereas the other conditions caused only a single order of magnitude reduction. Nevertheless, durability losses of this magnitude would likely compromise the useful application of these materials.

Another paper by the same researchers [74] compared materials similar to those they had prepared previously [73] with equivalent materials (nylon-polyaniline) prepared by a single bath variant. This used an addition of oxidant to the original impregnation bath to trigger polymerisation. Of most interest were the results of their studies into the durability of conductivity when the conductive fabrics were subjected to a range of treatments: abrasion, alternating acid/alkali treatments (doping/de-doping, although not identified as such in the publication), exposure to light, and washing with a detergent. Both preparation techniques behaved similarly in the various durability tests, but with the one bath version starting from a higher conductivity. The abrasion treatment did not change conductivity, although the nature of this abrasion was not stated and only 50 cycles were used. The specimens were able to be repeatedly doped and de-doped without any major change in conductivity in either state. Exposure to light for 100 hours reduced conductivity by approximately one order of magnitude (a change described as "slightly decreased" by the authors), but washing caused (after several cycles) a reduction in conductivity of several orders of magnitude. Not discussed by the authors was the subsequent boost in conductivity to near original levels that occurred when the specimen was re-doped. This is a clear indication that at least some of the loss of conductivity caused by washing was due to loss of dopant (in this case it will be chloride from the HCl doping), and would be recoverable with re-doping. Therefore one way of overcoming loss of conductivity of textile-ICP composites would be to incorporate re-doping into the laundering process.

The durability and application-related properties of cotton fabrics coated with polyaniline were reported by Bhat *et al.* [75]. A variety of polymerisation conditions were used, but the basic technique employed was to use a single bath in two stages to initially impregnate fabrics with aniline, then to polymerise with the addition of oxidant (APS) and dopant (HCl). Like the findings of Oh *et al.* [74], these specimens showed a decrease in conductivity when washed that could be reversed by re-doping in HCl (done by immersing the specimen in 1 mol/L HCl for two hours). Again this suggests that the loss of conductivity on washing was due largely to dopant loss, and not due to loss of the polyaniline itself. The cotton-polyaniline composite fibres had an improved flame retardence (burn time of 20 cm yarn length increased by up to 100%), and also showed electromagnetic interference shielding properties. Finally, the potential for these fabrics to be used as gas sensors was demonstrated by testing their response to ammonia vapour: the fabrics showed a marked (and reversible) drop in current flow when ammonia was introduced. (Applications such as these are discussed in more detail in Section 2.3).

Varesano *et al.* [55] carried out an extensive study of durability properties. Some aspects of their study were discussed earlier in this section, but they also assessed the effect on electrical properties (of wool-polypyrrole fabrics) of laundering with either perchloroethane (dry cleaning) or a typical domestic washing system; exposure to light and temperature (45°C); and abrasion. They used the relative resistance (the resistance after a designated test, relative to its original resistance) as a simple way of tracking the change in electrical properties. There was only a small change in resistance with dry cleaning (relative resistance after five cycles was 1.2), but a very large change with domestic laundering (relative resistance increased exponentially, and was about 45 after five cycles). De-doping was identified as the likely cause of this drastic deterioration in electrical properties. Exposure to light caused a linear increase in relative resistance, to about 5.5 after 160 hours. Heat exposure increased asymptotically until approximately 80 hours, after which there was no further increase. At this point the relative resistance was about 3.3. Oxidation of the polypyrrole coating was identified as the likely cause of both these increases. A third mechanism of conductivity degradation is physical erosion of the coating; after 40,000 abrasion cycles (using a Martindale-type tester) the relative resistance had increased to about 8.5. The effect of abrasion on the coating was very well illustrated by SEM images collected before and after abrasion, and these are provided in Figure 2.13. The specimens were not gold-sputtered, as they had sufficient conductivity from their ICP coating. As a result there are bright areas (due to electrical charging under the electron beam) where polypyrrole has been abraded from the substrate.

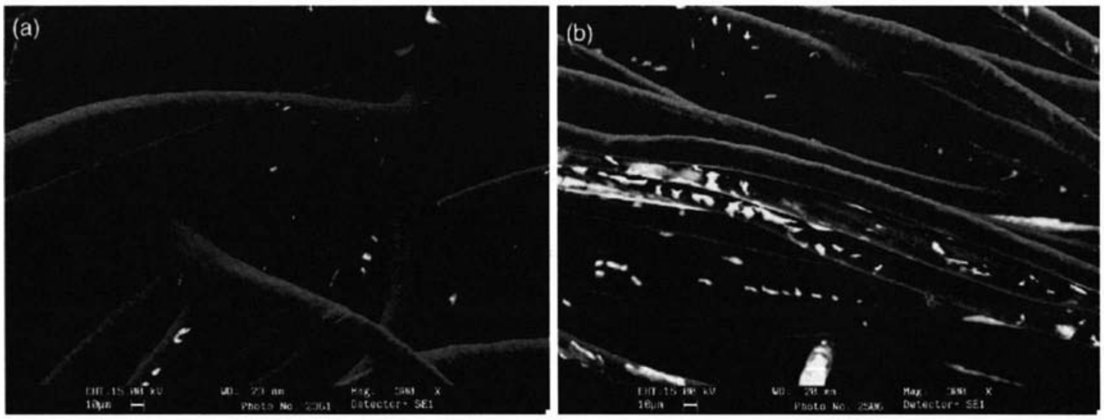


Figure 2.13. SEM images of wool-polypyrrole fabrics before (left) and after (right) abrasion testing (from Varesano *et al.* [55]).

2.2.3 *In Situ* Polymerisation by Vapour Phase Deposition.

The relatively high reactivity and volatility of pyrrole has been exploited by several researchers as a way of *in situ* polymerising it onto textiles. The basic principle is well exemplified by Tan and Ge [76], who used cotton thread as the substrate. The thread was impregnated with iron (III) chloride from a methanol solution by spotting it with a fixed volume from a glass capillary. The methanol was evaporated in air, and the thread was placed in a sealed vessel saturated with pyrrole vapour. Polypyrrole formed on the surface of the fibres on contact with the iron (III) chloride oxidant. The reaction was rapid, with minimum electrical resistance reached after just two minutes. Exposure of the specimen to vapour for longer than this time did not result in threads with lower resistance.

Some researchers have used a continuous vapour deposition approach to treat larger amounts of textile. Continuous deposition of polypyrrole onto poly(*p*-phenyleneterephthalamide) filaments (PPTA, e.g. Kevlar®) was demonstrated by Xu *et al.* [77]. They impregnated the oxidant (iron (III) chloride) onto the PPTA filaments from an aqueous solution at concentrations up to 60% w/w (~2.2 mol/L). They then dried the filaments and exposed them to pyrrole/H_2O vapour in an N_2 atmosphere. The filaments travelled through these various stages via rollers, and the treated filaments were produced at a rate of about one metre per minute. Hosseini and Pairovi [78] used a semi-continuous process with cotton and silk yarns. They pre-impregnated the yarns with iron (III) chloride, then ran them through a water-jacketed glass tube, through which pyrrole vapour in N_2 was circulated. The water jacket presumably maintained a temperature that prevented condensation of pyrrole onto the substrate, but the temperature used was not stated. This method was only semi-continuous, as the output side of the system had a unit attached that automatically made conductivity measurements on lengths of yarn that passed through. The yarn was periodically stopped to do this.

An elegant refinement of non-continuous vapour deposition was illustrated by Tessier *et al.*, who used a technique for covalently bonding polypyrrole onto poly(ethylene terephthalate) (polyester) fabric [79]. They phosphonylated fabric specimens by exposing them to phosphorous trichloride in the presence of ultrapure oxygen. A pyrrole variant called 1-(3-hydroxypropyl)pyrrole (shown in Figure 2.14) was then added, which bonded directly with the phosphonylated polyester through the hydroxypropyl 'tail'. The pyrrole 'head' of the molecule was then oxidatively polymerised with other pyrrole molecules, to produce polypyrrole that was periodically covalently attached to the polyester. This was done by impregnating the treated fabric with iron (III) chloride, then exposing it to pyrrole vapour. Surface resistance values of 10-100 kΩ/square were reported, but the durability of the coating (which might be expected to be very good) was not tested.

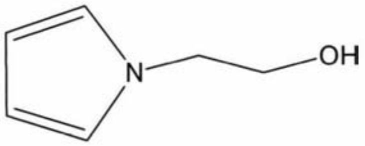


Figure 2.14. 1-(3-hydroxypropyl)pyrrole.

Sanyo and Mitsubishi researchers used a variety of substrates for the vapour-phase deposition of polypyrrole in 1996 [80]. These were mostly conductive materials, but did include a polypropylene non-woven. The substrates were impregnated with iron (III) perchlorate, then exposed to pyrrole vapour for 24 hours in a sealed vessel. As the oxidant was applied in an aqueous solution, a one-sided specimen could be prepared by treating one face of the fabric with a water-repellent agent before impregnation. The one-sided fabric was able to be used as an electrode, and the researchers concluded that vapour deposition was a useful method for preparing these types of materials.

In another variant on the basic approach, Stussi *et al.* [81] described a system for vapour deposition of conductive polymers onto substrates (not textiles, although it would be possible to extend aspects of the system to fibrous assemblies). Of most interest in this work was a novel means of patterning the polymer deposition. Thin layers of copper were deposited onto the substrate by vacuum evaporation through a patterning mask. The copper was then transformed to copper (II) chloride by exposure to hot chlorine vapour, which was then used as the oxidant for vapour deposition of the conductive polymer. In principle, miniature, multi-sensor systems could be prepared in this way. Also of interest in this research was the design of a reactor allowing solid ICP precursors to be volatilised by increasing the temperature, thus making them useable for vapour deposition. However, although some researchers (for example, Tan and Ge [82]) have used polyaniline, no reports have been found of less volatile ICP precursors (such as 2,2'-bithiophene) being used for vapour deposition.

2.2.3.1 Influence of Substrate Properties.

The choice of substrate used would be expected to have some influence on the properties of the textile-ICP composite. The extent to which oxidant is taken up before vapour exposure, and the extent to which the vapour can permeate the substrate, are likely to influence the ICP deposition process. However, relatively few researchers have focussed on this aspect of the system. While Hosseini and Pairovi used both cotton and silk yarns for their experiments [78], there was little comparison made of the two fibre types. SEM images suggested a heavier coating on silk, but the conductivity was only slightly higher (31 μS/cm compared with 14 μS/cm); values that were increased by two orders of magnitude after an additional doping step in iodine vapour.

Modification of the substrate fibres to alter their vapour deposition behaviour has been reported for wool [29] and polyacrylonitrile [63]. The wool was modified by either chlorination or acid treatment. Improved conductivity resulted, presumably as these fibre treatments would both have the effect of increasing the oxidant take-up. As is discussed later in this section, the amount of oxidant present on the substrate (typically controlled by oxidant solution concentration) is an influential parameter in the vapour deposition process [76,82-84]. For polyacrylonitrile fibre (commonly known as acrylic), a chemically modified version (with an amidoxime group, intended to absorb more Fe^{3+} ions from the oxidant, iron (III) chloride, solution) was compared with unmodified fibre [63]. In this case however, the modified fibre did not have any significant influence on resultant fibre conductivity. From this it was concluded that only physically-bound oxidant on the surface of the fibres was involved in polymerisation. The additional oxidant absorbed into, and held by, the modified fibres, was not involved.

While it is apparent that substrate properties do have an influence on the ICP deposition process (most directly though the extent to which they take-up the oxidant solution), there has not been any thorough investigation of this across a particularly wide range of substrates.

2.2.3.2 Reaction Parameters.

Several researchers have reported that composite electrical resistance decreased at higher concentrations of oxidant. Tan and Ge [76] observed a dramatic decrease (using pyrrole as the precursor and iron (III) chloride as oxidant) with concentrations up to ~0.5 mol/L, but more gradual at higher levels. The also found the same relationship when aniline [82] was used, with APS as oxidant and doping carried out in an after-treatment with 3M HCl. This created conductive polyaniline (green) from the non-conductive polymer (blue) initially formed. They recommended a oxidant concentration in this case of 1 mol/L or higher. Cho and Jung [83] found the same relationship between oxidant concentration and resistance, as did Dall'Acqua *et al.* [84]. In the latter, polypyrrole was deposited onto iron (III) chloride-impregnated viscose fibres by vapour deposition at 60°C, in research that was intended to compliment their solution polymerisation described earlier [36]. There was a clear decrease in resistance at higher oxidant concentrations, and the reason is apparent with reference to Figure 2.15: a much heavier loading of polypyrrole, as globular deposits on top of an underlying smooth coating, and also as loose ICP particles. It should be noted that the longitudinal striations were present on the pristine viscose fibres, and are not related to ICP deposition.

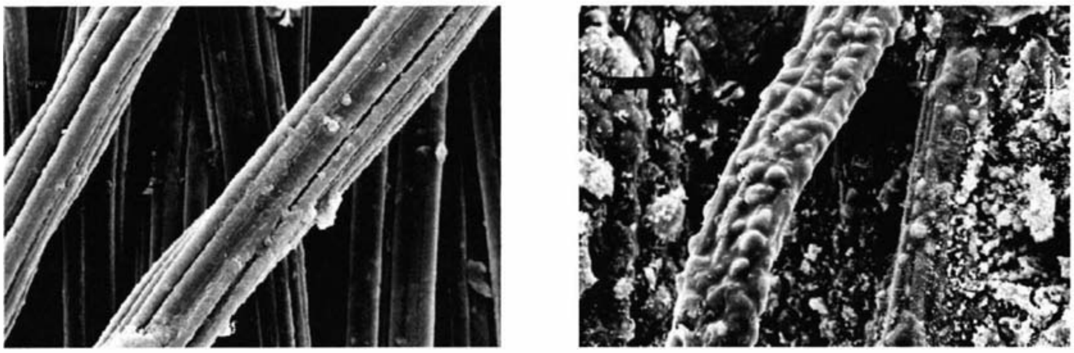


Figure 2.15. SEM images of vapour-deposited polypyrrole on viscose fibres (from Dall'Acqua *et al.* [84]). Left: oxidant concentration 9 g/L, 1290x magnification. Right: oxidant concentration 18 g/L, 1180x magnification.

In Tan and Ge's first paper [76], they reported that carrying out the polymerisation at lower temperatures (down to a minimum of -10°C) resulted in higher resistance, but it was not clear from the research if this was perhaps simply because the reaction was slower at the lower temperature, and therefore did not run to completion in the time allowed. Certainly the vapour pressure of pyrrole would be lower and the polymerisation reaction slower, at this reduced temperature. At higher temperatures (up to a maximum of 40°C), lower resistances were achieved, with a higher pyrrole vapour pressure and increased rate of reaction. In their second paper [82], Tan and Ge extended their research to the vapour polymerisation of aniline, again using cotton thread as a substrate, but APS as thc oxidising agent. On this occasion, high temperatures produced more-rapidly polymerised, but ultimately less-conductive composites. There appeared to be an advantage to long, slow polymerisation in forming a well-ordered polymer coating; a finding also supported by other researchers using polypyrrole on an aromatic polyamide fibre [83]. With longer times at high temperatures, there is a danger that the specimen becomes "overpolymerized". In general, the polyaniline composites reported in Tan and Ge's second paper were an order of magnitude higher in resistance than their polypyrrole composites [76], being in the range 5000-6000 Ω, compared to 500-1000 Ω.

Adding other volatile species (organic solvents) to the reaction vessel gave no advantage [76], although Cvetkovska *et al.*'s polymerisation carried out in the presence of iodine (I_2) vapour (intended to act as an additional dopant) had the effect of reducing the resistance by an additional order of magnitude, as compared to the set-up without iodine [63]. These researchers also found that specimens that were placed in the vapour 'wet' with oxidant solution (i.e. from which the solvent (water or diethyl ether) had not evaporated) had more homogeneous polymer deposition. Presumably the presence of solvent provides a degree of mobility for the reactive species involved in polymerisation.

In summary, it is clear that a high oxidant concentration results in a higher level of ICP deposition and lower resistance. Oxidant concentration is obviously a convenient way to directly control the amount of ICP deposited. On balance it seems that low temperature polymerisation results in lower resistance, with Tan and Ge's [76] first conclusion on this (that higher temperature was better) probably the outcome of an incomplete reaction. Polymerisation in the presence of a gaseous dopant appears to reduce resistance, but other species added to the vapour appear to offer no advantage.

2.2.3.3 ICP Morphology, Composition and Structure.

Vapour-deposited ICP coating morphology has been partly discussed in the previous section, and as shown in Figure 2.15, appears to consist of a smooth uniform coating, tending to become globular with loose polymer particulate present at high oxidant levels. Xu *et al.*'s observations [77] were consistent with this; their PPTA fibres appeared under SEM inspection to be coated with a smooth, uniform film. SEM images of filament ends suggested that the polypyrrole had even formed partially inside the fibre.

Xiao *et al.* made a more detailed study of the morphology of vapour-deposited polypyrrole in their work with polycaprolactam fibres [85] (polycaprolactam is a actually another form of nylon, usually referred to as nylon 6). They prepared the composite fibres with iron (III) chloride as oxidant and pyrrole in N_2 at room temperature. Two after-treatments were given: heat treatment (230°C in air for 1 hour) and phenol swelling (6.5% on weight of fibre aqueous phenol at 48°C for 1 hours). Cross-sectional TEM images of polypyrrole-coated fibres (with no after-treatment) indicated a two-layer structure to the polypyrrole coatings, particularly at heavy loadings: a compact layer with a more loosely constructed layer outside it. This could correspond to Dall'Acqua *et al.*'s SEM observation at high loadings (Figure 2.15, right), where a smooth layer appeared to form close to the fibre surface, with a rough globular layer covering it [84].

The heat treatment had the effect of destroying the conductive properties of the composite fibre, which is expected as it is a severe treatment. The effect on the morphology was examined with SEM, and is shown in Figure 2.16. The polypyrrole-coated fibre with no after-treatment was smooth, but with irregular deposits also apparent. After swelling, the coating appeared 'wrinkled' because of differential drying-shrinkage behaviour of the fibre and coating. This implies that the coating had no chemical interaction with the fibre surface, as they changed dimension independently, resulting in the wrinkling. Xiao *et al.* describe the heat-treated surface as "collapsed and compact", suggesting that the non-compact layer of the structure had become condensed by the treatment. There were no TEM images of after-treated fibres to confirm this.

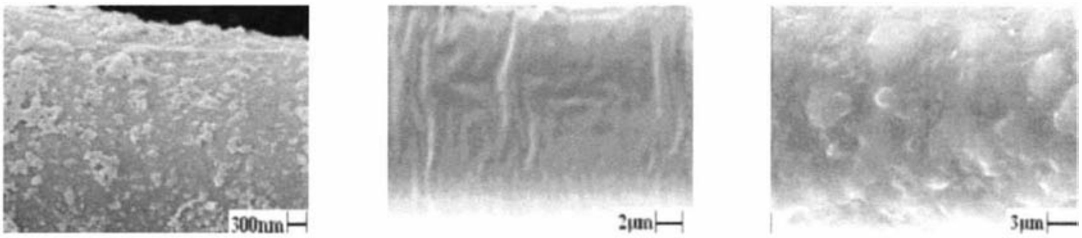


Figure 2.16. SEM images of polypyrrole-coated polycaprolactam fibres (from Xiao *et al.* [85]). Left: no after-treatment. Centre: after swelling in aqueous phenol. Right: after heat treatment.

Various researchers have attempted elemental analysis of vapour deposited ICPs. Xu *et al.* [77] did this for their iron (III) chloride-oxidised PPTA-polypyrrole composites, but the doping ratio (determined by examining the ratio of nitrogen atoms (on pyrrole) to chlorine atoms (in dopant)) could not be directly determined because of the presence of nitrogen in the substrate polymer (PPTA). Rector *et al.* [86] also worked with composite polypyrrole/PPTA fibres, and elemental analysis was performed on the composite (although it appears that the results relate to the polypyrrole component only). This indicated the presence of iron and chlorine in proportions that could not be correlated with any experimental variable. The elemental ratios were as expected for carbon, hydrogen and nitrogen (4:3:1, being the ratio present in the pyrrole molecule), with iron present in the range 0.085-0.116, chlorine present in the range 0.182-1.11, and oxygen present in the range 0.478-0.821 (all normalised relative to nitrogen). They stated that the presence of oxygen in the polymer was in agreement with Armes' earlier work [3] for oxidised polypyrrole. However, if the PPTA substrate (or residues of it) was still present, the oxygen could be related to that.

2.2.3.4 Textile Properties and Ageing Behaviour.

The influence of conductive polymer coating on the mechanical properties of textile fibres has rarely been addressed in the literature. An exception to this is work carried out at Deakin University [87]. They investigated the influence of a vapour-deposited polypyrrole coating on the frictional and tensile properties of wool and alpaca fibres. The polymerisation was carried out on scoured (cleaned) fibres, using iron (III) chloride impregnation followed by exposure to pyrrole-saturated air for 45 minutes. The fibres had an electrical resistance of about 2000 Ω over a 2 cm length. This reduced the coefficient of static friction by partially covering the scales that are present on most hair-type fibres, effectively levelling out the fibre surface. This was consistent with previous findings from these researchers when using the Milliken technique to deposit polypyrrole onto wool yarns [30]. The differential friction effect (whereby the friction against the scale growth direction is higher than that in the opposite direction) was also reduced. The effect on tensile properties was unclear, with no statistically significant difference in strength or elongation measured. Taken alone, the addition of the polymer coating might strengthen the fibre, but a commensurate reduction in strength might be caused by the oxidant degrading the fibre surface during polymerisation. The apparent lack of overall fibre degradation is an encouraging result, as it suggests that the fundamental properties of these fibres as they relate to textile processing and performance are not significantly altered by vapour deposition of an ICP. Other researchers [77] have also reported no change in fibre mechanical properties after vapour deposition of polypyrrole, or reported only slight reduction in tenacity and modulus of polypyrrole-coated aromatic polyamide fibres compared to untreated [83]. These fibres showed a gradual increase in resistance when they underwent tensile strain, with a rapid increase just before break. In theory this means the rupture of the fibre could be predicted in advance, although the strain-resistance relationship was not sensitive enough for these fibres to make particularly useful strain gauges.

By contrast, Dall'Acqua *et al.*'s viscose fabrics [84] were severely degraded by vapour deposition of polypyrrole, becoming weaker and less extensible (data provided in Table 2.6). Viscose is regenerated cellulose, a material which is certainly vulnerable to degradation when impregnated with a low pH, concentrated, oxidant solution. The fabrics and fibres that showed little or no degradation [77,83,87] were more resistant types, being wool (reasonably resistant to acid hydrolysis, although vulnerable to certain oxidants) and aromatic polyamides.

Table 2.6. Mechanical properties of viscose-polypyrrole composites (from Dall'Acqua *et al.* [84]).

Direction of test	Strength at break (N)		Elongation at break (%)	
	Untreated	Polypyrrole-coated	Untreated	Polypyrrole-coated
Warp	311.53	96.61	15.41	9.45
Weft	381.79	139.83	24.13	13.32

Ageing behaviour of vapour-deposited textile-ICP composites has not been studied, except as a brief observation by Xu *et al.* [77] that after ageing under environmental conditions for two months, the conductivity of their composites had decreased by ~80%, with no further decrease after another month.

2.2.4 *In Situ* Polymerisation by Electrochemical Techniques.

As all commonly used textiles are electrical insulators, it seems counter-intuitive to try and electrochemically deposit an ICP onto them. The fabric would need to be used as the anode in an electrochemical cell, and this is clearly not possible. However, a number of researchers have examined ways to circumvent this, and their work is reviewed in this section. The appeal of electrochemical deposition of the ICP is the additional control that can be had over the polymerisation process via the imposed electric current, and also the control over doping that can be exercised by electrochemical redox processes.

2.2.4.1 Attachment of Textile to Electrode.

A group of Indian researchers have experimented with a simple approach: Bhadani *et al.* [88] simply wrapped wool, cotton and silk yarns around the anode in an electrochemical cell, with pyrrole and thiophene used as ICP precursors, and tetrabutylammonium hexachloro-antimonate in 1,2-dichloroethane as the electrolyte. The ICP formed at the anode, but largely accumulated on the yarn. Resistivity with pyrrole was in the range 5-25 kΩ·cm, while for thiophene it was 7-65 MΩ·cm. Increasing the current used for electrolysis had no effect on resistivity, but did increase the mass of polymer added to the fibre.

The research was repeated with aniline as the precursor and *p*-toluenesulphonic acid as the electrolyte [89]. The effect of electrolysis time was reported; the mass add-on of polymer increased fairly steadily with time, while the resistivity decreased. Resistivity after five hours was 1.7, 1.6 and 5.2 kΩ·cm for cotton, silk and wool respectively, while the increase in weight was 83%, 224%, and 155% respectively. Similar experiments with pyrrole in place of aniline demonstrated similar trends, but with higher overall conductivity [90,91]. The difference in observed resistivity is not necessarily due to the different chemical nature of the substrates, but may also reflect the fibre diameter and shape (the total available surface area). The work was repeated with an aqueous solution of HBF_4 used as the electrolyte [92], with very similar results.

More recently Subianto *et al.* carried out similar work [93], using a cotton fabric that was attached to a stainless steel anode with a water-soluble adhesive (to allow it to be easily removed). They used pyrrole as the precursor and *p*-TSA as the dopant/electrolyte in an aqueous solution. The anode was oriented horizontally, and electropolymerisation took place for four to six hours, during which time polypyrrole accumulated in and on the fabric structure. For the purpose of comparison, films were created in the absence of the fabric, and also on cotton fabrics that were in contact with the anode but not glued to it. When the adhesive was used, the polypyrrole coating was mechanically attached to the fabric, having polymerised between the yarns and though the fabric as dendrites. The attachment was much less effective when the fabric was just placed on the anode, with a two-layer structure (fabric/polypyrrole film) apparent and no growth though the fabric occurring. Low current and high dopant concentration were the most effective conditions, as shown in Table 2.7.

Table 2.7. Electrochemical polymerisation parameters (from Subianto *et al.* [93]).

Current (dopant conc. = 0.5 mol/L)		Dopant (current = 100 mA/cm^2)	
Current density (A/cm^2)	Resistance (Ω/cm^2)	Dopant conc. (mol/L)	Resistance (Ω/cm^2)
2	0.75	0.01	0.44
3	1.19	0.02	0.033
5	210	0.05	0.0059

2.2.4.2 Electrochemical Flow Cells.

A novel technique for producing a conductive fibre from ICPs was described in a paper by Li *et al.* [94]. The method is more elegant than the other electrochemical techniques described so far, and used a 'flow cell'; 3-methylthiophene (3-MT) was pumped through a specially shaped narrow cylindrical (3 mm diameter) electrochemical cell, and polymerised as a thin linear structure from the anode towards the cathode. The inlet through which the precursor flowed was positioned just behind the anode (a platinum wire), while the outlet was just beyond the cathode. The continuous flow encouraged linear growth of the electrode deposit. The fibre was rather thick (0.6 mm) and grew slowly (0.8 cm/hour), but had conductivity (~20 S/cm) comparable with that of poly(3-MT) films. The influence of various parameters was reported, including precursor concentration (~0.5 mol/L was optimal), and current (1.0-3.0 mA produced reproducible smooth fibre growth). Fibre shape could be altered by modifying the flow cell shape, thus changing the character of the capillary flow.

The mechanical properties of the fibre were poor, being brittle and weak. This was addressed in a refinement of the technique [95,96], where a polyester or Kevlar® thread was suspended in the cell along the electrode axis. The conductive polymer was deposited onto this, creating a composite fibre/yarn with much improved mechanical properties. Unfortunately poly(3-MT) did not adhere to securely to the fibres, but polypyrrole synthesised in the same way did have good adhesion. Composite fibres were produced at rates of up to 30 cm/hour, with fibres of an acceptable flexibility having a conductivity of 24.3 S/cm. However, all fibres produced were of relative high diameter (the finest being 0.2 mm), which would limit the applicability in textile applications, where fibres are typically at least one order of magnitude finer. The technique was subsequently patented in 1995, without further refinement [97].

2.2.4.3 Combined Chemical and Electrochemical Polymerisation.

One way of overcoming the inherent difficulty of electrochemically polymerising onto a non-conductive substrate would be to first make it conductive. This may seem somewhat pointless – if it is possible to make the substrate conductive by other means why bother to use an electrochemical technique? It would however allow a moderately conductive substrate (having been ICP-coated by *in situ* polymerisation) to then be made much more conductive in a more controlled fashion via electrochemistry. A group of Korean researchers have taken exactly this approach, carrying out chemical and electrochemical deposition of the ICP onto a fabric in sequence [98-102].

Their initial step was to optimise their chemical oxidative polymerisation process [98] (they referred to this as 'COP'). They used a two-stage impregnation system (with 1-naphthalenesulphonic acid was present as an additional dopant) to deposit polypyrrole onto a polyester woven fabric (the work is also reported for nylon fabrics [99]). They established that iron (III) *p*-toluenesulphonate was a more effective oxidant (producing lower resistance composites) than APS; the addition of PVA to the monomer solution as a surfactant gave a denser, more uniform coating; and polymerisation at low temperature (0°C) resulted in lower resistance. These optimum conditions allowed a composite with 7% polypyrrole content to have a specific volume resistivity of 1 Ω·cm (with the mass of polypyrrole being controlled by multiple coatings). Fabrics similar to this, but with lower ICP content (to allow polypyrrole to be added electrochemically without making them excessively heavily loaded) were then used as the anode in an electrochemical cell, with pyrrole and the sodium salt of AQSA (Na-AQS) in an aqueous solution as the electrolyte (they referred to the electrochemical polymerisation as 'ECP'). The optimum conditions used a Na-AQS concentration of 0.05 mol/L, and electrolysis for two hours resulted in a fabrics with a specific volume resistivity of 0.2 Ω·cm, with 6% polypyrrole content.

The environmental stability of the ECP-COP specimens (electrochemical polymerisation on top of chemical polymerisation) was good, with almost no change in surface resistance over an 80 day period in a 25°C, 65% relative humidity environment. A COP-only specimen increased in resistance by about 50% over this period of time. This was attributed to the denser structure of polypyrrole formed by electrochemical polymerisation, as can be seen in SEM images that were taken of the specimens, provided in Figure 2.17. This denser structure better resists attack by oxygen. It should be noted that the ECP-COP reported by the same researchers for nylon fabric [99] was more globular in nature, suggesting a degree of substrate influence.

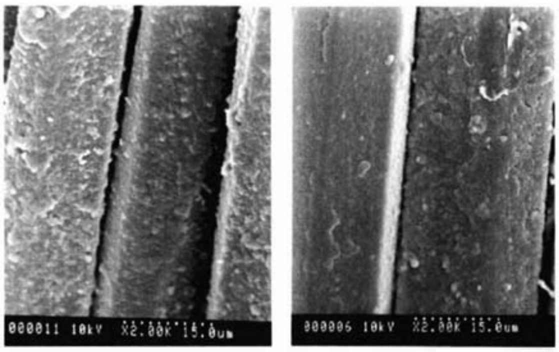


Figure 2.17. SEM images of polypyrrole on polyester (from Kim *et al.* [98]). COP on left, ECP-COP on right.

Related work assessed the potential for polymerising EDOT (see Figure 2.4) onto the textile by ECP-COP [100]. A variant on the two-stage impregnation process (described in Section 2.2.2) was used for COP, but produced composites that were unevenly coated, with large loose poly(EDOT) deposits in the fabric interstices. They also had lower conductivity, so the researchers did not continue with the ECP of EDOT, preferring to concentrate on polypyrrole. (This is disappointing, as given the better environmental stability of polythiophenes (compared to polypyrrole) a highly durable composite could have resulted, especially since the electrochemically prepared polypyrrole had excellent stability in its own right [98]). They used the ECP-COP process to put polypyrrole onto a nylon/elastane fabric, which had an electromechanical behaviour that might be useful for a strain gauge material, although the repeatability of resistance-deformation response was not evaluated. This application of textile-ICP composites is discussed in more detail in Section 2.3.

The thermal stability of the ECP-COP textile-ICP composites were assessed by Kim *et al.* [101], with material prepared using exactly the same process as previously described [98,99]. The thermal stability of COP composites was worse than for ECP-COP composites, with conductivity irreversibly dropping by nearly an order of magnitude for COP, compared to about 40% for ECP-COP. Presumably this was due to the coating morphology and molecular structure of the ECP-COP structure (discussed above) better resisting oxidative degradation and dopant loss. The application of these types of materials in electromagnetic interference (EMI) shielding was discussed in this and the other papers reviewed in this section; all had 'tunable' reflection and absorption properties, depending on the conductivity level of the composite. This was easily controlled during the electro-polymerisation process, and one novel approach was to create layers of low and high conductivity ICP on the substrate [101]. Low conductivity layers enhanced absorption, while high conductivity enhanced reflection. Another application as fabric electrodes was investigated in some detail by Kim *et al.* in a paper that is reviewed in Section 2.3 [102].

2.2.5 Deposition of Soluble ICPs.

ICPs are insoluble in most solvents, making the most straightforward polymer deposition process – application from a solution – unsuitable. However, as is also discussed in the next section (with reference to ICP fibre preparation), there are some combinations of polymer and solvent for which solution application is possible. This relatively new approach to polymer deposition is not a focus of the experimental part of the work described in this thesis, but it is worthwhile to review the potential it offers.

2.2.5.1 Deposition of Soluble Polyaniline.

Polyaniline solutions can be prepared by protonation with a functionalised protonic acid, creating a doped form of the ICP that is soluble in weakly polar or non-polar solvents such as *N*-methyl-2-pyrrolidone (NMP), dimethylsulphoxide (DMSO), xylene and *m*-cresol. Kim *et al.* [103] used dodecylbenzene sulphonic acid (DBSA) as the dopant, and created homogeneous solutions of polyaniline in xylene that they then used to coat polyester spun and filament yarns by a semi-continuous process, which involved drawing the yarns through several baths containing the polyaniline solution before drying. Yarn resistance was as low as 1.02 kΩ when a 10% polyaniline solution (the most concentrated) was used on the spun yarn, although for the filament yarn a 6% solution produced lower resistance than the 10% solution. This was thought to be due to the 10% coating being more viscous and 'gel-like', and not coating the smooth filament yarn fibre surfaces as well as it did for the less homogeneous spun yarn. This was confirmed by SEM examination of the yarns, with the heavier coating on and around the fibres apparent in the image of the spun yarn (Figure 2.18, left), compared to the filament yarn (right).

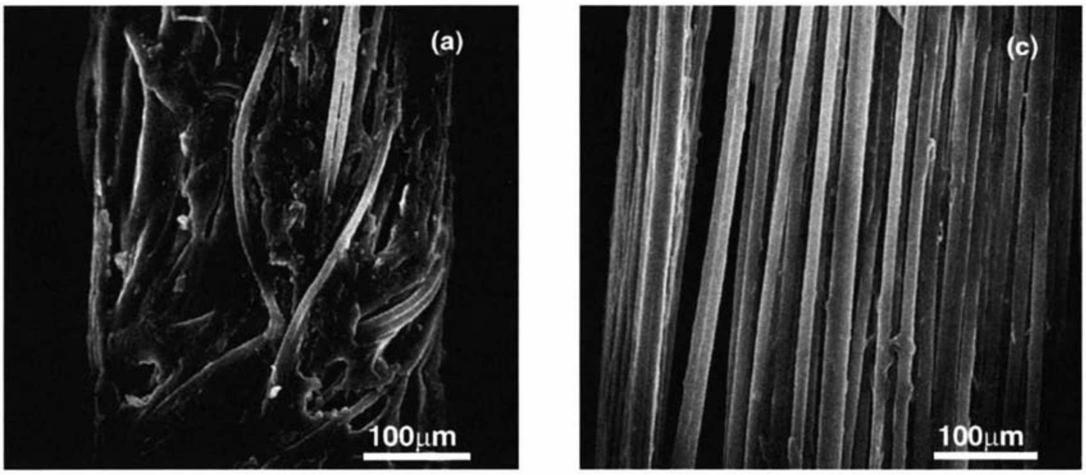


Figure 2.18. SEM micrographs of polyaniline-coated spun (left) and filament (right) yarns (from Kim *et al.* [103]).

Although the amount of polymer deposited onto the yarns was not reported, it is clear that it would be much greater for the spun yarn, with much of the polymer present in the fibre interstices rather than as a fibre coating. This would probably have the effect of substantially increasing the stiffness of these yarns, which could reduce their suitability for further processing (for example, knitting or weaving into a fabric). The obvious alternative is to coat the fabric with the ICP solution, and this was the approach reported by Fryczkowski *et al.* [104]. They also used DBSA-doped polyaniline, although the solvent used was not reported. The solution was 'padded' onto polyester fabric (padding is a commonly used textile wet processing technique whereby a fabric is dipped in a solution then put through a pair of rollers that squeeze it, forcing the solution into the fabric structure and controlling the amount that is taken up). The fabrics were given multiple coatings, with the resistance decreasing from approximately 50 kΩ with one coat, to approximately 2.5 kΩ with three. The resistance measurement system was not described.

Neither of the two papers discussed above went into any detail about the properties of the textile-ICP composites that resulted, but in a second paper from their research group, Kim *et al.* [105] examined these more closely. They coated polyester filament yarns with polyaniline by what appeared to be the same technique (a sol-gel process) as their previous work [103]. A range of yarn properties were evaluated:

- Ageing in ambient conditions: the electrical resistance of a 5 cm length increased from approximately 400 to approximately 1200 Ω over a 22-week period.
- Temperature sensitivity: the electrical resistance was fairly insensitive to temperature below 55°C. Above this, resistance increased with increasing temperature, suggesting some degradation of the ICP, as the expected behaviour of a semiconductor would be a decrease in resistance with an increase in temperature.
- UV sensitivity: the electrical resistance increased slightly after exposure to a UV light source for 80 hours.
- Mechanical properties: polyaniline-coated fibres had a slightly increased tensile modulus, while those treated with xylene (the polyaniline solvent) had reduced tensile modulus (the amorphous regions in the fibre polymer are vulnerable to damage from xylene).
- Electromechanical properties: the electrical resistance was largely unchanged by elongation until the yield point of the fibre was reached (at which point the load-bearing capability of the fibre drops) and the ICP coating was more readily deformed. After five successive load-recovery cycles there was a 12-15% increase in resistance.

While a number of these yarn properties are poor (particularly the ageing durability), the researchers point out that their polymer deposition conditions were yet to be optimised. At this stage however, it is difficult to see that deposition of polyaniline onto textiles from solution has any advantages over *in situ* polymerisation.

2.2.5.2 Deposition of Soluble Polypyrrole.

In two papers, Foitzik *et al.* described the preparation of soluble poly(3-alkylpyrrole) and its application to textile substrates [106,107]. Initially the work focused on preparing and comparing a range of poly(3-alkylpyrrole) variants, with differing carbon chain lengths [106]. The precursor was synthesised, then polymerised in solution with iron (III) chloride as oxidant and AQSA as dopant. As the carbon chain length increased (across the range 0 to 22), the polymer's solubility in chloroform increased, but its conductivity dropped. The optimum carbon chain length was between 10 and 14, giving a balance between solubility and conductivity. It was not explained why, but the researchers also carried out *in situ* polymerisation of their poly(3-alkylpyrrole) variants onto wool fibre samples. The conductivity of all variants up to a carbon chain length of 10 was comparable to that of unmodified polypyrrole.

The poly(3-alkylpyrrole) with a carbon chain length of 10 was employed in their subsequent work [107], which evaluated various techniques for depositing poly(3-decanylpyrrole) onto fabrics. Three solution-based techniques (spray, brush and dip coating) were compared with *in situ* polymerisation of 3-decanylpyrrole by one-step solution polymerisation and a technique referred to as vapour polymerisation. In reality the latter was not vapour deposition, but a variant on the two-stage impregnation technique described in Section 2.2.2, as it involved spraying the fabric with oxidant solution followed by spraying with precursor solution. This spray does not constitute 'vapour' of either reagent. Surface resistance of the fabrics before and after abrasion testing was measured, and is shown in Figure 2.19. The abraded samples are also shown (in the same order as in the chart). The dip-coating technique was excluded.

The initial resistance of the *in situ* polymerised specimens was lower, but all showed increased resistance after abrasion, as the ICP coating was worn away. This coating degradation is apparent in the specimen images, with the 'vapour polymerised' and spray-coated (five coats) samples showing a substantial colour change (comparing the central part of the fabric disc with the non-abraded outer edge). The *in situ* solution polymerised sample appears least abraded.

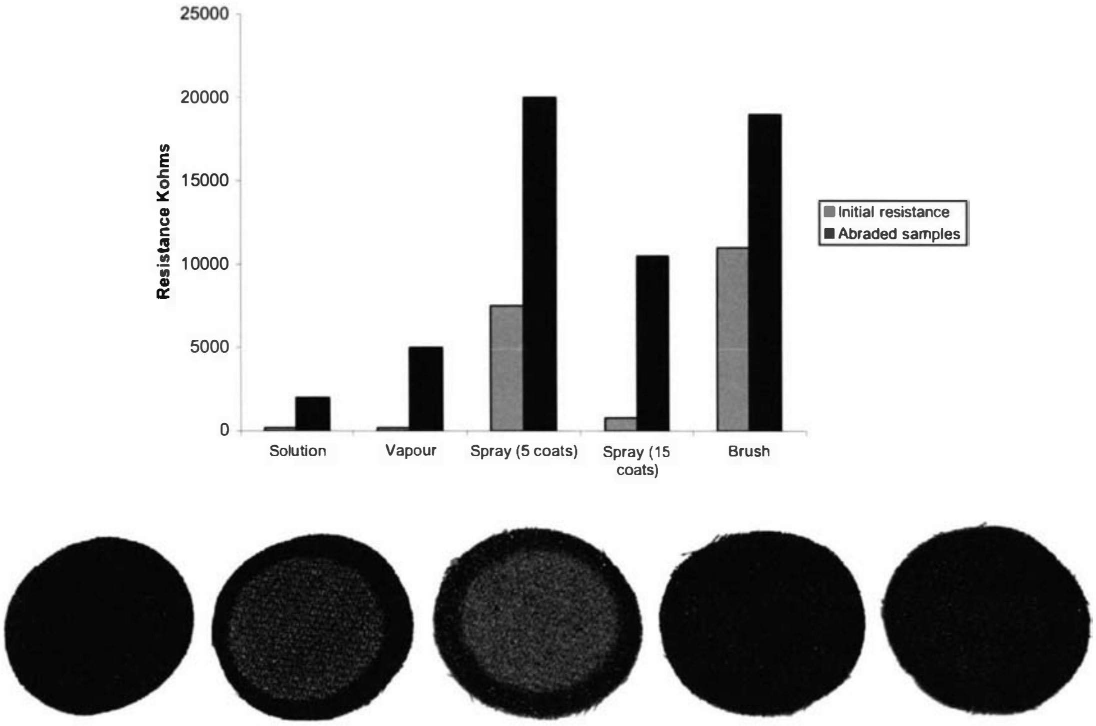


Figure 2.19. Change in surface resistance after abrasion testing for wool coated with poly(3-decanylpyrrole) by five techniques (top). Samples after abrasion (indicating loss of ICP) are also shown (bottom), in the same order as the chart (from Foitzik *et al.* [107]).

The main advantage of the deposition of the ICP from solution is that the substrate is not exposed to the potentially damaging oxidising agent that is required for *in situ* polymerisation. However, the electrical properties of solution deposited poly(3-decanylpyrrole) are inferior to *in situ* polymerised.

2.2.5.3 Deposition of Soluble Polythiophene.

Daoud and Xin [108] used an analogous approach to that taken by Foitzik *et al.* [106,107] in their experiments with 3-alkylthiophenes. They prepared poly(3-decylthiophene) and poly(3-dodecylthiophene) using 'ultraslow' addition (0.83 mL over four hours) of a low concentration precursor (2.97 mmol/L) to an iron (III) chloride oxidant solution. This technique was used to ensure preferential formation of the 'head-to-tail' coupled polymer, which is untwisted and therefore forms a more planar, compact (and thus more conductive) molecular configuration. This is shown in Figure 2.20. NMR and UV-Vis spectroscopy, and differential scanning calorimetry indicated that they had achieved approximately 85% of the preferred HT coupling (as shown on the left of Figure 2.20).

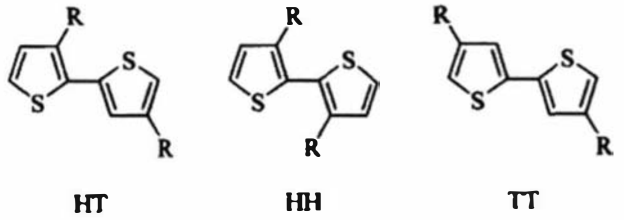


Figure 2.20. Possible linkages of poly(3-alkylthiophene). Head-to-head (HH) and tail-to-tail (TT) are twisted, while head-to-tail (HT) is planar (from Daoud and Xin [108]).

Both of the poly(3-alkylthiophene) variants were deposited (from chloroform solutions) onto nylon knitted fabrics, with poly(3-decylthiophene) giving a surface resistance of 100 Ω/square and poly(3-dodecylthiophene) giving 30 Ω/square. These are very low resistance levels, presumably attributable to the favourable molecular configuration of these regioregular polymers. If such polymers were readily available, this approach would represent an excellent potential alternative to *in situ* polymerisation. No durability assessment of the textile-ICP composites was reported, but as thiophenes, these would be expected to have good environmental stability.

2.2.6 Preparation of Conductive Polymer Textile Fibres.

With a few exceptions, textile fibres are polymers, so an obvious approach when preparing conductive textiles that use ICPs is to bypass the polymer deposition process completely and create fibres directly from the conductive polymer itself. Conductive fibres made in this way could ultimately allow the preparation of pure conductive polymer fabrics, with exceptionally low resistances. Unfortunately, conductive polymers are weak and brittle (certainly by comparison to textile fibre polymers), so this approach has so far had only limited success. As it was not a focus of the experimental part of this thesis, the following review is not intended to be comprehensive, but rather to give an overview of various approaches that have been used.

2.2.6.1 Bi-Component Fibres.

One approach is to create conventional fibres that incorporate a proportion of conductive polymer into their structure during manufacture. Finnish researchers have attempted to overcome the poor mechanical properties of conductive polymers by preparing polypropylene-polyaniline composite fibres [109]. This involved melt-spinning polypropylene with a percentage of a "polyaniline complex" (the latter was presumably a stable, thermoplastic form of polyaniline, but was not described further by the researchers). They varied both the type of polypropylene and the amount of polyaniline incorporated, and measured the mechanical and electrical properties of the resulting fibres. With some sets of conditions, they found discrete 'islands' of polyaniline in a polypropylene matrix; these fibres were weak and non-conductive. The lowest resistance reached was at only 5% polyaniline; this was of the order of 10^8 Ω (resistance measured according to Finnish standard test SFS-EN 1149-1). Non-woven fabrics were then prepared from these fibres, and the fabrics had surface resistances of the order of 10^9 Ω/square. These resistance values are certainly not low in comparison to the other conductive fabrics reviewed in this chapter, being at levels more appropriate for anti-static applications. In fact, the authors noted that fibre manipulation during non-woven manufacturing was made easier by the conductive nature of the fibres and their static dissipation behaviour.

Somewhat more-conductive bi-component fibres were described by Lee *et al.* [110], prepared by the extrusion of a conductive fibre from a mixture of polyacrylonitrile and sulphonated polyaniline dissolved in dimethyl sulphoxide (DMSO). The fibres were extruded into an aqueous acid solution, with a post-extrusion controlled elongation process (called 'drawing') in hot water following immediately. The ratio of polyacrylonitrile to polyaniline was varied from 9:1 to 1:1, while the draw ratio ranged from 5 to 7. Mechanical and electrical properties of the fibres were measured, and selected results are provided in Table 2.8.

Table 2.8. Selected mechanical and electrical properties of polyacrylonitrile/polyaniline fibres (from Lee *et al.* [110]).

Ratio of polyacrylonitrile to polyaniline	Draw ratio	Tenacity (MPa)	Modulus (GPa)	Elongation at break (%)	Conductivity (S/cm)
9:1	5	282.9	5.92	14.2	Not reported
4:1	5	274.8	5.71	13.5	Not reported
7:3	5	253.0	5.63	12.6	Not reported
3:2	5	156.7	4.60	9.2	Not reported
1:1	5	147.4	4.39	8.3	1.92×10^{-3}
1:1	6	162.3	4.21	9.7	2.98×10^{-3}
1:1	7	205.7	5.90	8.3	1.93×10^{-3}

Mechanical properties (tenacity, modulus and elongation at break) deteriorated as the amount of polyaniline was increased. Although not provided as data, a graph in the journal article showed the expected increase in conductivity as polyaniline content increased. The compromise between good mechanical properties (provided by the polyacrylonitrile component) and electrical properties (provided by the polyaniline component) is a fundamental issue for this type of bi-component fibre. Interestingly, the draw ratio had no clear effect on fibre properties – mechanical or electrical.

Takahashi *et al.* [111] also extruded bi-component fibres from a mixture of two polymers: poly(EDOT) that was doped with poly(4-styrenesulphonate) (PSS). This material was obtained from Bayer as a water suspension, and was extruded through a 70-180 μm diameter spinneret into acetone. Extruded fibres were 10 μm in diameter regardless of spinneret size used, because of the low concentration (1.3% w/w) of poly(EDOT)/PSS in the spinning dope. An SEM image of a poly(EDOT)/PSS fibre is shown in Figure 2.21. It had a smooth surface and a uniform diameter along its length, as far as this can be made out for the small amount of fibre illustrated. The electrical conductivity of the fibres ranged from 0.4-1.0 S/cm, which was lower than observed for polyaniline fibres (discussed in the following section), but the polyaniline fibres were substantially coarser. These poly(EDOT)/PSS fibres were also undrawn – their molecular chain orientation (and probably their conductivity) would be improved by fibre elongation (drawing) after extrusion. The mechanical properties of the fibres were not reported.

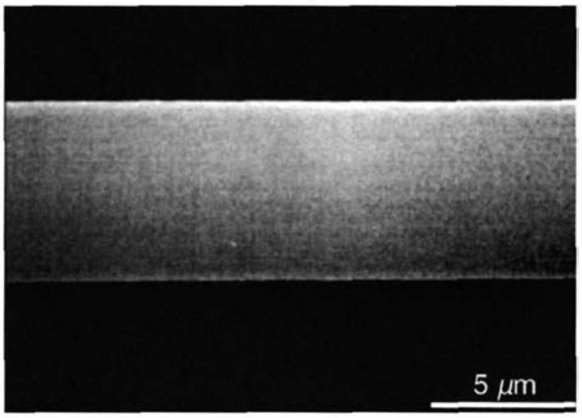


Figure 2.21. Poly(EDOT)/PSS fibre (from Takahashi *et al.* [111]).

An alternative approach was described in US Patent 6,228,492 [112], and summarised in a textile industry journal [113]. It perhaps has more in common with the ICP deposition techniques described in Section 2.2.5, in that the basic procedure was to coat partially solidified melt-extruded filaments with a polyaniline solution just below the spinneret. In a typical example of the process, aniline (or a variant) polymerised by APS was dissolved in xylene, washed in sulphuric acid and water, then distilled to concentrate the polyaniline. This was then applied to melt-spun polypropylene just after extrusion. Application to fibres that had not fully solidified was claimed to achieve better polyaniline-fibre adhesion (presumably on contact with the warm fibres the solvents are evaporated and solid polyaniline re-forms). Under light microscope examination, the fibres appeared to be uniformly coated with a thin layer of polyaniline (0.1-0.15 μm in thickness). Fibre resistivity reached a minimum of about 10^7 Ω/cm; a level probably only suitable for anti-static applications.

2.2.6.2 Pure ICP Fibres.

The ideal approach to the formation of conductive textiles would be to create conductive polymer fibres with adequate mechanical properties to allow them to be further processed. Wang *et al.* [114] reported on an investigation into the formation of conductive polyaniline fibres by spinning from a concentrated (20% w/w) solution of the emeraldine base (EB) form of polyaniline dissolved in *n*-methyl-2-pyrrolidinone. The EB solution was prepared with a gel inhibitor (2-methylaziridine), to allow a stable and homogeneous solution to be prepared at this very high concentration. It was extruded through a single spinneret into water, and kept in water (changed frequently) for more than one week to ensure complete removal of the solvent and gel-inhibitor. The filaments were then thermally stretched. This drawing process increased both fibre strength and Young's modulus, while reducing extension at break. Wide-angle x-ray diffraction revealed no increase in crystallinity in the filament.

Spinnerets of 250-650 μm were used, resulting in rather coarse filaments of 250-635 μm in diameter. The smaller spinneret produced filaments with a higher modulus, due to what the authors described as "enhanced flow alignment of polymer chains" through the smaller aperture. Before measuring the conductivity of the filaments, they were immersed in various acidic media for 48 hours to fully dope them, and vacuum dried to remove any residual moisture. They were tested in this dry state, with best results for benzenephosphonic acid-doped filaments (~10 S/cm), as opposed to hydrochloric acid or acetic acid. The fibres had a micro-porous structure, and the researchers postulated that the more volatile acid dopants had readily escaped the fibre. The porous structure also compromised the mechanical properties of the filaments, and eliminating this characteristic was identified as a major goal. Generally however, the thermal stability and conductivity of the filaments was similar to that of the EB powder starting material. A related patent has been granted [115], and the process further developed [116]. Polyaniline fibres trademarked Panion™ are reportedly commercially available [117] with high conductivity (200-1000 S/cm), and are claimed to have the mechanical properties of nylon.

2.3 Applications of Textile-ICP Composites.

2.3.1 Sensing Applications.

The capacity for conductive polymers to interact with their environment and reflect that interaction in their electrical properties makes them ideal for use in a range of sensing applications. Mechanical and chemical sensing applications have been identified, and these are reviewed in the following sections.

2.3.1.1 Textile Strain Gauge Fabrics.

Several researchers have evaluated textile-ICP composites for use as strain gauges. In a fairly comprehensive review of the work carried out at their laboratory, De Rossi *et al.* described textile-ICP sensor fabrics and an ICP fibre actuator [118] (the latter is discussed more fully in Section 2.3.2). The electro-mechanical sensor fabric was described as a "Lycra fabric" (although it was likely to be a nylon/Lycra® blend; pure Lycra® fabrics being very uncommon) that had been coated with polypyrrole via the Milliken technique [9]. The oxidant used was iron (III) perchlorate, with no additional dopant included. The fabric showed a decrease in resistance with increasing strain, levelling off at high strain, as shown in Figure 2.22.

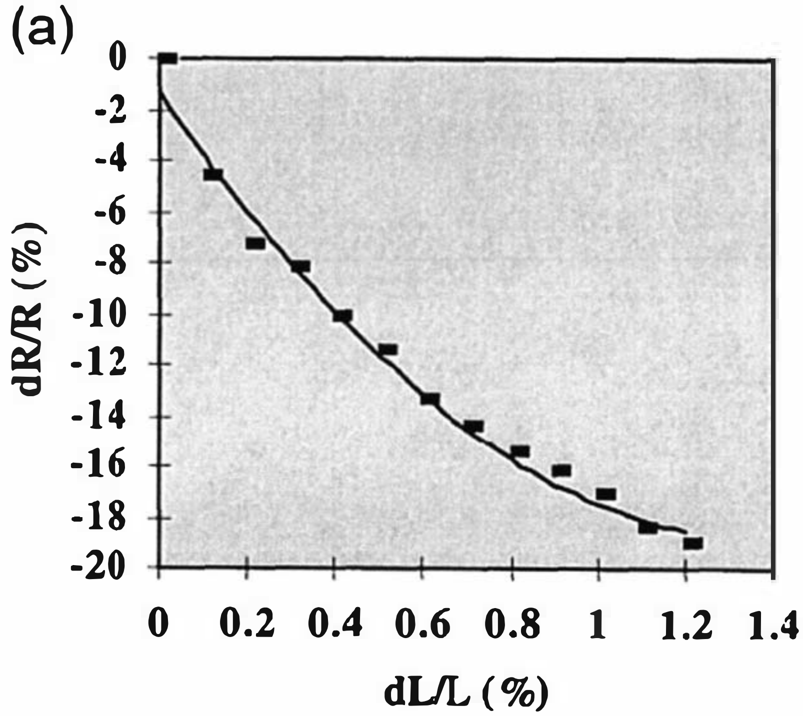


Figure 2.22. Change in electrical resistance (dR/R) of a polypyrrole-coated fabric with elongation (dL/L) (from De Rossi *et al.* [118]).

The authors noted that polypyrrole films behave differently to this, and conclude that "the intrinsic piezoresistivity of PPy can be excluded from being the cause of fabric properties". They also concluded that a progressive increase in the number of contacts between fibres was responsible for the decrease in resistance. This seems very likely, as most fabric deformation does not cause tensile strain on the fibres; rather it tends to cause changes to yarn and fibre geometry (bending and straightening). Exactly the same type of behaviour has been observed by the author of this thesis for fabrics made from conductive metallic or carbon fibres. The presence of an elastomeric fibre (the Lycra® in this fabric) provided recovery from stretch, giving the strain gauge reproducible stretch and recovery behaviour. A glove with sensing elements on each finger was made to demonstrate the potential for textile strain gauges. They also noted that the temperature coefficient of resistance of the material was negative (i.e. resistance decreases with increasing temperature) – a behaviour typical of semi-conductive materials.

In a subsequent paper [119], De Rossi *et al.* described several other textile strain gauge applications. All were prepared from polypyrrole-coated Lycra® fabrics (again probably nylon/Lycra®) prepared by the Milliken technique [9], some having been prepared with patterned polypyrrole tracks or sensors on them via a modified screen printing process (polymer deposition prevented in areas pre-printed with a wax-like 'print-resist' material); a similar approach to another Milliken technique [32]. They noted that the strain-resistance behaviour of the fabric sensors was a decrease in resistance with increasing strain, and the first strain recovery cycle was different to subsequent ones (lower resistance and a slightly different response). This may be partly because the ICP deposition technique was carried out on the fabric, resulting in some polymer accumulation in the fabric interstices, forming linkages between fibres. These conductive linkages were fractured in the first extension cycle, and were of course not re-formed in fabric recovery; hence the first stretch and recovery cycle will have a different response to subsequent ones. The devices described were a multi-sensor equipped glove, a leotard and a car seat. All showed potentially useful behaviour as "man-machine interfaces".

A nylon/elastane fabric was used by Australian researchers to prepare a textile strain gauge [37] by depositing polypyrrole onto it by the Milliken technique [9]. The resulting gauge could undergo repeated strain without mechanical damage, and was able to be used at strain levels up to 60%. The CSIRO/IPRI Intelligent Knee Sleeve was also briefly discussed, (although more fully described in a CSIRO media release [120]), and is shown in Figure 2.23. This device incorporates a strip of conductive polymer-coated elastic fabric linked to an audio feedback system. It is lightweight, wearable and portable, and emits an audible tone that varies depending on the strain level imposed. It is intended as a training aid for Australian Rules football players, to help teach safer techniques when landing after jumping.

Figure 2.23. The CSIRO/IPRI Intelligent Knee Sleeve (from [120]). Sensor is a strip of conductive polymer-coated fabric on the front of the knee bandage.

Other researchers have looked in more detail at the properties of fabrics that could be used as textile strain gauges. Li *et al.* [121] established that vapour deposition of polypyrrole carried out at low temperature (-27°C for 80 hours), resulted in fabrics that had lower strain sensitivity (that is, providing a smaller resistance change for a given elongation) but better cycle-to-cycle repeatability of behaviour than deposition carried out at room temperature. A heat treatment (60°C under vacuum for 40 hours) applied to the ICP-coated fabric gave higher strain sensitivity and better repeatability. It should be noted that in this work the oxidant was applied to the fabric in a 'paste', which was screen-printed onto one surface. As a result, the ICP coating was perhaps likely to be present on one face of the fabric only (that which was printed), and more in the form of a fabric-supported film than a coating around the fibres. One outcome of this was an electromechanical response of decreasing resistance with strain – presumably as the ICP film was stretched.

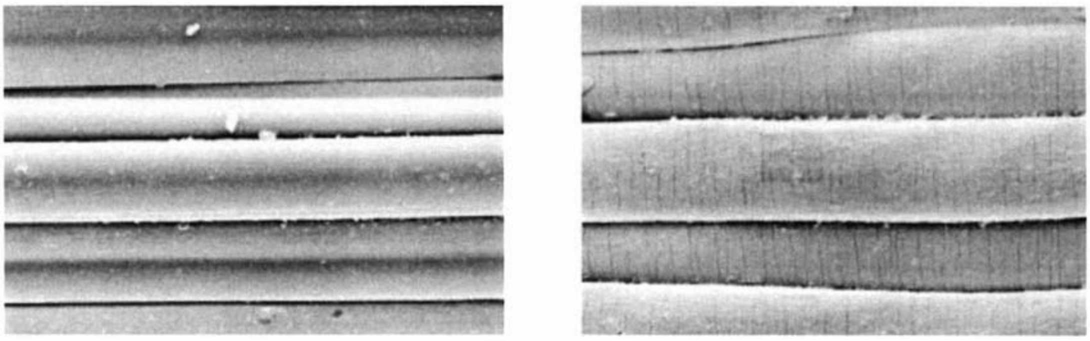
In a continuation of this research [122], the same group used vapour deposition to coat a Tactel®/Lycra® fabric (nylon/elastane) with polypyrrole – this time in such a way to apply a thin, all-over coating to the fibres. They also used the low temperature polymerisation and heat 'annealing' process used previously [121] to try and create an optimised strain gauge fabric. The resultant fabric (which used a bulky dopant anion – dodecyl benzene sulphonate – to improve durability) had good strain sensitivity, reproducibility, and reasonable ageing behaviour (an increase of 25% in resistance over a 9 month storage period). The fabric showed slight temperature sensitivity (resistance decrease of ~25% from 20-60°C), but was insensitive to changes in humidity.

While most researchers have used polypyrrole coatings, an alternative ICP for use in preparing strain gauge fabrics is a colloidal suspension of poly(EDOT) (see Figure 2.4) as a graft copolymer with poly(4-styrenesulphonate) in water. This commercially available preparation (Bayer) was used by Daoud *et al.* to coat a nylon/elastane fabric [123]. The fabric showed an increase in resistance with strain, compared to the typical decrease seen in other research. It is not clear why this would be; most likely it is an outcome of the structure of their substrate (this is not stated), but their explanation for this ("...the applied strain causes an increase in the distance between the delocalised π-orbitals hindering the hopping of electronics across the polymer chains...") seems improbable. It is unlikely that in this fabric deformation (up to maximum 35% strain), the molecular structure of the ICP coating on the fibres is being mechanically strained. Temperature (resistance decrease of 14% from 15-45°C) and humidity (resistance decrease of 50% from 25-90% relative humidity) sensitivity were also observed.

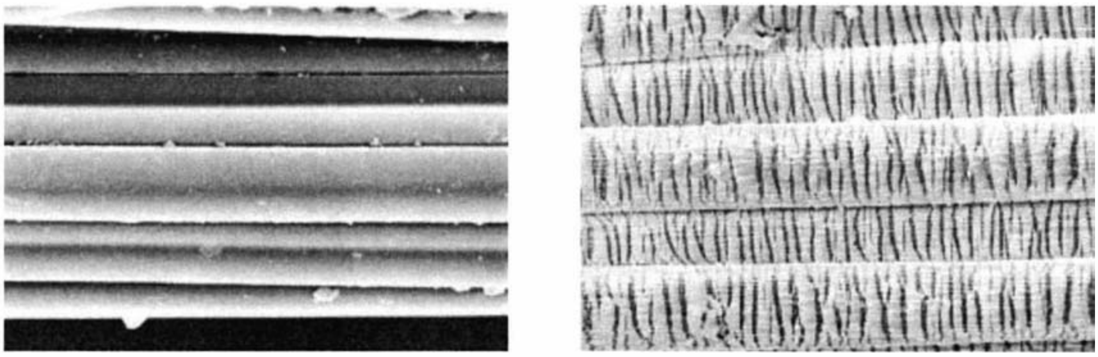
In concluding this sub-section, it is worth also reviewing a remarkably broad application patent [124], in which Smela describes a variety of conductive textile strain gauge constructions and applications. The system includes a "stretchable responsive material with electrical properties that change upon stretching", and a conductive polymer coated fabric is suggested for this purpose (however, the patent attributes a two-step impregnation method to a patent that is, in fact, the Milliken system [12]). Although De Rossi has already described a system that functions in this way [87], Smela argues that his system is wearable, but not portable (although it seems a trivial step to adapt De Rossi's system for full portability, and in fact for any of the applications described by Smela).

2.3.1.2 Textile Strain Gauge Fibres.

Hong Kong researchers have examined the potential use of fibres (as opposed to fabrics) as strain gauge materials [125,126]. Nylon and elastane fibres were coated with conductive polypyrrole via a vapour deposition technique, and a detailed study of the electromechanical behaviour of the fibres was made. As would be expected, the relationship between elongation and electrical resistance is different to the fabric case, with the fibres being directly subjected to tensile stress, rather than simply having their geometry within the fabric structure altered. For both nylon and elastane, resistance increased with elongation, but in different ways. For nylon the resistance increased linearly to twice its original value up to elongation of ~40%, then went to infinity as the fibre ruptured at this point. For elastane there was a non-linear increase in resistance, gradual at first, then more rapid as the fibre reached ~40% elongation (at which point it was still intact, with a resistance 20x its original level). An examination of the fibres under SEM revealed the reason for the different behaviour: as shown in Figure 2.24, there were transverse cracks in the ICP coating on the elastane fibres. As the fibre was stretched, these gradually opened, causing the resistance to increase rapidly. With nylon these cracks were not apparent, and the resistance increase was slower, until fibre breakage.



0% elongation



20% elongation

Figure 2.24. Nylon (left) and elastane (right) fibres coated with polypyrrole (from Xue and Tao [126]).

The cracks were thought to have been generated during the coating process or subsequent handling, and were present only on the elastane fibres because their low tensile modulus meant they were easily deformed, and thus the coating damaged.

2.3.1.3 Other Sensors.

Textile-supported ICPs are also capable of sensing other environmental parameters, such as temperature and humidity, as reported above for polypyrrole [122] and poly(EDOT) [123] coated fabrics. Brooks [127] reports on this behaviour in a research paper that also discusses single crystal organic conductors. The temperature dependence of the resistance of polypyrrole-coated polyester fibres obtained from Milliken Research Corporation was investigated for temperatures below room temperature (down to 4.2K). The resistance increased with decreasing temperature (a behaviour typical of semi-conductor materials; metals show the reverse behaviour) with a linear relationship thus:

$$\ln(R) \propto \frac{1}{\sqrt{T}}$$ where R is the resistance and T is the temperature (K).

The potential for such materials to be used as thermometers for cryogenic purposes was also discussed; advantages being fast response (an outcome of their low mass, and therefore low heat capacity) and small dimensions. The response above room temperature was not reported, but would be of interest in the development of temperature sensors for intelligent apparel systems.

The interaction of chemical species with the ICP coating could also influence its electrical properties, and to this end Collins and Buckley describe fabric-based chemical sensors prepared using a range of fabrics obtained from Milliken Research Corporation [128]. Conductive fabrics of this type provide a large surface area for exposure to chemical species, as well as a thin conductive layer and good mechanical properties. The materials were polypyrrole and polyaniline on polyester and nylon, with aromatic and simple anionic dopants. They also experimented with placing semi-permeable over-layers of non-conductive polymers on the fabrics, to allow selective absorption (and therefore sensing). They found a range of responses to ammonium and nitrogen dioxide vapour in dry air; the latter caused a small, reversible decrease in resistance (it acts as an oxidant, therefore increasing the number of 'hole' charge carriers), while the former caused an irreversible increase in resistance (it acts as a reductant, decreasing the charge carrying capacity). Humidity had a major effect on sensor performance – the chemical warfare agent dimethyl methylphosphonate (DMMP) gave a useful response in dry air, but could not be detected in humid conditions. They managed to achieve a better response in humid air when a polymer (either polyethylenimine or fluoropolyol) over-layer was added.

Hong *et al.* [129] also found ammonia sensitivity in polyaniline-coated nylon, but could not detect either of two other species of interest: carbon monoxide and propane. They experimented with various dopants, and found that (for ammonia sensing) formic acid was the most sensitive (giving a 100% increase in resistance) but was not fully reversible. Trichloroacetic acid was the least sensitive (giving only 1% increase in resistance), but had excellent reversibility. Stussi *et al.* also describe gas sensing using conductive polymer coated substrates (not textiles), prepared by a vapour deposition technique (discussed elsewhere in this review [81]). The system used could easily be extended to textile use, and was capable of discerning between three types of alcohol vapour (ethanol, propanol and butanol) with a response time of less than five seconds.

Polyaniline has found an unexpected use in the creation of fibre-optic-based sensors. This research, carried out as part of the US military's 'Soldier Integrated Protective Ensemble' (SIPE) research program, investigated the potential for incorporating fibre optic sensors for temperature and chemical agents into textiles [130]. Polyaniline coatings on glass were found to exhibit a useful colour change with doping and de-doping using HCl/NH_4OH, and these properties were transferable to a specially prepared fibre optic sensor. The polyaniline replaced the conventional optical fibre cladding, and its colour change influenced the transmission of a signal along that fibre. Optical fibre sensors were ultrasonically bonded to a textile substrate with no apparent damage, but their subsequent sensing behaviour was not reported.

Pressure can also be detected with a deformable conductive substrate. Brady *et al.* reported the development of a 'smart foam', created by depositing polypyrrole into the interstices of polyurethane foam by a form of two-stage impregnation [131]. The foam changed conductivity when compressed, as a result of improved surface contact within the porous structure. One use suggested is as a pressure sensor for shoe insoles to be used to monitor walking posture. It was also suggested that it could be used as a gas sensor (for ammonia in particular), consistent with Collins and Buckley's findings for textiles [128].

2.3.2 Other Applications.

There are numerous other applications for textile-ICP composites, some of which exploit their redox behaviour, while others simply use them as flexible lightweight conductive materials. Many of these applications are described in this section, but this is not intended to be comprehensive.

2.3.2.1 Actuators.

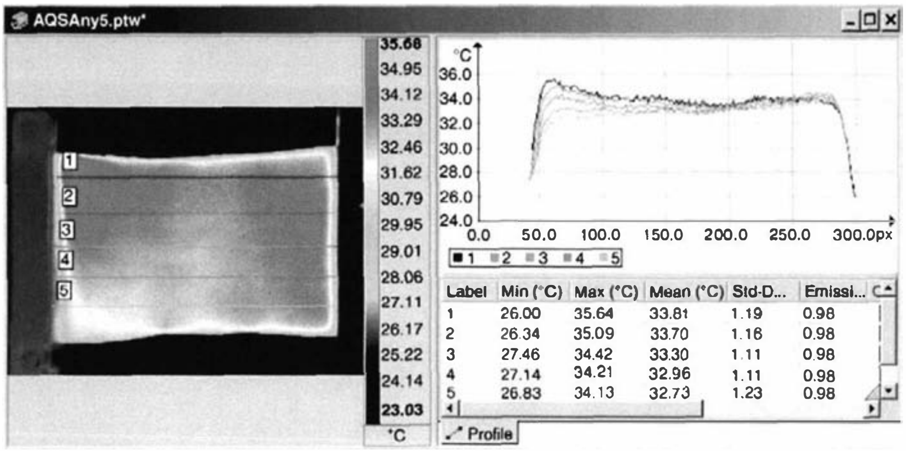
The use of conductive polymer actuators as artificial muscles was discussed by Otero and Sansiñena [132]. The basic mechanism of such systems exploits the redox behaviour of ICPs by moving counter-ions and water in and out of the polymer structure, with a resultant electrically-stimulated volume change. While the devices demonstrated so far have been based on bi-layer films, and have been limited to aqueous environments (where the electrolyte provides a means for ion exchange and water take-up/expulsion), it seems plausible that the bio-mimicry approach could be taken a step further, and fibre-like structures created from which to construct artificial muscles. The fibres could be bi-component (core/sheath, for example), or bundles of fibres could be bound together in a composite. In combination with solid polymer electrolytes [133], a 'dry' system is conceivable. Exactly such a system is in fact proposed by Carpi and De Rossi in their review paper [134]. A great deal of research is going on this area, but further analysis of it is beyond the scope of this review.

Another aspect of the work by De Rossi *et al.* reviewed earlier [118], concerns two actuators, both based on 200 μm, $HClO_4$-doped, polyaniline fibres. The fibre was held in an electrolyte of distilled water and $HClO_4$, with one end anchored to an electrode and the other to a load transducer. A small actuating effect was produced by exchanging ions with the electrolyte in response to applied electrical potential,. The exchanged charge density was 6.7%/(Cmm^{-3}), with an isotonic strain of 0.3% and stress of 3.5 MPa. As a dry system is preferable, they created a solid electrolyte jacket for the second actuator. The electrolyte was based on polyacrylonitrile dissolved in copper perchlorate in propylene/ethylene carbonate. A 50 μm layer of this was placed around the polyaniline fibre. Outside this and in contact with it, an electrode was created, either by deposition of polypyrrole, or by winding a fine copper wire helically around it. An actuation effect could be stimulated by applied electrical potential, with an exchanged charge density of 8.4%/(Cmm^{-3}) and estimated strain and stress of 0.2% and 2 MPa respectively. A wearable device made from bundle of these fibres was attached to a finger, and perceptible stiffening was felt. In conclusion, the authors noted that a better actuation effect may be achieved with a dopant anion other than perchlorate.

2.3.2.2 Heating and Cooling.

One outcome of the flow of current through a material is, if the electrical conditions are suitable, the emission of heat. There are potential applications for flexible, heat-emitting panels in clothing, furniture, bedding and medicine, so several researchers have evaluated the behaviour of textile-ICP composites for this application. One paper related to this has already been reviewed elsewhere [25]; those covered here specifically investigated resistive heating behaviour.

Håkannson *et al.* coated polyester/elastane knitted fabrics [38] with polypyrrole by the Milliken technique [9], varying the dopants employed. These fabrics were assessed by applying a fixed potential difference across a fabric piece (75 x 50 mm) and using a thermal imaging camera (with associated temperature analysis software) to assess the heating behaviour. Thermal imaging is ideal for this type of work, as it quickly highlights uneven heating behaviour across the area of the sample – something that is very difficult to detect with even large numbers of thermocouples. One example is shown in Figure 2.25. The slight unevenness of heating can be seen, although the cool edges are probably simply an outcome of heat loss to the environment being greater in these regions.



Label	Min (°C)	Max (°C)	Mean (°C)	Std-D...	Emissi...
1	26.00	35.64	33.81	1.19	0.98
2	26.34	35.09	33.70	1.16	0.98
3	27.46	34.42	33.30	1.11	0.98
4	27.14	34.21	32.96	1.11	0.98
5	26.83	34.13	32.73	1.23	0.98

Figure 2.25. Heating behaviour of a textile-ICP composite (from Håkannson *et al.* [38]), 30 seconds after the application of 24 V. The horizontal lines on the thermal image are cross-sections illustrated in the graph at top right.

The four dopants used were anthraquinone sulphonic acid (AQSA), naphthalene disulphonic acid (NDSA), *para*-toluene sulphonic acid and sodium perchlorate, and the first three of these gave a useful heating performance. These had power densities per unit area that exceeded 150 W/m^2 (considered the minimum level to be useful). The best performing was AQSA with 430 W/m^2. All maintained a steady heating behaviour over a 100 hour run, although there was a slight decrease in the power density for the AQSA-doped specimen. If this was due to oxidative degradation of the polymer backbone, it would be irreversible damage to the heating panel. The paper does not report if the specimens were re-tested to establish durability for repeated heat-up and cool-down cycles. Similar experimental techniques, and some textile-compatible power connectivity techniques (stitching and metal press-studs), were used in work the same researchers described elsewhere [39]. The connectivity techniques were largely unsuccessful, with uneven heating resulting. In the earlier paper [38], solid metal bars were clamped across each end of the fabric strip to make a good electrical contact.

Bhat *et al.* found that polypyrrole-coated cotton fabrics could also be used as heating panels [40], with many of the same properties observed as for the work described above. They deposited the ICP by the Milliken technique [9], with fabric mass increase from 4.5 to 45%, depending on the monomer concentration used in the polymerisation vessel. They claim that "good fabric properties were still retained up to 60% PPy", but it is likely that a fabric with this loading of polymer deposited onto it would be too stiff and inextensible for typical textile applications. They used a single thermocouple in the centre of the specimen (9 x 5 cm) to measure temperature (which could reach 90°C after 20 minutes with one unidentified fabric and a 9V input), so were unable to see if heating was uniform across the specimen. Their favoured sample was one that had a 35% loading of polypyrrole, as this stabilised at a temperature of 38.5°C, and drew 88.5 mA current at 9 V. Like the previous work, no detail was given of the repeatability of the heating effect for a given specimen.

Generating a cooling effect from a fabric is much more difficult that heating, but is of just as much interest for apparel (to be used in hot environments), or medical applications. The thermoelectric effect (sometimes referred to as the Peltier-Seebeck effect) is used to create a temperature differential across to dissimilar metals (or semiconductors) with an applied voltage, and Hu *et al.* attempted to demonstrate this behaviour for two dissimilar polypyrrole-coated fabrics [135]. One fabric had conductive polypyrrole deposited onto it by the Milliken technique [9], while the other was created by vapour deposition. The former had a resistance that was an order of magnitude lower than the latter. Initially the Seebeck effect (generation of a potential difference with an applied temperature differential) was tested, as this was easier experimentally. They were successful in generating a small voltage (around 0.05 mV) with a temperature difference of 55°C. The Peltier effect (where an applied voltage causes a temperature differential, which could be used for cooling or heating effects) was harder to demonstrate, as the fabrics were insufficiently dissimilar, and their rig lacked sufficient thermal insulation to allow reliable temperature measurements to be made. However, indications were that a slight (albeit transitory) cooling effect did take place.

2.3.2.3 Miscellaneous Applications.

Italian researchers described an application for textile-conductive polymer composites that only indirectly makes use of their conductivity [136]. They found that glass fibre fabrics coated with polypyrrole or other doped conductive polymers performed well at removing viruses from water. The fabric was compared with filter paper onto which polypyrrole had been deposited (both treated by a two-stage impregnation technique), and had superior performance. Fabrics coated with doped conductive polymers were seen as a potential alternative to 'charge modified' filters. In this type of filtration there is an electrostatic interaction between the filter material and the contaminant, and the unique charge distribution properties of conductive polymers can be exploited for this purpose. The conductivity is only measured as a means of assessing the efficiency and reproducibility of the polymerisation. ICP films are likely to behave the same way, but lack the mechanical strength required for this application.

Another filtration application for textile-ICP composites was described by Ding *et al.* [137]. In this work, silk, cotton and linen fabrics were coated with polypyrrole by the Milliken technique [9], then placed into solutions of 10 ppm $(AuCl_4)^-$ with 0.1M HCl or 70 ppm $(Au(CN)_2)^-$ with 255 ppm NaCN. Residual gold concentration in the solution was measured at intervals by atomic absorption spectroscopy. While even the uncoated fabrics recovered gold from the solutions, the efficacy of the coated fabrics was much greater – after 30 minutes the polypyrrole-coated linen fabric had recovered 95% of the gold present, compared with only 5% for the uncoated fabric. While the uncoated fabrics could absorb the gold ions onto the fabric surface, the researchers postulated that when the ICP was present, the gold uptake occurred by a redox mechanism, whereby the ICP was 'over-oxidised' and the gold anion reduced to elemental gold. This appeared to then accumulate in particles on the surface of the fibres, as shown in Figure 2.26.

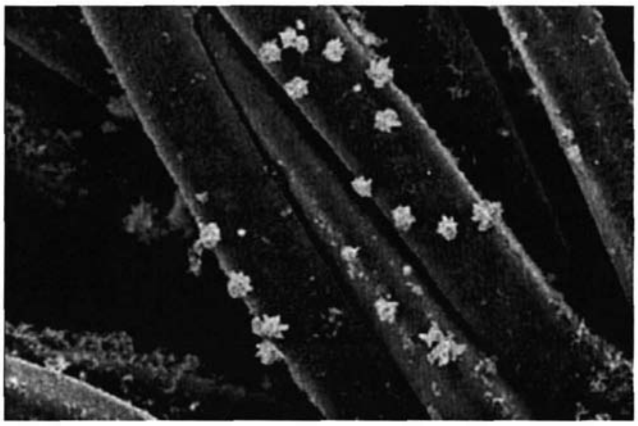


Figure 2.26. Particles (presumed to be recovered elemental gold) present on polypyrrole-coated fibres (from Ding *et al.* [137]).

There is substantial interest in the use of conductive polymers in biochemical and medical applications, including detecting proteins [138], screening for Rhesus antigens [139], stimulation of cell growth via the application of an electrical potential [140], and, in the future, as artificial muscles [132] As many of these applications may involve implantation into the human body, the biocompatibility of conductive polymers is of great importance. Zhang *et al.* [141] have investigated this property for polypyrrole-coated polyester fabrics. Such fabrics allow the formation of structures that would be impossible with an un-supported ICP, because its mechanical properties would be inadequate. The polyester fabrics chosen represent materials that are potentially suitable for the construction of vascular prostheses. They were coated with polypyrrole by the same techniques previously used by these researchers [79], and were assessed in a range of ways that relate to their use as a blood-contacting biomaterial. Full details of the tests are beyond the scope of this review, but the fabrics showed good biocompatibility. They did not cause haemolysis (destruction of blood cells) or alter coagulation properties. They were able to be sterilised with ethylene oxide with acceptable residue levels, and were non-toxic to human umbilical vein endothelial cells.

Continuing the medical theme, Korean researchers examined the suitability of polypyrrole-coated fabrics as electrodes for functional electrical stimulation. Their initial work [142] focussed on quantifying a range of fabric properties that would influence electrode performance, including resistance change with moderate deformation (for which they established that up to 40% extension caused no irreversible change), and stability of current flow (for which they established that over the course of a 10-minute electrotherapy treatment the current would not change). In another paper [102], they reported on a trial using fabric electrodes to apply a TENS (transcutaneous electrical nerve stimulation) treatment to rats. They compared copper-coated fabrics (copper deposited by an electroless plating procedure) with polypyrrole-coated fabrics; these having had the ICP deposited in two steps: via chemical oxidative polymerisation followed by electrochemical deposition (in a similar manner to that described by Kim *et al.* [98]). The clinical tests were designed to determine which of the conventional adhesive electrode, the textile-copper electrode and the textile-ICP electrode were the most effective in treating nerve-damaged rats. The textile-copper electrode had a statistically significant effect (as did the conventional electrode), but the textile-ICP electrode did not, and the researchers concluded that it would be more suitable for applications where a lower-strength electrical pulse is required.

The electromagnetic (EM) radiation shielding properties of conductive fabrics have already been briefly discussed in reviewing a range of papers focussed on ICP deposition techniques [26,54,75,98-101]. One additional paper worth reviewing is that of Håkansson *et al.* [41], where the EM shielding application was assessed in more detail. High total shielding effectiveness levels were achieved with several fabrics (prepared with the Milliken technique [9], with varying dopant levels and ICP deposition times). The behaviour across a frequency range from 1 to 18 GHz is shown for three of these fabrics in Figure 2.27. In these types of materials, a relatively large amount of the shielding effect was by absorption (approximately 45-50% of incident radiation for the three best fabrics), with less from reflection (approximately 20-40% of incident radiation). These combined gave the approximately 70-85% total transmission loss shown in Figure 2.27. By comparison, in metallic materials the very good shielding effectiveness these materials show is almost exclusively due to reflection. This may provide some advantage for the textile-ICP materials in certain shielding applications where 'retro-reflection' needs to be minimised.

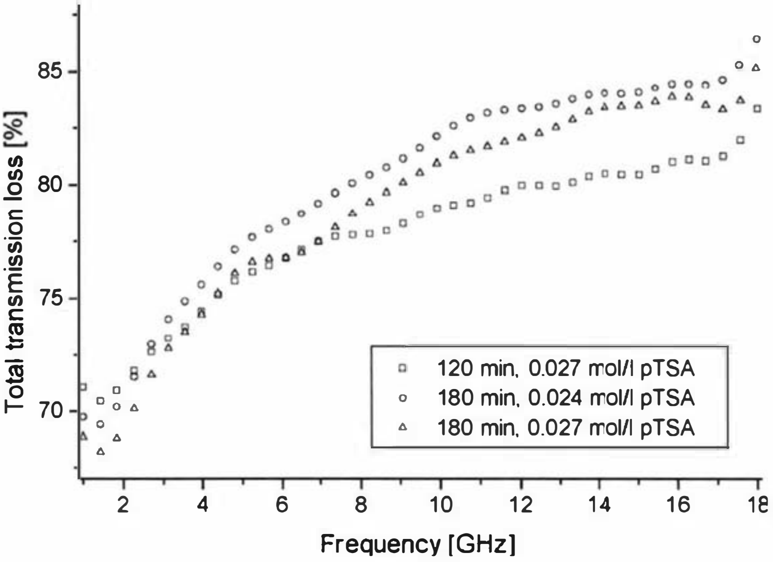


Figure 2.27. Total EM shielding effectiveness for the three best fabrics from [41]. Their dopant (*p*-TSA) concentrations and polymerisation times are shown.

A wide range of current and potential applications for conductive polymers (referred to in their paper as electro-active polymers) were described Carpi and De Rossi in their extensive review of applications [134]. These included strain gauge sensors and actuator fibres, which have been reviewed elsewhere in this chapter. Most importantly, they discussed the general application area of "fiber electronics", where electronic functions are actually embedded into fibres. Power sources are one type of electronic function that could be embedded, and the 'PowerFiber' was described: a fibre battery concept proposed by ITN Energy Systems [143], which schematically is a similar structure to the actuator system proposed earlier (due of course to the fact that both systems are electrochemical devices, so therefore require two electrodes and an electrolyte). Other applications discussed were less reliant on the type of electrically conductive polymers that are the focus of this thesis.

Chapter 3 Research Aims.

The overall aim of this research was to use *in situ* polymerisation techniques to prepare textile-ICP composites with the following properties:

- Moderate electrical conductivity. High conductivity (or low resistance) is useful as it makes more applications possible, but stability and durability at a lower conductivity is probably more valuable. For ease of measurement, surface resistance values in the kilo-ohm to mega-ohm range (that is, from 1×10^3 to 1×10^6 Ω/square) are appropriate. These resistance levels are comfortably within the measurement range of a conventional multimeter.
- Good mechanical properties. The composite should be as close as possible to the original textile in terms of flexibility, extensibility and strength. These intrinsic textile properties are highly desirable features, and should be compromised as little as possible.
- A high level of durability of conductivity to ageing and to typical textile care procedures (such as laundering). A worthwhile goal is that the surface resistance of the composite should not change by more than 10% after 10 domestic wash cycles. Similarly, it should not change by more than 10% after storage in standard conditions (see Section 4.1.3) for 6 months.

To achieve these aims, ICPs based on pyrrole and thiophene were concentrated on. Variants of thiophene (3-methylthiophene, 2,2'-bithiophene and 3,4-ethylenedioxythiophene) were of particular interest because of their expected greater reactivity than thiophene and better durability than pyrrole [4,5]. Aniline was excluded because of its more complex oxidation behaviour.

Secondary aims of the research were to:

- Determine the influence of textile fibre properties on the ICP polymerisation process and the resultant composite properties, as this has not been clearly established.
- Determine the influence of various polymerisation parameters, such as reagent concentration, reaction temperature and additional dopants, on the 'quality' and 'quantity' of ICP deposited.
- Compare the range of possible ICP deposition systems for suitability with textile substrates and potential for commercial scale-up.
- Determine a suitable testing procedure for assessing the influence of ICP deposition on key textile properties (flexibility, extensibility and strength).

- Examine the morphology of ICP coatings on textile fibres; determine coating thickness and the extent to which ICP forms inside the fibre.
- Determine the elemental composition of ICP coatings and estimate their level of doping.

In the early stages of the research, it was intended to investigate the preparation and properties of a particular type of sensor based on a textile-ICP composite: the textile strain gauge. However, as work progressed, it became apparent that it would be much more valuable to focus on creating a durable conductive material that could be used for this and other applications.

Chapter 4 Experimental Work – Basic Techniques

4.1 Fabric Preparation, Handling and Storage.

4.1.1 Specimen Preparation and Identification.

In much of the experimental work reported in this thesis, the same preparation and specimen identification protocols were followed. For many experiments, 40 x 40 mm square specimens were used. This size is convenient to treat on a small scale, and is suitable for the surface resistance measurement technique adopted (see Section 4.3.2). For knitted fabrics, specimens were cut out to exactly these dimensions, with the sides of the square parallel to the courses and wales (for definitions of these and other textile terms see the glossary in Appendix 1). For woven fabrics an alternative approach was used; necessary because the cut edges of woven fabrics often easily fray, and any loss of edge threads during treatment could cause substantial errors in measurement of the mass change of the specimen. For woven fabrics, the specimens were cut out at 45 x 45 mm dimensions, with the sides parallel to the warp and weft yarns. Yarns were then carefully removed from the edges, until the specimen consisted of a central section measuring 40 x 40 mm with a short fringe surrounding it. The remaining edge yarns were essentially protected by the fringe of yarns perpendicular to them, and were therefore much less likely to be dislodged and lost during subsequent processes. An obvious alternative to this would be to overlock the specimen edges, securing the edge yarns in place. However this is an awkward procedure on such small specimens, and also introduces a percentage of fibre (the overlocking thread) that is not representative of the specimen.

Identification of the specimens also presents some challenges. Marking the specimens with an indelible marker of some sort is unhelpful, because the conductive polymers deposited on them are typically dark in colour and would obscure any markings of this type. Also any marking, whether ink from a pen or graphite from a pencil, is effectively adding a surface treatment that may interfere with the way that the ICP is deposited on the substrate, or could even change the electronic behaviour of the composite. Pencil graphite is conductive, so could certainly act in the latter way. Another method would be to attach loops of thread to the specimen, indicating a number that could then be referenced to the treatment applied, but this would be an excessively time-consuming process.

The chosen method was to clip the corners or sides of the specimens in such a way as to make them instantly identifiable from their shape. The area of specimen clipped is away from areas required for surface resistance measurements, and as it is carried out before the preparatory rinse (see Section 4.1.2), does not compromise before and after measurements of mass. Up to six specimens can be distinguished using corner-only clipping. For more than this, notches can be clipped into the sides of the specimens. Figure 4.1 illustrates the identification protocol for up to 10 specimens.

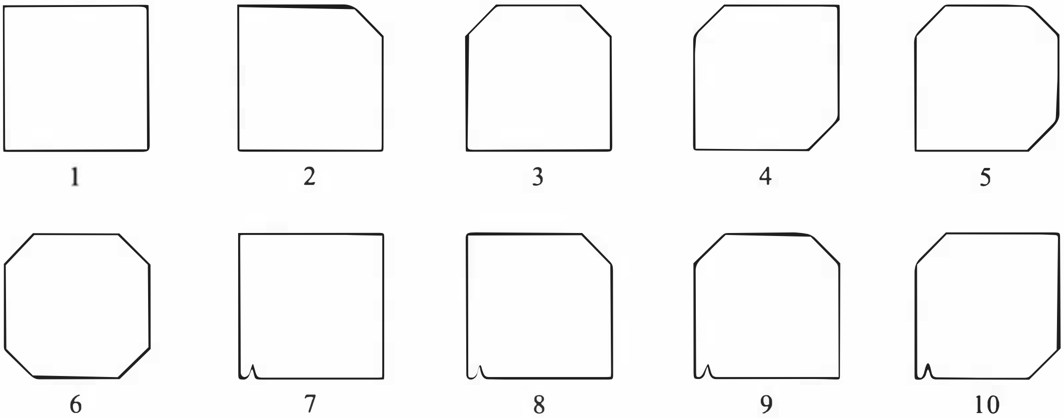


Figure 4.1. Identification protocol for up to 10 specimens.

4.1.2 Pre-Treatment Rinse.

Textiles are often treated with chemical agents to improve processing performance during their manufacture, to impart special attributes or to improve customer appeal at point of sale. Generally these are treatments to modify surface properties. For example, lubricants are added during early-stage processing of wool to help reduce mechanical stresses on the fibre during carding. These are often mineral oils, which can be removed by subsequent wet finishing processes. Similarly, synthetic multi-filaments have a 'spin finish' that has a lubricating and anti-static effect to aid in subsequent processing. Cotton yarns to be woven into fabrics are often 'sized' – impregnated with a substance which makes the surface fibres adhere to one another, thus improving the abrasion resistance of the yarns and their weaving performance. Yarns for knitting are usually waxed, to lubricate them as they pass over the many guides and knitting elements involved in manipulating yarns on a knitting machine. An example of a finish that is imparted to give a special fabric property is the use of agents to improve the 'wicking' behaviour of a textile for active sportswear or next-to-skin use (wicking is the spontaneous dispersion of liquid moisture, such as perspiration, through a material). Furthermore, fabric softeners (typically cationic surfactants) are often applied to fabrics to improve their handle (the way they feel) at point-of-sale.

These treatments are often not intended to be durable. Efforts are made during late-stage processing to remove the agents that were added to improve processing performance, although some residue can remain through to the finished fabric. Fabric softeners added to improve point-of-sale appeal are often removed in the first wash of the product, and even finishes intended to improve fabric performance may be removed after several laundering cycles. Regardless, the presence of these finishes means that the properties of the constituent fibre polymer are not the sole influence on the deposition and subsequent behaviour of surface coatings such as conductive polymers. A certain behaviour observed for a fabric may reflect the surface finish, rather than the fibre type. For this reason, in all of the work reported in this thesis, a pre-treatment was carried out on all fabric specimens to remove any non-durable finishes. The fabrics were chosen to not have any unusual finishes present, so after pre-treatment the fabric behaviour can be considered to be representative of its fibre type and construction, and not of surface treatments. The pre-treatment process described here also has the effect of dislodging any loosely adhering fibres or yarns. This prevents their loss during polymer deposition, where they could introduce errors in the measurement of polymer mass add-on.

The pre-treatment was carried out as follows:

1. Specimens were immersed in a large excess of acetone, and gently agitated for several minutes.
2. They were then removed and placed flat on clean glass sheets under a fume hood, and the acetone allowed to fully evaporate.
3. When free of acetone, the specimens were immersed in a large excess of de-ionised water, and agitated for several minutes.
4. The specimens were then removed from the water and pressed against absorbent paper, before being placed onto clean glass sheets and allowed to dry at room temperature.
5. When dry, they were placed into a room which is maintained at 65% relative humidity (± 5%) and 20°C (± 2°C). These are the standard conditions for textile testing, as set out in ISO 139:2005 [144]. This is discussed in more detail in the next section.

The choice of solvents was partly based on the literature. Xu *et al.* used an acetone rinse to prepare yarn for conductive polymer deposition [77], although most researchers have not detailed what preparatory measures were undertaken, if any. Use of an organic solvent followed by water was intended to remove as wide a range of non-durable agents as possible. Note that the use of a detergent to aid this process was avoided, in order to prevent any surfactant residue being left on the specimens, as this could strongly influence polymer deposition.

4.1.3 Standard Conditions.

On most occasions, the next step before carrying out conductive polymer deposition was to allow the specimens to remain in the standard conditioned room for at least 24 hours before weighing them (the initial mass of the specimen was compared with the mass after polymer deposition, to calculate the polymer mass add-on). All measurements were made on specimens after a minimum of 24 hours in the conditioned room, because many textile materials have properties (including mass and electrical properties) that vary substantially with moisture content, and the variable ambient conditions in an uncontrolled environment introduce errors to measurements made in those conditions. As an example of how textile properties can change depending on the moisture content of the atmosphere, Table 4.1 provides moisture content data for some of the fibre types used in this work.

Table 4.1. Moisture content of textiles (from WIRA Textile Data Book [145]).

Fibre type	Standard moisture content[1]	Mass of a specimen[2] at 20% RH	Mass of a specimen[2] at 80% RH
Nylon	4.31%	9.70 g	10.10 g
Polypropylene	0.10%	10.00 g	10.00 g
Polyester	0.40%	9.97 g	10.01 g
Acrylic	1.48%	9.91 g	10.09 g
Wool	14.53%	9.15 g	10.23 g
Cotton	7.83%	Data not available	Data not available

Notes:

1. The standard moisture content is simply the mass of water in the material as a percentage of its total mass (textile + water), under standard conditions. Another term that is regularly used is 'regain'. This is the mass of water in the material as a percentage of its dry weight.
2. A 10 g specimen at standard conditions.

As the data in Table 4.1 indicates, the mass of a small specimen of wool fabric can vary by more than 10% in two environments that are not particularly extreme. This is because the natural fibres are hygroscopic, due to polar groups in their molecular structure. They readily absorb moisture vapour from the environment, the amount depending on the humidity (i.e. the moisture content of the air). The synthetic fibres are much less sensitive, but even the mass of a nylon specimen can vary by about 4% and acrylic by about 1%. With single depositions of ICP likely to be as low as one or two percent mass add-on, it is obviously important that the mass of the specimens is always measured in the same environment. In addition, some conductive polymers have polar chemical groups (such as the –NH groups in polypyrrole) that result in hygroscopic behaviour. Measurements of polymer mass add-on and surface resistance that are not carried out in standard conditions, on specimens that have equilibrated with that atmosphere, may have significant errors due to the variable moisture content in the substrate and polymer.

Another excellent reason for carrying out all testing on specimens that are in equilibrium with standard conditions is the possibility of the conductive polymer having electronic behaviour that varies with moisture content and temperature. Several researchers have highlighted the moisture and temperature sensitivity of polypyrrole, for example [127,128]. The resistance of polypyrrole is lower when its moisture content is higher, and, as has been discussed above, it is capable of absorbing moisture from the atmosphere. Also, as semiconductors, conductive polymers have a positive thermal coefficient of conductivity [86,118] (in comparison, metals are known for having a negative thermal coefficient of conductivity, hence they become super-conducting at extremely low temperatures). At higher temperatures conductive polymers have lower resistance, and vice versa. Although the difference in resistance is not likely to be great across normal laboratory temperature conditions (perhaps fluctuating across a range of 15-30°C), it is still sensible for all comparisons of the surface resistance of textile-ICP composites to be carried out in standardised conditions of temperature and humidity. It should be noted that for the thiophene-based conductive polymers that are the focus of this work, moisture sensitivity is likely to be less important, as they are unlikely to be hygroscopic to any great degree. They could still exhibit temperature sensitivity, so it is essential to carry out their assessment in controlled conditions.

4.1.4 Storage.

When no longer required for on-going measurements, the textile-ICP composite specimens were retained in ambient laboratory conditions, away from direct light and heat sources. Usually they were kept in clearly identified 'snap-lock' plastic bags, and they were always handled with clean laboratory forceps to prevent contamination. The storage and handling of a typical specimen is shown in Figure 4.2.

All of the specimens prepared during the work described in this document have been retained, except where destructive testing of them (such as microanalysis) has been carried out.

Figure 4.2. Handling and storage of a typical textile-ICP composite specimen (polyester interlock fabric with poly(EDOT) deposited on it).

4.2 Standard Fabrics.

Early in this work, it became apparent that one of the key variables to address in the development of a technique for preparing textile-ICP composites is the influence that the fibre type has on the properties of the composite. All textile fibres are based on polymers (except carbon fibres, mineral fibres and glass), but they all have different chemical and physical properties, and different morphologies (some of these differences are discussed in Appendix 2). These differences also have an impact on the type of fabrics that tend to be available made from certain fibre types. Often, cotton and polyester fabrics are made to be smooth and lightweight, while acrylic and wool fabrics tend to be softer and loftier. In both cases, this reflects the typical end-uses and exploits the fibre properties, for example wool's natural crimp, which makes wool fabrics soft, resilient and bulky. Similarly, cotton's fineness and absorbency results in it being found in thin, smooth-surfaced fabrics. The result of this is that it is very difficult to investigate the effect of fibre type in the fabric, because of the presence of other variables related to the fibre diameter, yarn linear density and twist, as well as fabric weight, tightness and structure.

One option would be to carry out an investigation into the effect of fibre type by treating single fibres of different types and measuring electrical properties. This would be quite difficult and time consuming, given the dimensions of fibres (typically < 20 μm in diameter and a few centimetres in length), and, for natural fibres, the variability between fibres of a certain type. An easier approach is to select fabrics that have been deliberately prepared, as far as possible, to be equivalent in every property except fibre type. Using commercial fabrics is not feasible, as it has proved impossible to get fabrics that are at all close to equivalent. Manufacturing them to a strict specification at the WRONZ processing plant was also an option, but would have been expensive and time consuming. Fortunately, other textile researchers and testing laboratories have also found a need for equivalent fabrics with different fibre types, so it was possible to carefully select and purchase 'standard' fabrics, intended purely for testing and research purposes. These are similar enough to allow direct comparisons of fibre type to be made.

For this work, seven fabrics were purchased from Testfabrics Ltd (West Pittson, Pennsylvania, USA), and used in much of the research described in this thesis. They are referred to as the 'standard fabrics', and were selected from Testfabrics' range to represent seven different fibre types (including all those in common use), with both synthetic and natural fibres represented. Basic variants of each fibre type were chosen, with no non-circular fibre cross-section variants of the synthetics included, and no fabrics with special finishes.

The yarns in the fabrics were all spun from staple fibre (that is, discrete lengths, like natural fibres) rather than continuous filament. The fabrics were all plain weave construction (the simplest weave structure), which is shown in Figure 4.3. The fibre diameter and the fabric area density (usually referred to as the fabric 'weight') were chosen to be as similar as possible for all fabrics. This means that the fabrics all provide approximately the same fibre surface area for polymer to be deposited upon per unit mass of fabric.

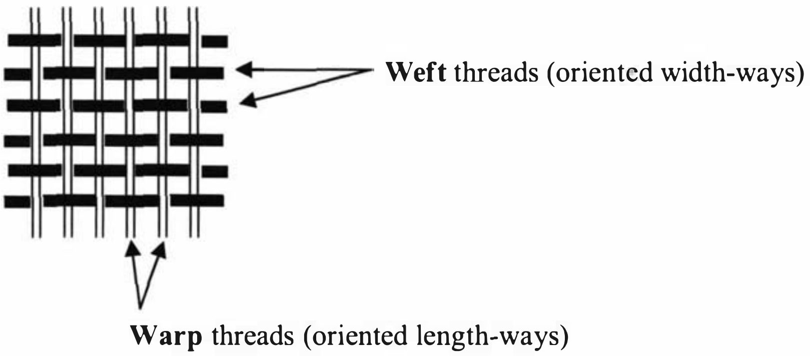


Figure 4.3. Plain weave structure (chosen for all standard fabrics).

Although the nominal fabric weight was provided by Testfabrics, it was sensible to confirm this by measurement, and also to confirm that the fibre diameters were similar. Fibre diameter was measured in the WRONZ Testing Laboratory, using the OFDA apparatus. This is a system for automated measurement of fibre diameter, using a computer controlled image analysis technique. The test is carried out on a small snippet of fibres taken from the textile, according to the standard test method [146]. Fabric details and weight measurements are provided in Table 4.2.

Table 4.2. Fabric description and mass per unit area (weight).

Style #[1]	Description[1]	Code	Nominal weight[1] (g/m^2)	Measured weight[2] (g/m^2)
361	Spun nylon 6.6 DuPont type 200	N	124	134
983	Spun polypropylene fabric	P	170	196
777	100% Dacron Type 54 (polyester)	D	126	126
864	Spun Orlon Type 75 (acrylic)	O	135	161
537	ISO wool adjacent fabric	W	Not given	135
493	60 x 60 cotton sheeting	C	151	153
978	Glass fabric	G	122	209

Notes:

1. Taken from the Testfabrics catalogue.
2. Based on the mass of a 10 x 10 cm square of fabric in standard conditions (20°C, 65% relative humidity).

Some of the fabrics differed substantially from their nominal weights. However, there were five of the fabrics (N, D, O, W, C) that fell into a fairly narrow weight range: about 135-160 g/m^2. The polypropylene and glass fabrics were a little further outside this range, which must be considered during the analysis of results.

The fabric specific surface area (α, the total fibre surface area per unit mass) was calculated from a formula derived as follows:

$$\alpha = A / m \qquad (1)$$

where A is the total surface area of fibres in a piece of fabric, and
m is the mass of the same piece of fabric.

$$A = \pi \, . \, d \, . \, \ell \qquad (2)$$

where d is the average fibre diameter, and
ℓ is the total length of fibre in the piece of fabric.

Also we can use the total fibre volume, V:

$$V = \pi \, . \, (d/2)^2 \, . \, \ell \qquad (3)$$

and:

$$V = m / \rho \qquad (4)$$

where ρ is the fibre density.

Equating (3) and (4) gives:

$$m / \rho = \pi \, . \, (d/2)^2 \, . \, \ell \qquad (5)$$

Rearranging (5) yields:

$$\ell = m / [\rho \, . \, \pi \, . \, (d/2)^2] \qquad (6)$$

Substituting (6) into (2), and rearranging gives:

$$A = (4 \, . \, m) / (\rho \, . \, d) \qquad (7)$$

Making the obvious rearrangement to (1) and equating with (7) yields a simple formula for the fabric specific surface area, thus:

$$\boldsymbol{\alpha = 4 / (\rho \, . \, d)}$$

Table 4.3 contains these data for the standard fabrics.

Most of the fibre types had similar fibre diameter measurements, with the range being approximately 11-20 μm. The extremes are the polypropylene and glass fabrics, as they were for fabric weight. It was expected that the variability of the wool and cotton fibres would be higher than that of the synthetic fibres, but this has not proved to be the case. The CV (defined in Note 1 under Table 4.3) of the natural fibres is lower than that of acrylic (O), and that of glass (G). The glass fabric was heavier than required for comparative purposes and its fibre diameter was by far the lowest, so it was likely to be of limited use. The fabric specific surface area values were quite similar, with a range of 0.147 to 0.247 m^2/g, and again the glass fabric was an extreme value. Wool was slightly lower than the others, but the closeness of the values across the range (excluding glass) provided some confidence that comparisons made between these fabrics would largely reflect the different fibre properties, and not fabric structural differences.

Table 4.3. Fibre density, diameter and calculated fabric specific surface area (α).

Code	Fibre diameter			Fibre density [147] (g/cm^3)	Fabric specific surface area (m^2/g)
	Mean (μm)	Standard deviation (μm)	Coefficient of variation[1]		
N	16.32	3.22	19.8%	1.14	0.215
P	20.50	2.76	13.4%	0.90	0.217
D	12.63	2.00	15.8%	1.38	0.229
O	13.98	3.98	28.5%	1.16	0.247
W	18.43	4.32	23.4%	1.31	0.166
C	13.16	3.66	27.8%	1.55	0.196
G	10.85	5.86	54.0%	2.50	0.147

Notes:

1. The coefficient of variation (CV) is a commonly derived parameter for fibre diameter measurements. It is the standard deviation expressed as a percentage of the mean and is a useful way of comparing the variability of samples with different means.

One limitation of the fabric specific surface area calculation is that it does not take into account the degree of accessibility of the fibre surfaces. In some structures with identical fabric weight, fibre type, and fibre diameter, the fabric may be so tightly constructed as to restrict access to fibres that are not on the surface of the fabric or yarn. For the fabrics chosen here, only the glass fabric appeared to be more tightly constructed than the others. All the other types were very similar in tightness, so the specific surface area comparisons should be valid.

Scanning electron microscope (SEM) images were used as a means of examining fibre and ICP coating morphology throughout this work, and were taken of the standard fabrics (shown in Figures 4.4 to 4.9). These fabrics were sputter-coated with gold before the SEM work was carried out, although even with this in place, capturing good images of some of the fibres was difficult. Standard fabric P (polypropylene) is absent from the SEM images as it was not used for SEM imaging at any stage during the work.

Another fabric was used regularly throughout this work: a polyester knit fabric in a structure called interlock. Knit fabrics are easier to handle in many of the experiments as they generally do not fray, and the interlock structure is particularly good in this regard. It is referred to as a 'balanced structure', and as such does not have the edge curl that many knit fabrics show. It was a lightweight fabric (~150 g/m^2) obtained from a local fabric importer. As such, its commercial specification (which might include the yarn linear density, the fabric 'tightness' and its finishing processes) is not precisely known, but its structure (interlock) and composition (100% polyester) has been confirmed. An SEM image of this untreated fabric is also provided, in Figure 4.10.

Many of the images in Figures 4.4 to 4.10 show a degree of loose material on the fibre surfaces. These could be the remnants of fabric finishes, such as delustrants or lubricant powders. In the case of the natural fibres, they may be scale fragments on the wool or foreign vegetable material (known as 'trash') on the cotton fibres. The preparation routine (described in Section 4.1) was intended to remove much of this material, which could otherwise interfere with the chemical or physical properties being investigated.

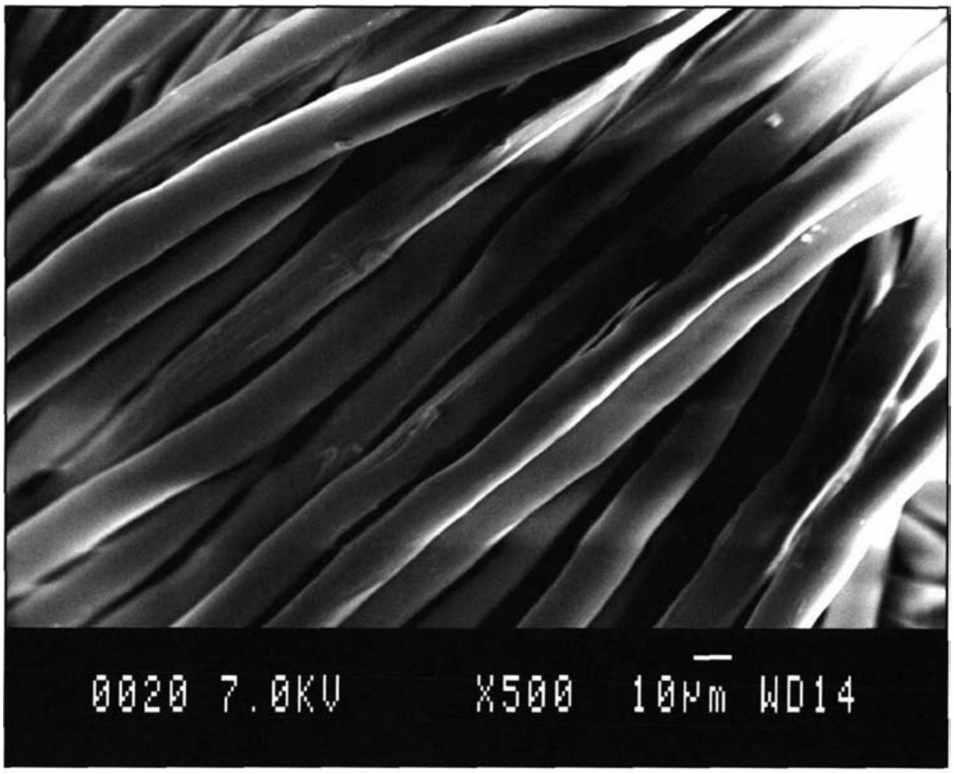


Figure 4.4. SEM image of nylon standard fabric (N).

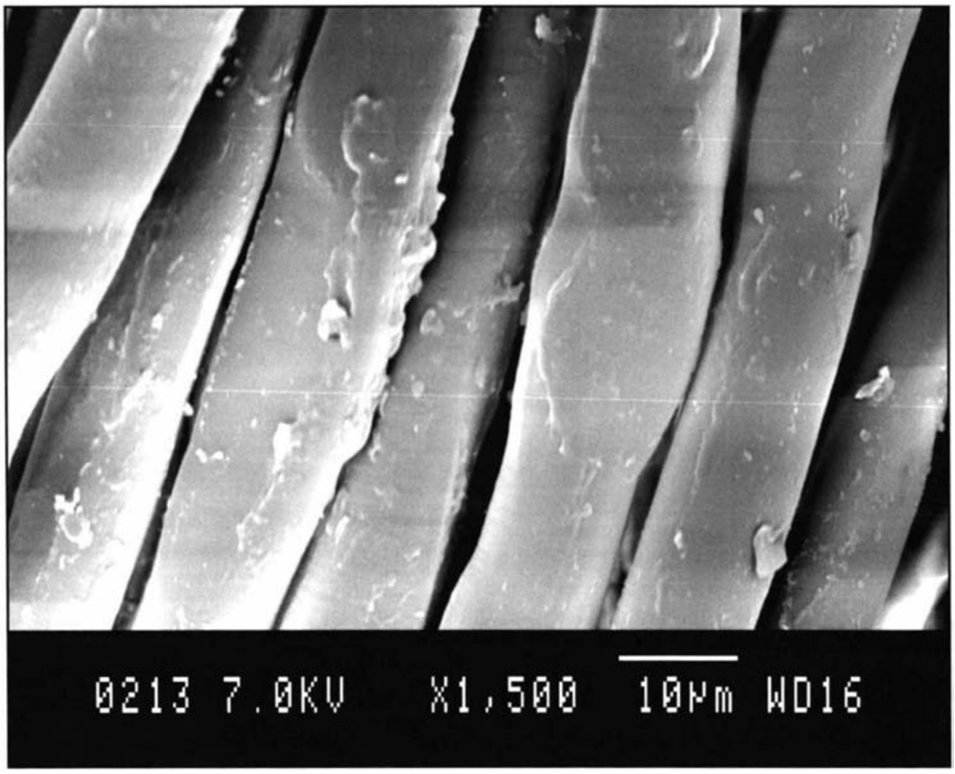


Figure 4.5. SEM image of polyester standard fabric (D).

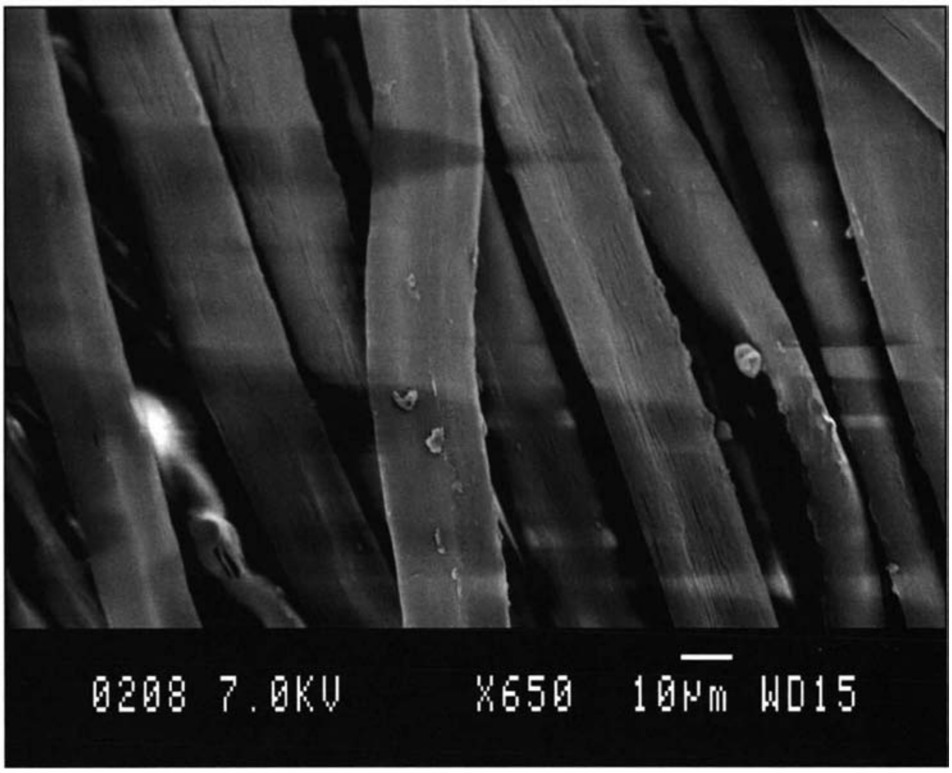


Figure 4.6. SEM image of acrylic standard fabric (O).

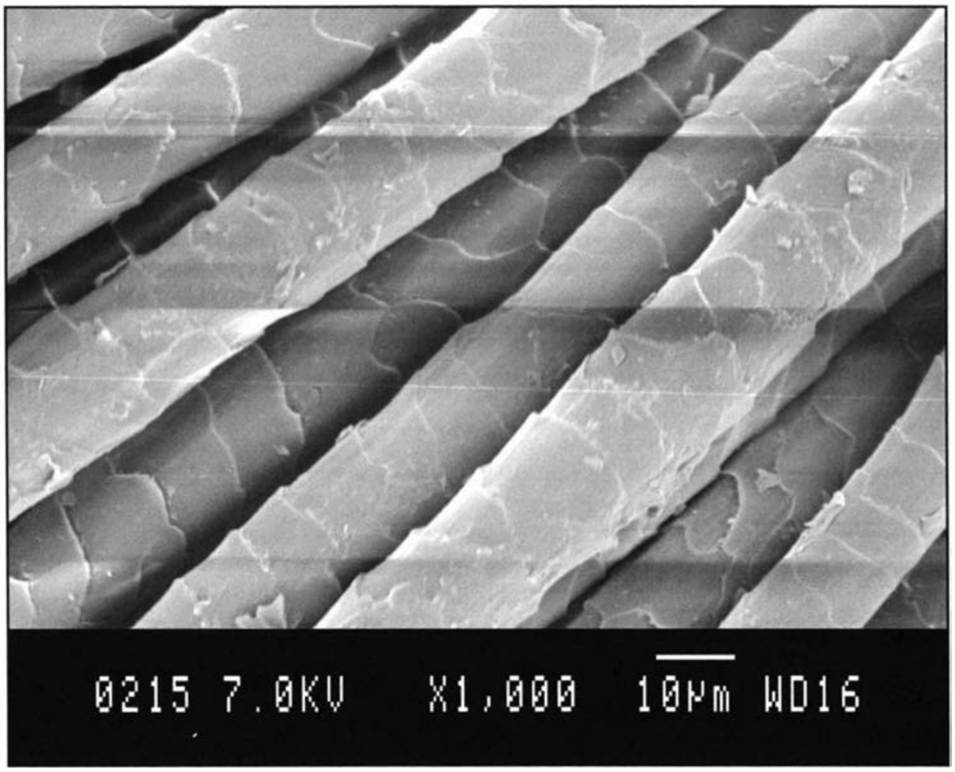


Figure 4.7. SEM image of wool standard fabric (W).

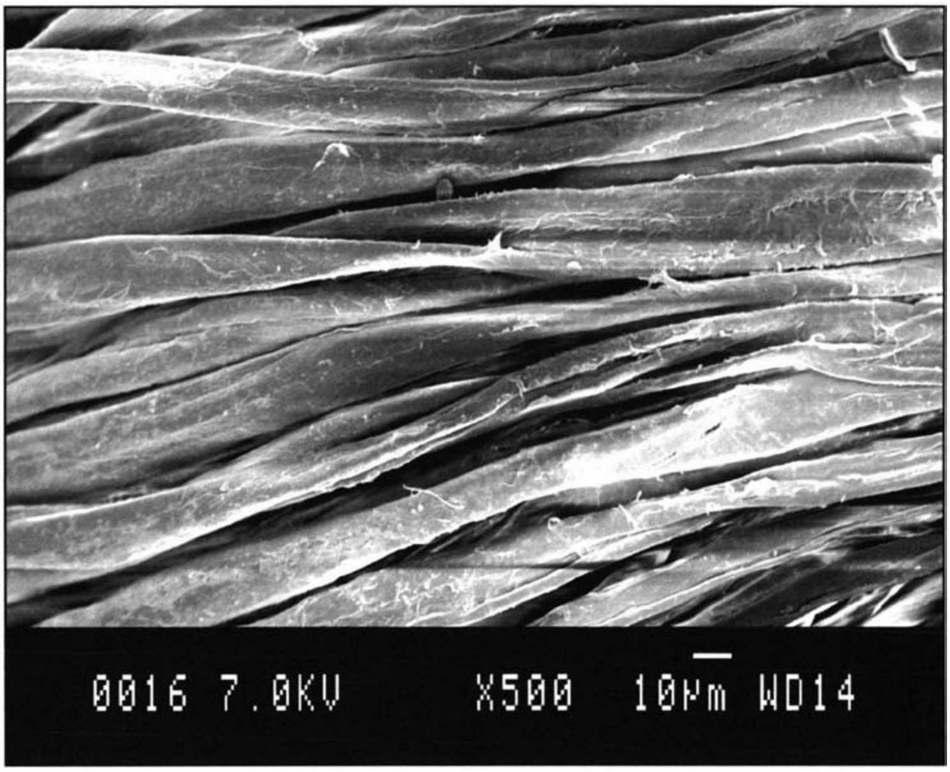


Figure 4.8. SEM image of cotton standard fabric (C).

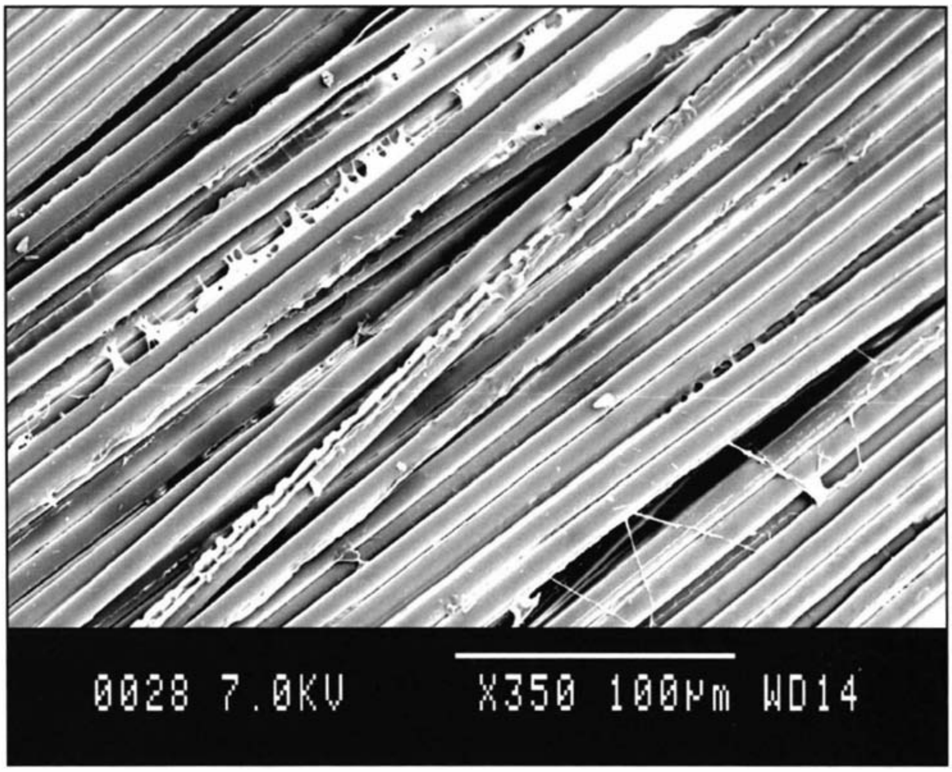


Figure 4.9. SEM image of glass standard fabric (G).

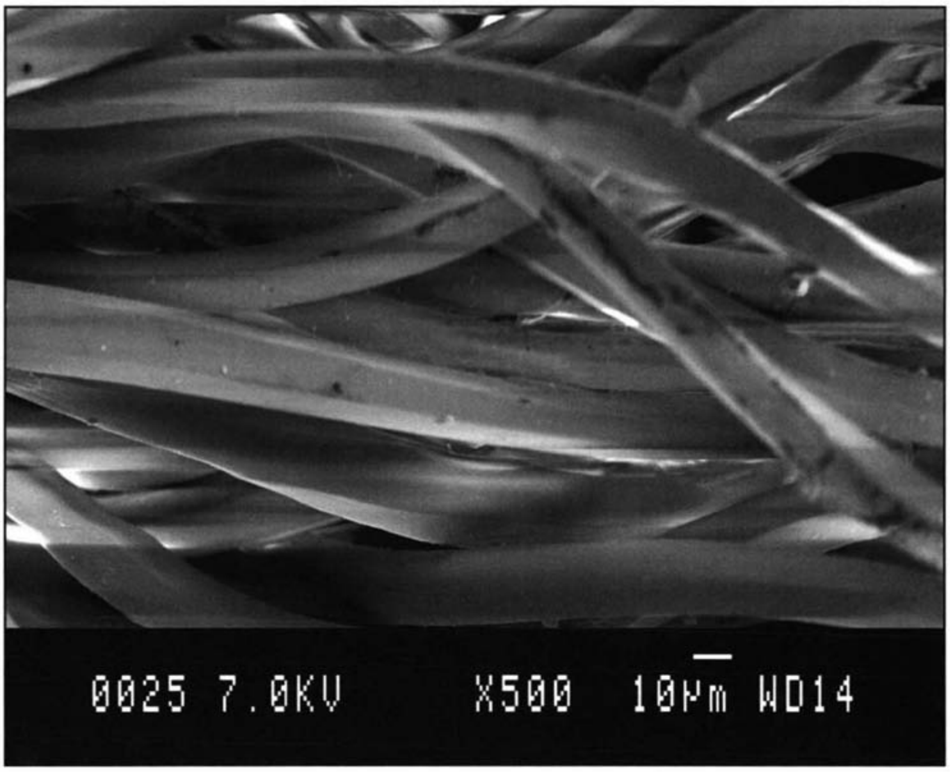


Figure 4.10. SEM image of polyester interlock fabric (P INT).

4.3 Measurement of Specimen Parameters.

Throughout the work reported in this thesis, two key parameters were used to determine the efficacy of polymer deposition onto textile specimens: the amount of polymer deposited onto the substrate, and the electrical properties of the resultant textile-ICP composite.

4.3.1 Measurement of Mass Add-On.

This is simply the difference in sample mass from before to after ICP deposition, expressed as a percentage of the initial mass, i.e.:

$$\Delta M = \frac{m_f - m_i}{m_i} \times 100$$

Where ΔM is the percentage mass add-on,

m_f is the mass of the specimen after ICP deposition, and

m_i is the initial mass of the specimen.

Mass add-on can also indicate how the mechanical properties of the specimen may have changed. A high mass add-on is likely to lead to a stiffening of the fabric, as the interstices in the structure become occupied by ICP. A low mass add-on is more likely to retain the mechanical properties of the underlying substrate. It is likely that specimens having a higher mass add-on will have lower electrical resistance, as there is more conductive material present through which a current can flow. However, mass add-on does not provide any indication of the 'quality' of the deposited ICP, so it is possible that this direct relationship will not hold.

A four-decimal-place analytical balance was used for specimen mass measurements, giving an error in each measurement of ± 0.00005 g. If we consider a typical specimen mass of ~0.2 g and a typical mass add-on of ~3% (giving a typical mass change of ~0.006 g) we can analyse how the error propagates through the mass add-on calculation:

- As stated, the specimen mass (in g) has a maximum error of ± 0.00005 in 0.2 g (0.0025%)
- Therefore, the mass change (in g) has a maximum error of ± 0.0001 g (= 2 x 0.00005 g) in 0.006 g, which is 1.67%.
- Therefore, the proportional mass change has a maximum error of ± 1.6725% (= 1.67 + 0.0025).
- Therefore the mass add-on percentage itself also has an error that is of the order of 1.67% (that is 1.67% of 3% mass add-on, so 3% ± 0.05%, not 3% ± 1.67%).

If this analysis is repeated with a much lower mass add-on, such as 0.5%, the error in the mass add-on is of the order of 10% (that is, the mass add-on would be 0.5% ± 0.05%); for a much larger mass add-on, such as 20%, the error in the mass add-on is of the order of 0.05% (that is, the mass add-on would be 20% ± 0.01%). These errors should be taken into account when considering the differences between mass add-on results. In general, small differences are treated with caution.

In all experiments reported in this thesis, the mass add-on was calculated on the whole specimen, before removing samples from it for further analysis.

4.3.2 Measurement of Surface Resistance.

The most important parameter (of those which it is feasible to routinely measure) is the electrical resistance of the textile-ICP composite. The SI unit for electrical resistance is ohms (Ω), defined by the statement that the potential drop across a resistor is directly proportional to the current flowing across it. The ratio of current to potential drop is the resistance.

In order to define the resistance of a material, rather than a specific object, it is necessary to consider the specific resistance, or resistivity, as it is known. Resistivity is defined by the statement that the electric field at a point in a resistive material is proportional to the current density at that point. Resistivity is the ratio of the electric field to current density. Unit analysis reveals that the unit for resistivity is ohm-metres (Ω·m).

The conductivity is simply the reciprocal of resistivity, and therefore has the unit 'reciprocal ohm metres'. A reciprocal ohm is sometimes referred to as a 'mho', but the SI unit for conductivity is siemens per metre (S/m), although for small specimens S/cm is used.

The most common technique for measuring the electrical properties of conductive polymers is the four-point probe measurement of conductivity, where two outer probes supply current, and the two inner probes measure voltage. However, on an irregular sample such as a piece of fabric, it seemed more appropriate to use a fabric surface resistance technique. This could have been done in a variety of ways, and while it may have been sufficient to develop a method specific to this work, there are at least two standard methods that could be used: BS6524 and AATCC Test Method 76-1995 [148,149]. These are, in principle, the same, and specify either a concentric or parallel two-electrode arrangement. In both cases, the resistance of the fabric is measured by placing an electrode assembly on the fabric, and directly measuring the electrical resistance between the positive and negative electrodes with an ohmmeter.

The concentric ring electrode method is particularly useful, in that it is non-destructive. The electrode assembly can be placed on a fabric sample that is of any size, provided it is larger than the assembly. In comparison, the parallel electrode method requires that the specimen be no wider than the length of the electrodes, so specimens must either be prepared to an exact size, or cut from a larger piece. The parallel electrode method does, however, have the advantage, provided the separation of the electrodes is identical to their length, of giving a direct measurement of surface resistance in 'ohms/square', while an additional calculation is required for the concentric ring electrode system. Also, a standard assembly for the concentric ring method is quite large (about 8 cm in diameter), whereas the parallel electrodes can (in principle) be any size and separation. In theory, the surface resistance of a square sample across opposite edges is the same regardless of the size of the square [150], so a small assembly can be used with small specimens.

(Aside: The unit 'ohms/square' seems unusual. An explanation of its derivation is beyond the scope of this work, but it has been argued that the units of surface resistance could be simply expressed as 'ohms'. However, ohms/square is the accepted unit for this parameter and is recommended by key researchers in the field [26], so has been used throughout the work described in this thesis).

After considering the advantages and disadvantages of the two methods, it was decided to use a small parallel electrode assembly. This is shown in Figure 4.11, placed on a strip of ICP-coated fabric. The strip width (and length of the electrodes) was 1.5 cm, and the electrodes were 1.5 cm apart. The electrodes were brass, and were profiled to give a narrow line contact with the specimen. They were separated by a plastic (highly resistive) 'bridge', and had lightweight wires attached which run to the terminals of an ohmmeter. A small metal weight was placed on the assembly to ensure that, in all experiments, the surface resistance measurements were made with the fabric compressed to the same load at the point of electrode contact. This is because the contact resistance (between electrode and specimen) and the resistance of the specimen under the electrode is influenced by the compression applied by the electrode assembly. Therefore it is essential to fix the load of the assembly. The AATCC method [149] states that the contact pressure between specimen and electrode should be such that "when additional pressure is applied between the fabric and the electrodes, the test results are not affected". This was the case for all the specimens used in this work, when the overall mass of the electrode assembly and additional weight was 125 g.

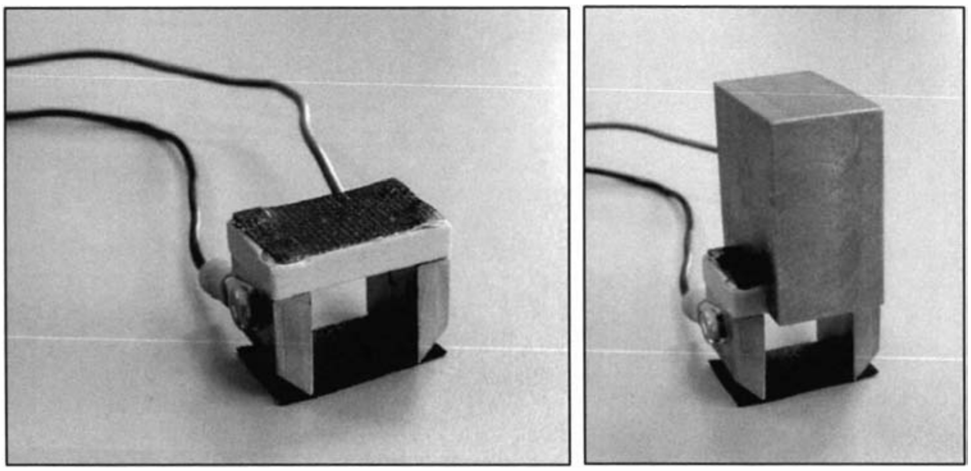


Figure 4.11. Parallel electrode assembly used for surface resistance measurements (left – without additional weight, right – with additional weight in place).

The ohmmeter used in this work was the resistance measurement setting of a digital auto-ranging multimeter. Two multimeters were used at various times, regularly calibrated and verified to give the same results. They were a Fluke 19 and a Center 122. With both meters, resistance was measured using a DC voltage of 1.5 V.

Specimens were typically prepared with a 40 x 40 mm area available for resistance testing. They were cut into four strips, two in each orientation, as shown in Figure 4.12. By measuring both faces of the fabric strip, a total of four measurements could be made in each direction of the fabric, and a total of eight overall. The mean and standard deviation of these eight measurements is usually reported in this work.

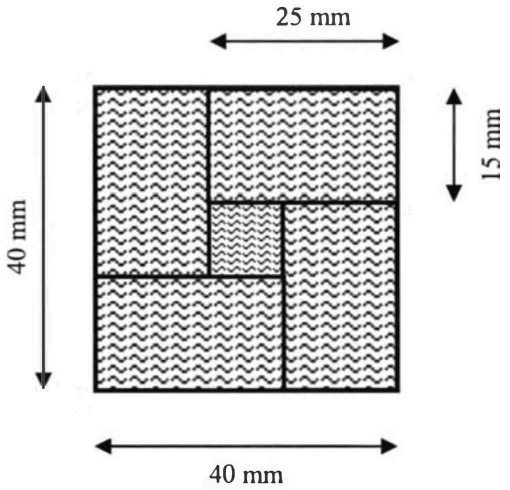


Figure 4.12. Cutting of samples for measurement of surface resistance from treated specimen.

4.4 Summary of Polymer Deposition Techniques.

In the work reported in the following chapters, four techniques were used to deposit ICPs onto textile substrates. A description of the basic features of each technique is provided below, while the specific conditions and/or experimental variations are described in the relevant section of the following chapters. The first three techniques have also been discussed in the literature review, while the fourth was developed in the course of this research.

4.4.1 One-Step Aqueous Technique.

The use of this technique by previous researchers is discussed in Section 2.2.1. In this work it is often referred to as the 'Milliken' technique, as it was developed and patented by the Milliken Research Corporation in the 1980s and 1990s. The technique has been widely used by researchers as it is particularly straightforward: all reagents are dissolved (at relatively low concentrations) in water in a vessel to which the fabric specimen is added. Over time, with agitation, the ICP polymerises onto the surface of the fabric.

In the experimental work reported in this thesis, the *in situ* polymerisation of ICP precursors onto textile substrates by the one-step aqueous technique was carried out as follows:

1. A vessel was filled with an aqueous oxidant solution of iron (III) chloride hexahydrate at a concentration of 0.04 mol/L in de-ionised water. This solution was prepared immediately before use. The vessels used in this work were 'Schott' laboratory reagent bottles, with screw-top lids. 250, 500 and 2000 mL bottles were used, depending on the volume of the solution.
2. An additional dopant was added to the oxidant solution. This was usually 1,5-naphthalenedisulphonic acid (NDSA), although *para*-toluenesulphonic acid (*p*-TSA) was also used. Its concentration in the polymerisation solution was 0.005 mol/L. It was dissolved in the solution by shaking the vessel.
3. Samples were wet out in de-ionised water and pressed against absorbent paper to remove excess water before adding to the vessel. Wetting out in this way ensured that the polymerisation solution rapidly impregnated the specimen; particularly when hydrophobic fibres (such as wool) were used. This caused a marginal decrease in the reagent concentration in the vessel as it slightly increases the volume of water. The amounts of fabric and the solution volume were related, with a ratio of 30 g textile to 1 L of solution being used. Therefore in 250 mL, 7.5 g of textile was treated; in 500 mL, 15 g of fabric was treated, and so on.

4. The precursor was then added to the vessel. This was done last to prevent any polymerisation from being able to occur before the vessels were being agitated (see below). Precursor concentration was 0.015 mol/L. The vessel was sealed then vigorously shaken by hand.
5. The vessel was then placed in a laboratory flask shaker and agitated vigorously for four hours at room temperature (typically between 18 and 22°C).
6. At the completion of the polymerisation period, the vessel was removed from the shaker, the textile specimen removed and rinsed in copious amounts of de-ionised water to remove any unreacted reagents or poorly adhering polymer. It was then allowed to dry in air.

The research that relates to this technique is described in Chapter 5.

4.4.2 Vapour-Phase Deposition.

This technique has also been widely used by researchers, as described in Section 2.2.3. As it relies on the reaction of the ICP precursor in vapour form with an oxidant-impregnated substrate, more volatile precursors (such as pyrrole) have typically been used. In the work reported here, this technique is referred to as 'vapour-deposition'.

The principle of vapour deposition is quite simple. An oxidant-impregnated piece of the substrate is suspended in a sealed vessel above a dish containing the precursor in sufficient quantity to still be present as liquid/solid at the completion of the treatment. If the temperature is maintained at a constant level, the vapour pressure will remain unchanged throughout the process. A schematic of the process is shown in Figure 4.13.

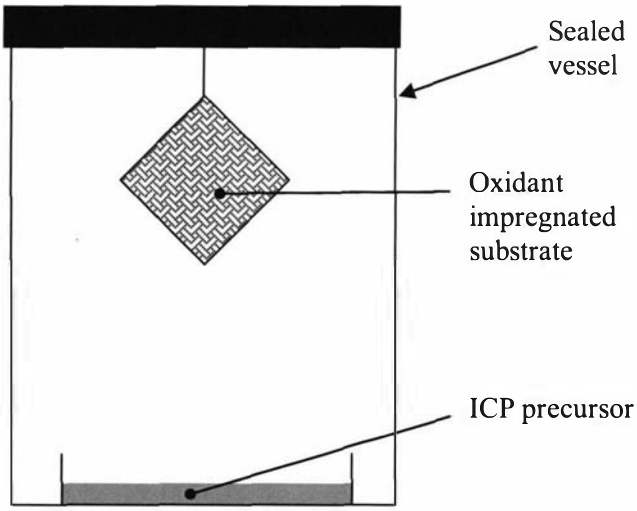


Figure 4.13. Vapour deposition set-up.

This arrangement was used because it is easy to replicate and modify, and requires no special apparatus. Alternatives could be to force vaporised precursor through a more densely packed substrate (perhaps in a pressure vessel by evacuation then introduction of the precursor), or by pumping the vapour through the substrate in a circulating system.

In situ polymerisation of ICP precursors onto textile substrates by vapour phase deposition was carried out as follows:

1. A polymerisation chamber was prepared by placing a small quantity of ICP precursor into a small Petri dish which was then placed in a larger vessel (typically a flask or jar with an airtight lid). It was left for a period of time for the vapour of the precursor to reach an equilibrium vapour pressure in the vessel.
2. The textile specimen was impregnated with a solution of the oxidant. This was done by placing the specimen into a vessel containing the oxidant solution and gently agitating. Vigorous agitation (e.g. shaking the vessel) was only carried out if the oxidant solution did not readily wet-out the specimen. If an additional dopant was used this was dissolved in the oxidant solution prior to impregnation. Various solvents were used, including methanol, de-ionised water and acetonitrile. The oxidant used most commonly was iron (III) chloride hexahydrate.
3. The specimen was then removed from the solution and allowed to dry flat under a fumehood for 30 to 120 minutes. It was turned periodically during the drying time to prevent the oxidant from 'pooling' on one face of the fabric.
4. After drying, the specimen was placed into the polymerisation chamber for a period of time, during which the precursor vapour and impregnated oxidant reacted, forming a conductive polymer coating.
5. Upon removal from the chamber (the time of exposure varying widely, depending on the precursor type and temperature, the latter of which was also varied), the specimen was rinsed in copious amounts of de-ionised water before being dried in air.

Deviations from the technique given above and investigations into the effect of the critical process parameters (such as exposure time, temperature, and so on) are described in the relevant section of Chapter 6, where the experimental work that used this technique is reported.

4.4.3 Two-Step Impregnation.

ICP deposition onto textiles by two-stage impregnation is widespread in the literature (as discussed in Section 2.2.2), and has been successfully used to polymerise thiophene variants.

Thus it is of particular relevance to the work reported here. Again, the technique in its basic form is simple: the specimen is impregnated with precursor then oxidant in successive treatments (or vice versa, although this approach was not used in the research reported in this thesis).

In situ polymerisation of ICP precursors onto textile substrates by two-stage impregnation was carried out as follows:

1. A precursor solution was prepared by dissolving an amount of precursor in acetonitrile. The concentration of this solution was varied between 0.034 and 1.422 g/10 mL. The volume of this solution was usually only ~10 mL, as the specimens were small (less than 1 g), and it was prepared in a small vial with a lid. A range of precursors were used.
2. An oxidant solution was prepared by dissolving an amount of oxidant (typically an iron (III) salt, such as iron (III) chloride) in a suitable solvent. The concentration of this solution was varied between 0.1 and 1.0 mol/L. The volume of this solution was also ~10 mL, and was prepared in a small vial with lid. A range of organic solvents, plus de-ionised water was used. If an additional dopant was used this was dissolved in the oxidant solution prior to impregnation.
3. The textile specimen was placed into the precursor solution for a few minutes and agitated gently to thoroughly impregnate the specimen. The specimen was removed and the acetonitrile allowed to evaporate. As acetonitrile is much more volatile than any of the precursors, this leaves the precursor evenly dispersed through the substrate.
4. The specimen was then placed into the oxidant solution for a few minutes with no agitation (to minimise diffusion of the precursor off the specimen). The specimen was then removed and the oxidant solvent allowed to evaporate, during which time a conductive polymer coating formed on the substrate. It was turned periodically during the evaporation time to prevent the reagents from 'pooling' on one face of the fabric.
5. After the oxidant solvent had evaporated, the specimen was rinsed in copious amounts of de-ionised water before being dried in air.

Deviations from the technique given above and investigations into the effect of the critical process parameters (such as reagent concentration, oxidant type, and so on) are described in the relevant section of Chapter 7, where experimental work that used this technique is reported.

4.4.4 'Single-Dip' Technique.

The so-called 'single-dip' technique is a refinement of the two-stage impregnation technique described earlier. It is a new technique, developed in the course of the work reported here, and as such is not described in the literature. It uses a single, simultaneous impregnation of precursor and oxidant, but reaction conditions should be such that polymerisation does not take place in the solution. This reaction should only occur when solvent evaporation takes place.

In situ polymerisation of ICP precursors onto textile substrates by the single-dip technique was carried out as follows:

1. A oxidant solution was prepared with oxidant (typically an iron (III) salt) in a suitable solvent. A range of organic solvents, plus de-ionised water, were used. The concentration of the oxidant was varied between 0.05 and 1.50 mol/L. If an additional dopant was used this was also added to the polymerisation solution at this stage. Unless otherwise noted in the text, the oxidant solution was iron (III) chloride hexahydrate at a concentration of 1 mol/L in methanol.
2. A precise amount of the oxidant solution was added to a small vial in which a known quantity of precursor had previously been placed. This created a polymerisation solution with oxidant, precursor and additional dopant (if used) all present. The concentration of precursor in the polymerisation solution was varied from 0.007 to 0.248 g/10 mL. Unless otherwise noted, the precursor was EDOT, and its concentration was 0.03 g/10 mL.
3. The textile specimen was placed in the polymerisation solution for several minutes and periodically agitated to ensure thorough impregnation. Unless otherwise noted, impregnation time was four minutes, with agitation for 10 seconds every minute. The specimen was then removed and the solvent allowed to evaporate, during which time a conductive polymer coating formed on the substrate. It was turned periodically during the evaporation time to prevent the reagents from ‘pooling’ on one face of the fabric. Evaporation time was 60 minutes with the specimen turned after 5, 10, 20, 30 and 45 minutes, unless otherwise stated.
4. After the solvent had evaporated, the specimen was rinsed in copious amounts of de-ionised water before being dried in air.

Polymerisation solutions were prepared just before use, and were usually 10 mL volume. Because the appropriate amount of EDOT is very small (approximately one drop from a 1 mL disposable pipette), and somewhat variable (the drop size is not always exactly the same), a technique was employed to ensure that precisely the 0.03 g/10 mL concentration was achieved. The process was as follows:

a. One drop of EDOT was placed in a vial and the mass of EDOT added was recorded.
b. The volume of the polymerisation solution required to give 0.03 g/10 mL EDOT concentration (= (mass of EDOT added ÷ 0.03) x 10 mL) was calculated.

c. This volume of oxidant solution was added (from a graduated pipette).

This gives approximately 10 mL of polymerisation solution, with exactly 0.03 g/10 mL precursor concentration, ignoring the additional volume added by the precursor. This volume is very low (approximately 0.023 mL) and represents only about 0.23% of the solution volume, assuming no reduction in volume due to EDOT solubility in methanol. Because of the solubility of EDOT in methanol, the volume addition from the presence of EDOT is in fact even less than that calculated here. The reduction in oxidant concentration is also ignored as this is very small (the concentration remains at 1 mol/L to two decimal places with these quantities of EDOT added). The variable volume of solution might influence the polymerisation process in some way, although this variability is only approximately ± 10%, so this is unlikely given the large amount of solution relative to the size of the specimen.

Deviations from the technique given above and investigations into the effect of the critical process parameters (such as reagent concentration, solvent type, and so on) are described in the relevant section of Chapter 8, where experimental work that used this technique is reported.

4.5 Chemical Reagents.

All chemical reagents used in this work were purchased specifically for this research, and were used as received. Previous researchers (see Section 2.2.1) had found no benefit in using distilled water instead of tap water, and also found that distillation of pyrrole prior to use had no effect. Therefore, while high quality reagents were purchased specifically for the project (appropriately stored and discarded in accordance with the manufacturers recommendations), no special efforts were made to achieve especially high levels of purity in the polymerisation systems. Despite the preparation process for the fabrics, they were probably still 'dirty' from an analytical viewpoint, so it seemed somewhat pointless to attempt to achieve particularly high levels of purity in the reagents to be used with them.

The following reagents were used in this work, and obtained as indicated:

ICP precursors: Pyrrole, aniline, thiophene, 3-methyl thiophene, 2,2'-bithiophene and 3,4-ethylenedioxythiophene were purchased from Aldrich.

Oxidants: Iron (III) chloride (hexahydrate), iron (III) chloride (anhydrous), iron (III) nitrate, iron (III) perchlorate and ammonium persulphate were purchased from Aldrich, and were generally ACS grade reagents. Hydrogen peroxide was purchased from BDH.

Dopants and acids: Aromatic sulphonates and sulphonic acids were purchased from Aldrich. Other acids were used from laboratory stocks, having been previously purchased from BDH.

Solvents: Methanol, ethanol, acetonitrile, acetone, and di-ethyl ether were purchased from BDH, and were their 'Analar®' grade. De-ionised water from the laboratory supply was used unless otherwise indicated.

Chapter 5 Experimental Work – Aqueous System.

5.1 Background.

The one-step aqueous polymerisation system pioneered by the Milliken Research Corporation [9] is well proven and widely known, so it was sensible to initially trial it for the *in situ* polymerisation of thiophene variants. The abstract of one paper [26] suggested that thiophenes could be used in this system, but no data was found in that paper or in any of the literature that confirmed this. Part of the reason that the system works very well for pyrrole is because of pyrrole's moderate solubility in water, meaning that it can be dissolved in the polymerisation solution at low concentrations, then as polymerisation progresses and the molecular weight of the oligomers increases, the oligomers precipitate out of solution and deposit onto available surfaces [33]. Thiophenes however, are not soluble in water, and alternative solvents may not allow the system to work in the same way. The outcomes of a trial of this system for thiophene variants are described in this section.

The technique as described in the literature has been reviewed in Section 2.2.1, and the details of how it was used in this work provided in Section 4.4.1.

5.1.1 Initial Attempts.

A first attempt at poly(thiophene-variant) deposition was attempted using the technique as described in Section 4.4.1, with thiophene and 3-methylthiophene replacing pyrrole. The dopant was *p*-TSA, and a 7 g specimen of wool fabric was treated in a 250 mL volume.

There was no apparent change to either of the fabric specimens after 16 hours of treatment. It was thought that the low reactivity of these two precursors could have been preventing polymerisation from occurring, so additional oxidant was added in the form of a few drops of hydrogen peroxide, and the vessels agitated again. After eight more hours, the specimens had darkened slightly. They were removed, rinsed and dried, but although they were slightly orange-grey coloured (some of which is attributable to iron (III) chloride staining) they were non-conductive (> 40 MΩ/square).

A second attempt was made with the solutions prepared in acetonitrile rather than water and 2,2'-bithiophene and 3,4-ethylenedioxythiophene (EDOT) in place of thiophene and 3-methylthiophene. Other experiments had indicated that chemical polymerisation of thiophene and 3-methylthiophene with iron (III) chloride was difficult to initiate, so alternative thiophene variants were expected to have a greater reactivity and therefore be more likely to polymerise.

After 20 hours it appeared that polymerisation had occurred, but much of it was particulate in solution, rather than on the specimens. The bithiophene specimen was a blotchy reddish-brown colour, and particles of reddish brown material were removed when rinsed. That which remained seemed to be reasonably well-attached the fibres. The EDOT specimen was a blotchy blue colour, and also released a large amount of particulate when rinsed. The residual pale blue coating on the fabric was not well attached, and could be rubbed off with a finger. The bithiophene specimen was non-conductive, but the EDOT specimen had a just-measurable resistance of approximately 35 MΩ/square.

The use of acetonitrile in such large volumes is not practical from either a safety or economic perspective, so a third variant of the experiment was carried out. In this case, the precursors were dissolved in 20 mL of acetonitrile before being added to the aqueous solution of oxidant and dopant. Otherwise the conditions of polymerisation and specimens were the same as previously.

After 20 hours the specimens were removed, with no substantial change observed. After rinsing and drying, the EDOT specimen was a pale grey-blue colour, and non-conductive. The bithiophene specimen was slightly yellow-brown in colour, and also non conductive.

The results of the second and third experiments suggest that some conductive polymer deposition was occurring. Polythiophene (perhaps more accurately poly(2,2'-bithiophene) in this case) is a reddish brown colour, and poly(EDOT) is bluish. However the level of deposition seemed to be low, and the polymer seemed not to be fully oxidised, so was not very conductive. The compromise (experiment three) was less effective than using acetonitrile as the only solvent.

5.1.2 Summary and Conclusions.

These results were disappointing, but not unexpected. It may just be possible to deposit thiophene-based polymers onto textiles by this approach, but only when an impractical solvent is used (acetonitrile). In fact, given the relatively large solution volume (250 mL to treat ~7 g of fabric), the use of any organic solvent is probably not practical. The technique is in many ways analogous to textile dyeing, requiring a relatively long slow process at low reagent concentrations. To the author's knowledge, no practical textile dyeing process uses a solvent other than water.

It was also apparent that when acetonitrile alone was used as the polymerisation solvent, much of the polymer formed was not attached to the fibres. This is consistent with the findings of Gregory *et al.* [22], who noted that if organic solvents were used as the polymerisation medium, the reaction took place exclusively in the solution and not on the fibre surfaces. It is likely that the polymer coating found on the specimens accumulated there after polymerisation, rather than being created *in situ*. Therefore this technique was abandoned for thiophene-based precursors for the remainder of this work, although some experiments using pyrrole are reported in the following section.

5.2 Effect of Fibre Type.

5.2.1 Background.

Although polymerisation of thiophene variants was unsuccessful by this technique, there are still relevant investigations to be carried out using pyrrole. Previous researchers have concluded that substrate fibre type has little or no influence on the polymerisation process [22,26]. This is difficult to accept, as different fibre types have very different surface chemistry and adsorption properties. The adsorption of polymerisation reagents will surely be influenced by these differences, and thus a difference in polymer formation will occur. This is likely in turn to influence the surface resistance of the composite. Two experiments were carried out to test this. In the first, a specimen of each of the standard fabrics was treated separately in its own vessel; while in the second, specimens of all fabrics were treated together in one larger vessel. In the former case, each specimen (of equal mass) had access to the same amount of adsorbable material. In the second, they competed for the full quantity, so substrates with a greater affinity should have increased their 'share' of reagents, with subsequent change in polymer mass add-on and surface resistance. The differences between fibre types should therefore be exaggerated under these conditions.

5.2.2 Experimental Work.

Square specimens of the seven substrates were cut from the bulk to weigh 7.5 g. They were prepared as described in Section 4.1 before treatment. They were not fully dried after their final rinse in de-ionised water, but simply pressed against absorbent paper (leaving the specimens damp in this way facilitates rapid 'wetting-out' in the polymerisation solution, and makes only a marginal difference to the concentration of reagents in the solution). The polymerisation conditions were as described in Section 4.4.1, with seven individual solutions of 250 mL and a 'shared' solution of 1750 mL. The dopant was NDSA and substrates were the seven standard woven fabrics – nylon, polypropylene, polyester, acrylic, wool, cotton and glass (see Section 4.2 for details).

After treatment all specimens were dark to light grey in colour with deposited polypyrrole. The glass fabric was the lightest (and not uniformly coated), and cotton the darkest in colour. Surface resistance was measured as described in Section 4.3.2, but mass add-on was measured by comparing the fabric mass per unit area (by cutting a small specimen out of the bulk treated piece) with that calculated previously (Section 4.2, Table 4.2). These results are provided in Table 5.1, and graphically in Figures 5.1 and 5.2. The standard deviation of surface resistance is provided in parentheses in the table.

Table 5.1. Mass add-on and surface resistance – seven fibre types.

Fibre type	Mass add-on (%)		Surface resistance (Ω/square)	
	Separately	Together	Separately	Together
Nylon	6.7	0.7	5.69 (1.74) x 10^2	4.81 (1.55) x 10^2
Polypropylene	0.5	-2.0	1.12 (0.24) x 10^3	1.40 (0.38) x 10^3
Polyester	-0.8	4.0	5.84 (1.38) x 10^2	7.39 (2.53) x 10^2
Acrylic	2.5	2.5	4.31 (0.92) x 10^2	2.98 (0.27) x 10^2
Wool	4.4	5.9	7.96 (1.55) x 10^3	6.20 (1.10) x 10^3
Cotton	11.1	11.8	4.73 (1.41) x 10^3	3.60 (0.82) x 10^3
Glass	-4.8	-3.3	3.07 (0.95) x 10^4	1.90 (0.87) x 10^3

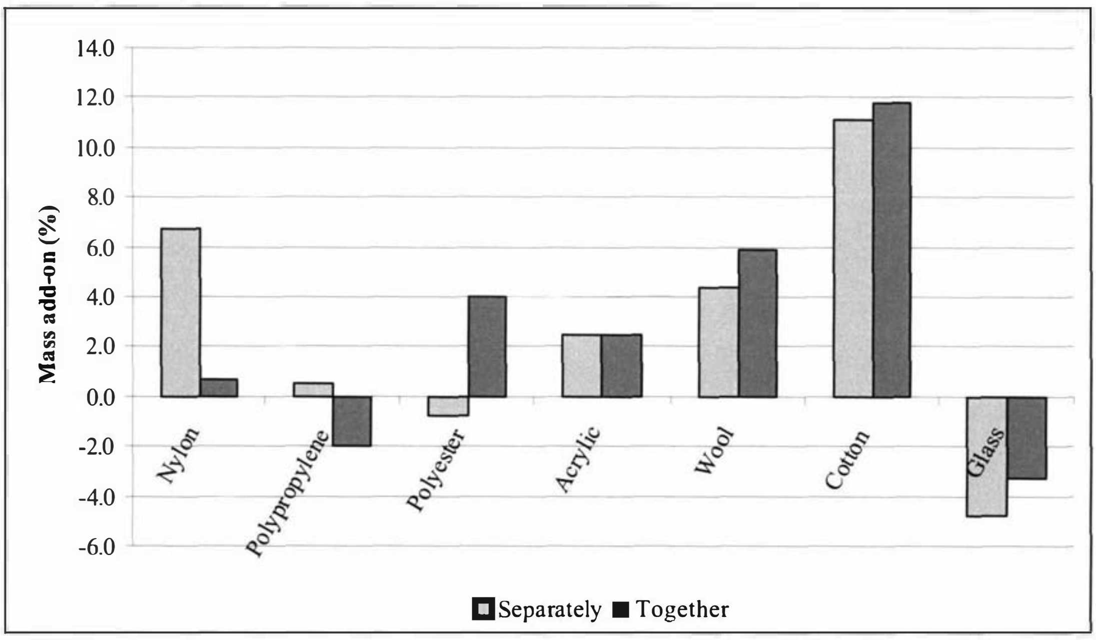


Figure 5.1. Mass add-on – seven fibre types.

There was a substantial difference between the fibres, regardless of whether they were polymerised together or not. The synthetic fibres were the best (lowest resistance), with the two (more absorbent) natural fibres actually being less conductive, and, in the case of cotton, having a very high mass add-on. It is possible that the high absorbency of these fibres encourages the reagents to migrate inside the fibre, where it is perhaps difficult for polymer chain formation to take place (and where if it does, it is not necessarily contributing to reducing surface resistance, which relies on the surface of the substrate being conductive). The glass fibre fabric had a high resistance when polymerised on its own (the worst), but improved substantially when polymerised with the other specimens. This may have been due to improved solution circulation in the latter case, as it was observed that the relatively stiff glass fabric tended to sit partly out of the polymerisation solution, and did not allow good circulation of the polymerisation solution around it when in a separate, smaller vessel. Previous work has indicated that glass does not perform well in this system [26], and it was certainly inferior to the synthetic fibres in both situations.

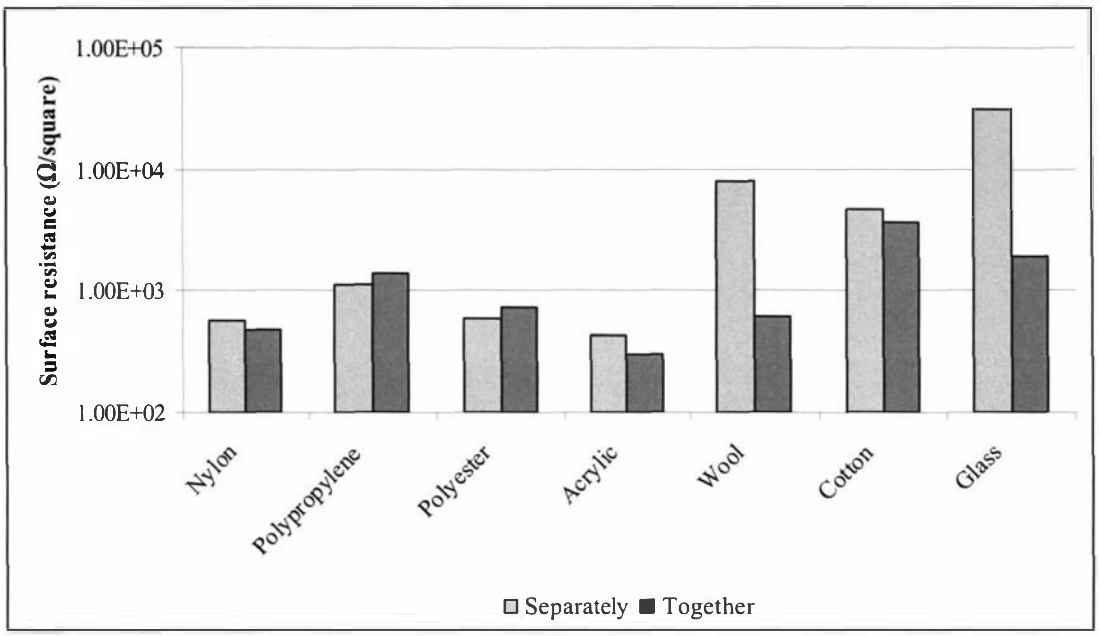


Figure 5.2. Surface resistance – seven fibre types.

While the surface resistance changed only slightly depending on whether the specimens were polymerised together or not, the mass add-on was dramatically different. However, these mass add-on values may have to be ignored for two reasons: firstly, they are only a single measurement (that is, a sample size of one), and secondly the mass add-on was calculated indirectly, from two values that were also arrived at by calculation. On face value they appear to show some interesting behaviour when the 'together' and 'separately' values for each are compared, but they may each incorporate large errors that render any conclusions drawn invalid.

5.2.3 Summary and Conclusions.

The influence of fibre type has been demonstrated for a set of standard woven fabrics. Natural fibres performed worse than synthetic ones, in that they had higher surface resistance. It is difficult to draw conclusions regarding the mass add-on, as the values obtained may be unreliable.

Chapter 6 Experimental Work – Vapour Deposition.

6.1 Background.

As described in the literature review (Section 2.2.3), many researchers have attempted to deposit intrinsically conductive polymers onto porous substrates (including textiles) via a vapour deposition technique. The principle of this technique is briefly described in the next section, and has proven quite successful with pyrrole used as the precursor. Pyrrole is a relatively volatile substance, so in a sealed vessel with liquid pyrrole, the vapour pressure in the atmosphere above the liquid pyrrole is relatively high, and vapour deposition process can be expected to be more rapid than in the atmosphere above a less volatile substance.

Vapour pressure is dependent on the inter-molecular forces present in the substance, which are dependent on molecular weight and the dipole moment of the molecule. Vapour pressure information could not be found in the literature for all of the ICP precursors used in this work, but those that were available, plus all precursors' boiling points (which are a good indication of volatility) are given in Table 6.1.

Table 6.1 Vapour pressure and boiling point data for ICP precursors.

ICP precursor	Vapour pressure (Pa)		Boiling point (°C) [3]
	At 20°C [1]	At 60.3°C [2]	
Pyrrole	157	8386	130
Thiophene	9182	44930	84.4
3-Methylthiophene	3825	15465	114
2,2'-Bithiophene	Not available	Not available	260
3,4-Ethylenedioxythiophene	Not available	Not available	193

Notes:

1. Extrapolated to 20°C from data provided in the *CRC Handbook of Chemistry and Physics* [151]. Extrapolated value for thiophene is in agreement with that reported by Wu and Ondruschka [152].
2. From Eon *et al.* [153].
3. From the *Aldrich Handbook of Fine Chemicals and Laboratory Equipment* [154].

Given the strong negative correlation between boiling point and vapour pressure for the three precursors for which full data is available ($r = -0.998$ for vapour pressure at 20°C), it is safe to assume that the rank order of vapour pressure (from highest to lowest) will be thiophene, 3-methylthiophene, pyrrole, 3,4-ethylenedioxythiophene and 2,2'-bithiophene. In fact bithiophene has a melting point of ~33°C [154], so the vapour pressure above it would undoubtedly be very low at room temperature. As is also confirmed by the data in Table 6.1, vapour pressure of ICP precursors is increased at higher temperatures. This may be a way of accelerating the vapour deposition process, especially for 2,2'-bithiophene which is otherwise likely to react very slowly. The potential limitation of increasing temperature is that higher temperatures may cause some degradation of the precursor before it can react with the oxidant. The polymerisation reaction will also be influenced by the reactivity of the precursor, as well as its vapour pressure. Therefore, the relatively unreactive thiophene would probably be less likely to polymerise than its variants, despite its high vapour pressure.

The main appeal of a vapour deposition system is its apparent efficiency. The polymerisation reaction is confined to the surface of the substrate, as this is the only place where precursor and oxidant come into contact (although it is possible that both oxidant and precursor could penetrate into the fibre structure, resulting polymerisation inside the fibre). Also, the only precursor used up in the process is that consumed by the polymerisation reaction. Provided there is liquid precursor present in the base of the reaction vessel, the vapour pressure will remain unchanged regardless of the actual quantity of precursor. This means that it is easy to replicate the polymerisation conditions for repeated treatments.

6.1.1 Initial Attempts.

Initial attempts were made to confirm the vapour deposition behaviour of pyrrole as reported in the literature, and to see if it was possible to use the same system for the *in situ* polymerisation of thiophene-based precursors onto textile substrates. These experiments also had the purpose of identifying relevant parameters to investigate further. The basic system described in Section 4.4.2 was used for this work.

6.1.1.1 Verification and Preliminary Investigation of Pyrrole Behaviour.

In most of the work described in this section, the ICP precursor was pyrrole and polymerisation was carried out at room temperature. Several basic parameters were assessed with this general technique, as described below. It should be noted that the technique was being modified during this process, so there are differences in vessel size and substrate used. As a result, comparisons should not be made between different experiments, but only within each experiment.

A. Oxidant Solvent and Concentration.

In the first experiment, specimens (polyester/cotton knit) were impregnated with 1 mol/L $FeCl_3.6H_2O$ in methanol, de-ionised water and acetonitrile, dried (210 minutes for water, 80 minutes for methanol, 20 minutes for acetonitrile; these timings having been previously determined to be sufficient for all solvent to be removed) then placed in the vapour polymerisation vessel for 30 minutes. The results are provided in Table 6.2, and indicate that methanol performed the best as it had the lowest resistance. The mass add-on of all oxidants was similar. Methanol was used throughout subsequent work, as it is both safer to handle than acetonitrile and faster drying than water.

Table 6.2. Preliminary experiment – oxidant solvent.

Oxidant solvent	Surface resistance (Ω/square)	Mass add-on (%)
Methanol	5.08×10^3	0.94
De-ionised water	29.3×10^3	0.95
Acetonitrile	19.8×10^3	0.87

In the second experiment, specimens (polyester interlock) were impregnated with $FeCl_3.6H_2O$ in methanol at a range of concentrations. The method and other reagents were as used previously. The results are provided in Table 6.3.

Table 6.3. Preliminary experiment – oxidant concentration.

Oxidant concentration (mol/L)	Surface resistance (Ω/square)	Mass add-on (%)
1.00	11.8×10^3	0.69
0.76	51.3×10^3	0.60
0.50	10.5×10^4	0.49
0.26	28.0×10^4	0.56
0.10	69.9×10^6	0.45
0.06	50.0×10^9	0.41

There was an obvious graduation in depth of colour, from dark grey at 1.00 mol/L to light grey at 0.06 mol/L, confirming the general trend of less polymer deposited at lower concentrations, as indicated by the mass add-on. It is apparent that a high oxidant concentration is preferable, as it brings about a lower resistance. The higher mass add-on indicates that this may have been partly due to the presence of more conductive polymer. However, even at the lowest concentration there is 0.41% mass add-on, suggesting that perhaps the conductive polymer that has formed at higher concentrations is better doped (in other words, more fully oxidised) than that which forms at lower concentrations. In subsequent work a high oxidant concentration was used.

B. Exposure Time.

Specimens (polyester/cotton knit) were impregnated with 1 mol/L $FeCl_3.6H_2O$ in methanol, dried and exposed to pyrrole vapour for a range of times. The method was otherwise the same as previously used. The results (given in Table 6.4) show a clear trend of decreasing resistance with increased exposure time, possibly beginning to level off at the longer exposure times. The mass add-on seems to generally increase, but somewhat inconsistently. The latter phenomenon indicates that there may a degree of variability in mass add-on, if not surface resistance (examined more closely in Part D of this section). This experiment was repeated (reported on in Section 6.2) for longer times and other precursors.

Table 6.4. Preliminary experiment – exposure time.

Exposure time (minutes)	Surface resistance (Ω/square)	Mass add-on (%)
1	1.3×10^5	1.9
2	3.6×10^4	2.5
4	6.0×10^3	1.9
8	1.4×10^3	7.2
16	8.0×10^2	5.7
32	5.1×10^2	9.7

C. Alternative Oxidants/ Dopants.

Tan and Ge [82] found that ammonium persulphate (APS) was effective for the polymerisation of aniline vapour, so it was trialled for pyrrole. As APS is not very soluble in methanol, de-ionised water was used as the oxidant solvent, at a maximum achievable concentration of 0.8 mol/L. An initial experiment indicated that the polymer deposited was non-conductive, so hydrochloric acid was used as a source of dopant anions. 30 minute vapour exposure was used, with the results given in Table 6.5. These are very high resistance values with high mass add-on levels, suggesting that while polymer is being deposited in reasonably large quantities, it is poorly doped and therefore has poor conductivity. Iron (III) chloride is therefore a preferable oxidant.

Table 6.5. Preliminary experiment – alternative oxidant.

Oxidant set-up	Surface resistance (Ω/square)	Mass add-on (%)
APS only (no HCl)	6.41×10^9	7.61
APS then HCl as after-treatment	2.00×10^9	5.82
APS with HCl in oxidant solution	6.65×10^6	8.51

D. Reproducibility of Results.

Because of some indications of variability between similar trials, a brief assessment of this was made for two different exposure times (2 and 20 minutes). Five specimens (polyester interlock) were prepared for each exposure time, and treated one after the other in the same vessel. Liquid pyrrole was still present in the base of the vessel at the end of the trial. The oxidant solution was 1 mol/L $FeCl_3.6H_2O$ in methanol. The resistance and mass add-on results are provided in Table 6.6.

Table 6.6. Reproducibility of results.

Specimen	2 minute exposure		20 minute exposure	
	Resistance (Ω/square)	Mass add-on (%)	Resistance (Ω/square)	Mass add-on (%)
1	1.3×10^5	0.46	2.0×10^5	0.45
2	2.1×10^5	0.33	0.7×10^5	0.55
3	2.1×10^5	0.11	1.0×10^5	0.58
4	2.3×10^5	0.11	1.5×10^5	0.45
5	3.7×10^5	0.23	1.3×10^5	1.27
Mean	2.3×10^5	0.25	1.3×10^5	0.66
Standard Deviation	8.7×10^4	0.15	5.0×10^4	0.35
Coefficient of variation	37.9%	60.5%	38.1%	52.4%

Note: Coefficient of variation is the standard deviation expressed as a percentage of the mean, and gives an indication of the spread of data that is independent of magnitude.

Clearly there is appreciable variability between otherwise identical treatments. The resistance values however, are reasonably close, and the same order of magnitude. Regardless, this result emphasises the need for replicates to be used, and in subsequent trials a minimum of three specimens of each variant were treated, and their results averaged. There didn't appear to be a substantial difference in reproducibility between the two exposure times.

6.1.1.2 Feasibility of System for Thiophene Variants.

In parallel with the experiments reported on in Section 6.1.1.1, several attempts were made to polymerise thiophene-based ICP precursors by a vapour deposition technique. It had already been determined (from the work reported on in Section 5) that the thiophene-based precursors were more difficult to polymerise than pyrrole, so it was expected that longer exposure times would be required, if any reaction occurred at all.

In the first experiment, four specimens (polyester/cotton knit) were impregnated with $FeCl_3.6H_2O$ in methanol and exposed to ICP precursor vapour for 24 hours. This length of time was chosen because initial observations indicated that the rapid darkening – indicative with pyrrole of polymer deposition – did not occur. Results for four different precursors are given in Table 6.7. Even though bithiophene is a solid, there was sufficient vapour pressure above for polymerisation to slowly occur. Some slight darkening of the specimen was observed after 40 minutes, and after 24 hours the specimen was uniformly dark reddish-brown. With EDOT some darkening was observed after only five minutes, and the specimen was uniformly dark blue after 24 hours. For both bithiophene and EDOT the mass add-on indicates substantial polymer deposition. For 3-MT and thiophene there was no change in the appearance or mass of the specimen. Although thiophene and 3-MT are more volatile than bithiophene, they are very unreactive, and do not seem to be readily polymerised by a vapour deposition system. EDOT has a low resistance but a high mass add-on when polymerised in this way, resulting in the specimen being somewhat stiffened by the deposition of conductive polymcr. As the reaction was relatively fast, it may be possible to reduce the exposure time and thus the mass add-on (as was the case for pyrrole in Section 6.1.1.1, Part B) to achieve a more acceptable level.

Table 6.7. Preliminary experiment – thiophene variants.

ICP precursor	Surface resistance (Ω/square)	Mass add-on (%)
Thiophene	> 20 x 10^6	0.0
3-Methylthiophene (3-MT)	> 20 x 10^6	0.0
2,2'-Bithiophene	10 x 10^6	5.7
3,4-Ethylenedioxythiophene (EDOT)	1.2 x 10^3	10.0

A second experiment repeated the previous procedure, except that 0.16 mol/L *para*-toluene sulphonic acid (*p*-TSA) was added to the oxidant solution, and the exposure time was limited 18 hours. Aromatic sulphonic acids are recommended as alternative dopant sources to the oxidant counter-ion, as they seem to increase conductivity and improve durability [9,19,68]. The amount of *p*-TSA to add was an estimate, based roughly on the oxidant to additional dopant ratio used in the aqueous system described in Chapter 5. Polymerisation proceeded as it had previously, and although a very slight greenish darkening of the 3-MT specimen was observed, it was lost after rinsing. The results were as given in Table 6.8, and suggest that conductivity can be improved by using an additional dopant (although the unreactive precursors were still non-conductive). It is possible that the greenish darkening on 3-MT may have been reduction of the iron (III) chloride to an iron (II) species, although corresponding oxidation of the precursor to form a polymer did not appear to have taken place.

Table 6.8. Preliminary experiment – thiophene variants with *p*-TSA.

ICP precursor	Surface resistance (Ω/square)	Mass add-on (%)
Thiophene	$> 20 \times 10^6$	0.0
3-Methylthiophene (3-MT)	$> 20 \times 10^6$	0.0
2,2'-Bithiophene	1.2×10^6	1.0
3,4-Ethylenedioxythiophene (EDOT)	0.7×10^3	7.6

6.1.2 Summary and Conclusions.

This preliminary work indicated that the vapour deposition approach works very well for pyrrole, and can also be used – although with much longer vapour exposure times – for bithiophene and EDOT. The work reported in subsequent sections of this chapter was a further investigation into the vapour deposition of thiophene-based precursors onto textile substrates, attempting to optimise the deposition conditions for low resistance at reasonably low mass add-on, and with an accelerated polymerisation reaction.

This work has also identified the key parameters that control the polymer deposition reaction for pyrrole; subsequent work attempted to determine if these are also the key parameters for the thiophene variants. These key parameters are:

- Oxidant concentration.
- Vapour exposure time.
- Temperature of the vapour deposition system.

- Presence of additional dopants.

Finally, an acceptable basic technique, with reasonably reproducible results, has been established. This technique is simple to carry out in the laboratory environment, and is easily modified.

6.2 Effect of Vapour Exposure Time.

6.2.1 Background.

The influence of vapour exposure time was clearly demonstrated for pyrrole in Section 6.1.1.1 (Part B), with an increase in polymer mass add-on and a decrease in surface resistance at longer times. There was an indication that this behaviour levelled-off at approximately 30 minutes exposure time, and exceeding this would not lead to any further change in properties. It is important to identify the point at which this levelling off occurs, as leaving the specimen in contact with reaction species (oxidant and precursor) for any longer than necessary may have a deleterious effect on its mechanical properties.

In the work reported in this section, the effect of exposure times of up to two hours were investigated for pyrrole, up to four days for 3,4-ethylenedioxythiophene (EDOT), and up to eight days for 2,2'-bithiophene.

6.2.2 Experimental Work.

The technique for vapour deposition of conductive polymers onto a textile substrate was as described in Section 4.4.2. Polyester interlock (P INT) and cotton woven (C WVE) fabrics were impregnated for 20 minutes with an oxidant solution of 1 mol/L iron (III) chloride in methanol, dried for 90 minutes, then exposed to the ICP precursor vapour at 20±2°C. It should be noted that zero-time control specimens were also prepared, by impregnating the specimen with the oxidant solution and allowing it to dry as for the other specimens, but then rinsing the specimens without exposure to vapour. These control specimens indicate the mass change and surface resistance when no polymer deposition is carried out.

Surface resistance and polymer mass add-on was measured as described in Section 4.3. Three replicates of each set of conditions were used, and the results averaged. These data are provide in Table 6.9 (standard deviation in parentheses), and presented graphically in Figures 6.1 (pyrrole), 6.2 (bithiophene) and 6.3 (EDOT). The last row of Table 6.9 gives the results for the control specimens.

The substantial reduction in mass for the control (presumably caused by oxidative degradation of the substrate) suggests that the actual polymer mass add-on may be much higher than that indicated. However, as any reduction caused in this way on the substrate will be the same for all variants, it can be ignored for comparative purposes. The mass add-on relative to the initial mass probably gives a better indication of how the fabric's mechanical properties may have changed. Adjusted values (assuming that the same mass reduction occurs on all occasions) could be calculated, but it is important to consider that the action of the oxidant on the substrate is likely to be different in the presence of the ICP precursor. For these reasons, unadjusted values are used in this work.

Table 6.9. Mass add-on and surface resistance – vapour exposure time.

Precursor	Exposure time	P INT		C WVE	
		Mass add-on (%)	Surface resistance (Ω/square)	Mass add-on (%)	Surface resistance (Ω/square)
Pyrrole	1 min	0.08 (0.07)	1.56 (0.81) x 10^{5}	-0.05 (0.16)	3.58 (2.37) x 10^{4}
	2 min	-0.08 (0.35)	1.57 (1.30) x 10^{5}	0.00 (0.28)	1.98 (1.00) x 10^{4}
	5 min	0.05 (0.29)	5.57 (2.14) x 10^{4}	0.05 (0.08)	9.17 (5.03) x 10^{3}
	10 min	0.23 (0.31)	1.64 (1.14) x 10^{4}	0.62 (0.18)	2.35 (0.65) x 10^{3}
	30 min	0.63 (0.04)	1.63 (0.25) x 10^{4}	0.55 (0.03)	1.22 (1.26) x 10^{3}
	60 min	0.42 (0.26)	1.07 (0.25) x 10^{4}	0.23 (0.29)	1.35 (0.33) x 10^{3}
	120 min	0.46 (0.02)	2.18 (0.49) x 10^{4}	0.40 (0.15)	2.20 (0.54) x 10^{3}
BT	24 hr	0.00 (0.12)	3.11 (1.02) x 10^{10}	---	---
	48 hr	0.36 (0.13)	1.39 (0.56) x 10^{10}	---	---
	96 hr	0.58 (0.27)	3.98 (3.35) x 10^{10}	---	---
	161 hr	1.13 (0.26)	5.57 (1.40) x 10^{7}	---	---
	194 hr	1.91 (0.54)	4.95 (2.75) x 10^{7}	---	---
EDOT	8 hr	0.30 (0.22)	2.35 (2.80) x 10^{5}	1.04 (0.19)	1.59 (0.75) x 10^{3}
	16 hr	0.49 (0.28)	1.64 (1.06) x 10^{4}	1.67 (0.33)	8.12 (0.24) x 10^{2}
	24 hr	0.77 (0.16)	3.47 (1.73) x 10^{3}	0.73 (0.22)	8.42 (4.40) x10^{2}
	48 hr	1.58 (0.51)	1.19 (0.68) x10^{3}	2.58 (0.59)	2.52 (1.37) x 10^{2}
	96 hr	3.47 (0.50)	5.45 (0.39) x 10^{2}	4.76 (0.64)	6.98 (1.55) x 10^{1}
None	0 min	-0.20 (0.14)	> 1 x 10^{11}	-1.15 (0.30)	1.10 (0.23) x 10^{10}

For pyrrole, it appeared that maximum mass add-on and minimum surface resistance were achieved at about 30 minutes vapour exposure time, and that increasing exposure time beyond this did not give any further change. As expected, the reaction times with the two thiophene variants were much longer, but it is clear that they can be polymerised in this way without needing to alter the basic technique. In both cases there was a general increase in mass add-on and a decrease in surface resistance as more polymer was deposited at longer times. The mass add-on values were still quite variable, as indicated by their large standard deviations relative to the mean values. Surface resistance was less variable, and the differences in values tended to be larger (orders of magnitude), so the high variability is less of a concern.

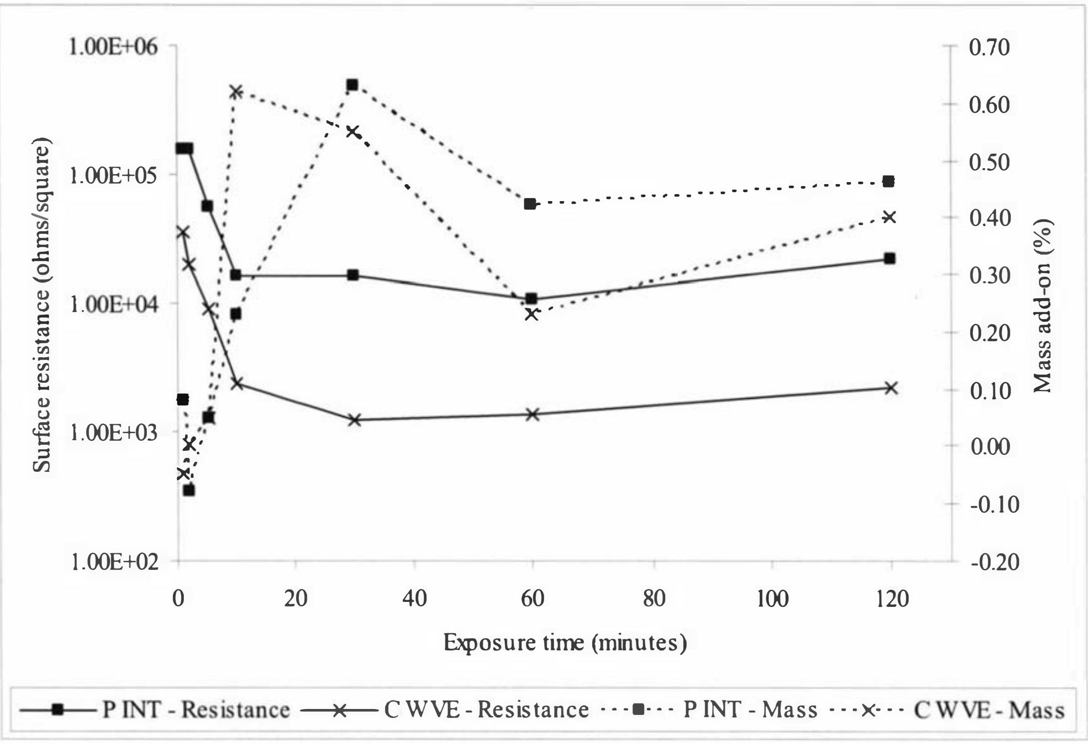


Figure 6.1. Mass add-on and surface resistance – vapour exposure time (pyrrole).

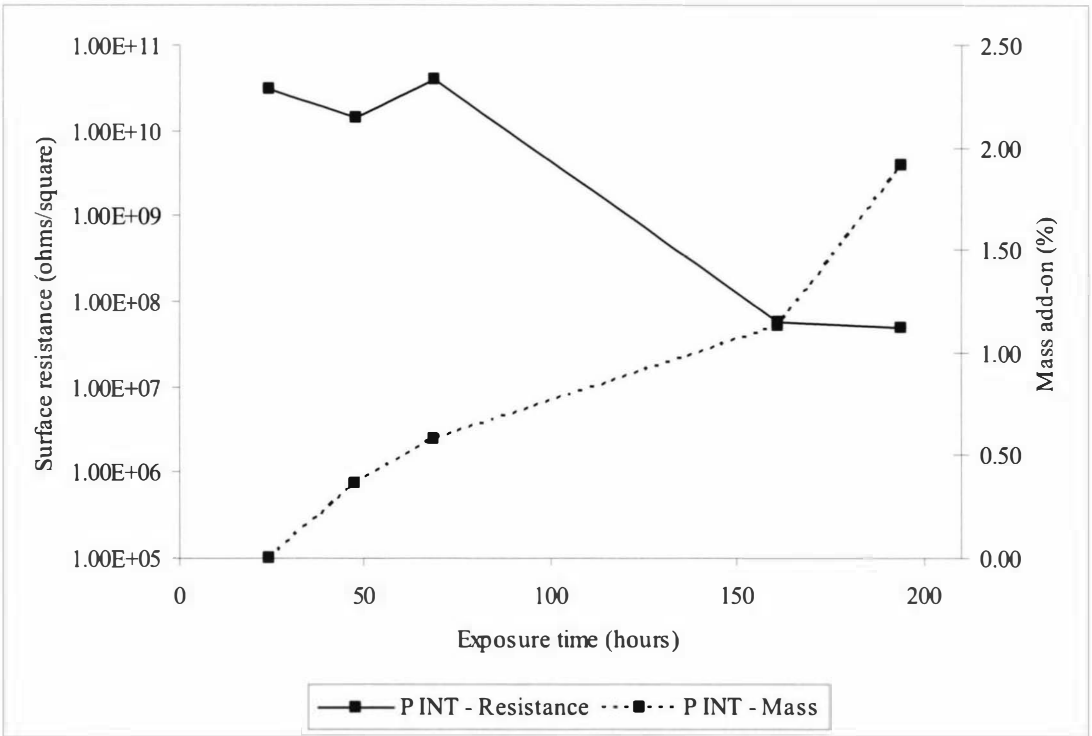


Figure 6.2. Mass add-on and surface resistance – vapour exposure time (2,2'-bithiophene).

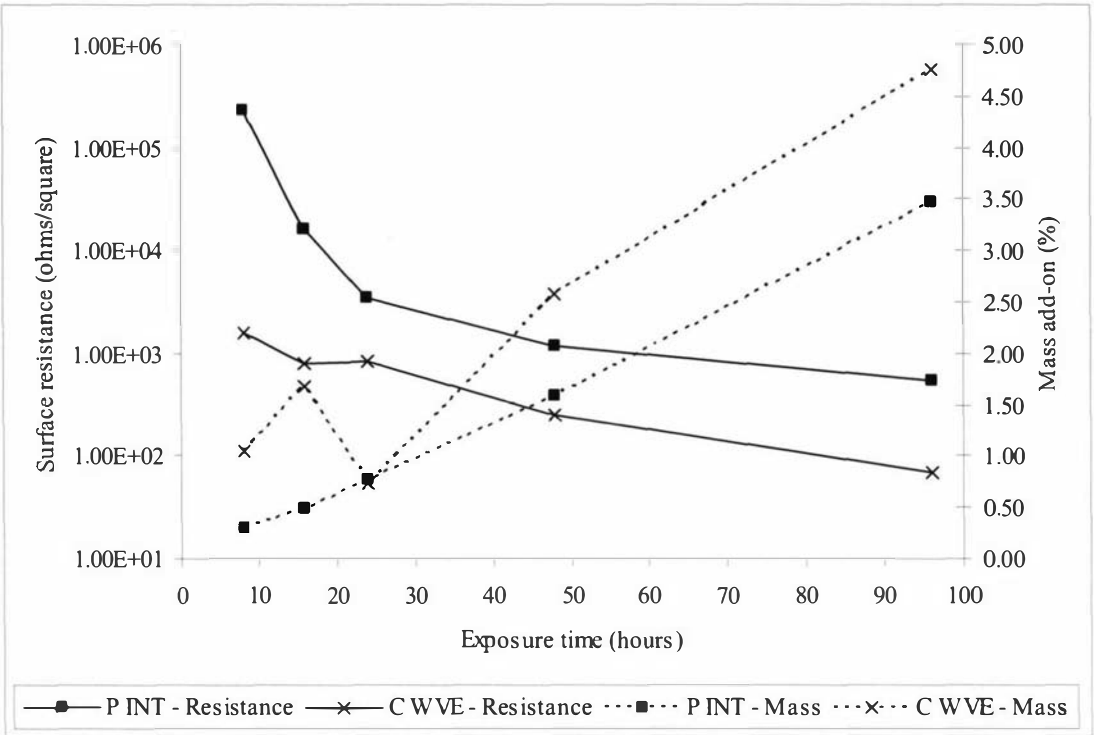


Figure 6.3. Mass add-on and surface resistance – vapour exposure time (EDOT).

EDOT reached resistance levels that were lower than those of pyrrole. Pyrrole levelled-off at approximately 20 kΩ for P INT and 2 kΩ for C WVE, while after 96 hours exposure EDOT had resistance of approximately 545 Ω for P INT and 69.8 Ω for C WVE. The mass add-on for EDOT was also much higher. Although the reaction took four days to reach this point, it was shorter than bithiophene, which took 8 days to reach only 50 MΩ, with a relatively low mass add-on of about 2%.

The 'efficiency' of the three precursors is compared in Figure 6.4 for P INT. Surface resistance has been plotted as a function of mass add-on, with the ideal behaviour placing the data points in the lower left-hand corner. EDOT and pyrrole have data points close to this quadrant of the graph, while bithiophene appears only in less favourable quadrants. Where they overlap in terms of mass add-on (indicated by the oval), EDOT and pyrrole have similar surface resistance. The lower surface resistance that can be achieved with EDOT comes at the cost of a much higher mass add-on. Overall, the generally linear nature of the relationship between mass add-on and surface resistance for all precursors indicates a strong correlation between these properties. The correlation coefficients for all five precursor/substrate combinations are provided in Table 6.10.

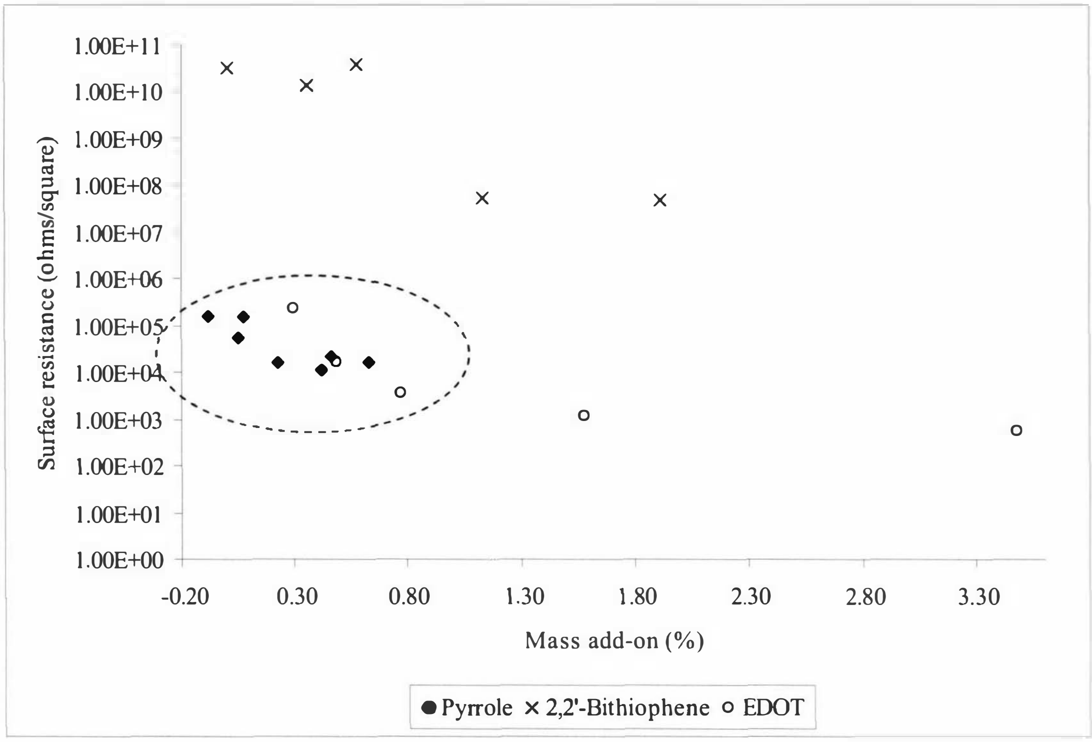


Figure 6.4. Surface resistance vs. mass add-on for three precursors on polyester interlock (P INT).

Table 6.10. Correlation coefficients (mass add-on vs. surface resistance) for all precursor/substrate combinations.

Combination	Correlation coefficient (r)
Pyrrole / P INT	-0.78
Pyrrole / C WVE	-0.77
2,2'-Bithiophene / P INT	-0.73
EDOT / P INT	-0.48
EDOT / C WVE	-0.80

In all cases other than EDOT / P INT the correlation coefficient is large and negative, which is probably skewed somewhat by the two very high mass add-on values for long exposure times.

6.2.3 Summary and Conclusions.

It is encouraging that the two thiophene-based precursors can be polymerised by the vapour deposition method, and can, with sufficient time, produce quite conductive composites. The time required to achieve that level of polymer deposition and resistance is the main drawback of the system, with eight days of vapour exposure required for bithiophene to get down to the MΩ level. EDOT was much faster, but still took 16 hours of vapour exposure to reach 16 kΩ (on P INT); a level that was achieved with pyrrole in ten minutes. This behaviour is not at all unexpected, and is probably due to the low vapour pressure (for bithiophene particularly) and low reactivity of the two precursors as compared to pyrrole. Accelerating this process is critical to the practical use of these two precursors for vapour deposition.

Another interesting outcome is the different behaviours of the two substrates. These can only be compared for pyrrole and EDOT, as the length of time taken to carry out the trials with bithiophene prevented the C WVE set from being undertaken. In every case, the surface resistance with the cotton fabric was lower, regardless of the mass add-on. Because the two fabrics are structurally different there are many possible reasons for this, but one likely cause is the higher absorbency of cotton compared to polyester, meaning that the oxidant was probably more readily taken up by cotton, allowing a higher final level of polymer deposition. The cotton may also have absorbed oxidant into the fibre structure, possibly allowing polymer formation inside the fibres.

6.3 Effect of Elevated Temperature.

6.3.1 Background.

At increased temperatures, the vapour pressure inside the sealed polymerisation vessel (as shown in Figure 4.13) will be increased. This results in a higher availability of the ICP precursor to the oxidant impregnated substrate, and should result in an increased rate of polymer deposition. Alongside that phenomenon is the increased rate of reaction due solely to the increased temperature. Overall therefore, increasing the temperature at which the system is held should result in accelerated vapour deposition. This is particularly important for the thiophene variants used in this work, as their very slow rate of polymerisation (established in the work reported on in Section 6.2) is a major limitation of their use in this way.

In the work reported in this section, accelerated polymer deposition was attempted by increasing temperature for 3,4-ethylenedioxythiophene (EDOT) and 2,2'-bithiophene. Pyrrole was also included for direct comparison. It is possible that elevating the temperature of polymerisation for a more reactive substance (such as pyrrole) may be counter-productive, as it may lead to degradation of the precursor before it has the opportunity to polymerise on the surface of the substrate.

6.3.2 Experimental Work.

The technique described in Section 4.4.2 was used, with the same procedure as given in Section 6.2. Polyester interlock (P INT) was the only substrate. In order to attain a higher temperature than ambient, the bottom of the reaction vessel was placed into a water bath set to maintain a fixed temperature for the duration of the reaction. This raised the temperature of the precursor in the base of the vessel; but the temperature at the specimen was more relevant. This was measured by inserting a thermometer into the reaction vessel through an opening in the lid. The opening had a rubber grommet in it, making an airtight seal around the thermometer. The bulb of the thermometer was positioned in the vessel at the same level as the centre of the specimen. Vapour exposure times were 30 minutes for pyrrole, 24 hours for 2,2'-bithiophene and 8 hours for EDOT. The polymerisation was carried out at nominal temperatures of 19, 34 and 52°C, but the exact temperature varied slightly from this.

All the pyrrole specimens darkened rapidly; the elevated temperature specimens fastest. At the completion of the reaction (and after rinsing) they were all uniformly dark grey, and were not noticeably different from each other. At 19 and 34°C the bithiophene specimens were only slightly darkened, while at 52°C the specimen was a uniformly dark reddish brown. The EDOT specimen at 19°C was moderately dark blue, but not uniform. At 34°C it was already darkening after 30 minutes, and was uniformly dark after 8 hours. At 52°C the specimen was uniformly dark after only 30 minutes, and very dark blue at completion. The mass add-on and surface resistance measurements for the specimens (average of three, standard deviation in parentheses) are provided in Table 6.11.

Table 6.11. Mass add-on and surface resistance – temperature.

Precursor	Vapour temperature (°C)	Mass add-on (%)	Surface resistance (Ω/square)
Pyrrole	19.0	1.82 (0.12)	3.88 (0.26) x 10^3
	35.5	1.74 (0.27)	2.40 (0.79) x 10^3
	56.0	1.54 (0.26)	2.40 (0.31) x 10^3
2,2'-Bithiophene	19.0	-0.21 (0.18)	> 1 x 10^{11}
	37.0	0.07 (0.06)	> 1 x 10^{11}
	55.0	4.90 (2.52)	1.23 (0.08) x 10^5
EDOT	19.0	0.32 (0.11)	1.16 (3.47) x 10^4
	36.0	2.52 (1.28)	1.90 (1.17) x 10^3
	54.5	17.23 (2.19)	4.82 (0.63) x10^2

These data are also provided graphically in Figure 6.5 (pyrrole), 6.6 (bithiophene) and 6.7 (EDOT). It should be noted that the resistance scale in the graphs is logarithmic for bithiophene and EDOT, but not for pyrrole.

It appears for pyrrole that there is no real advantage in increasing the temperature of the reaction. There was only a small difference in surface resistance for the three temperatures, and the mass add-on actually decreased slightly as the temperature increased. This indicates that the reaction proceeds best at room temperature. It may be that the polymer deposition process for pyrrole would be enhanced by a reduction in temperature.

In the case of bithiophene, increasing the temperature to just above its melting point (~33°C) had no beneficial effect. At this vapour exposure time a conductive composite was not formed. However, at a temperature of 55°C there was finally some polymerisation, and a moderately conductive composite was formed.

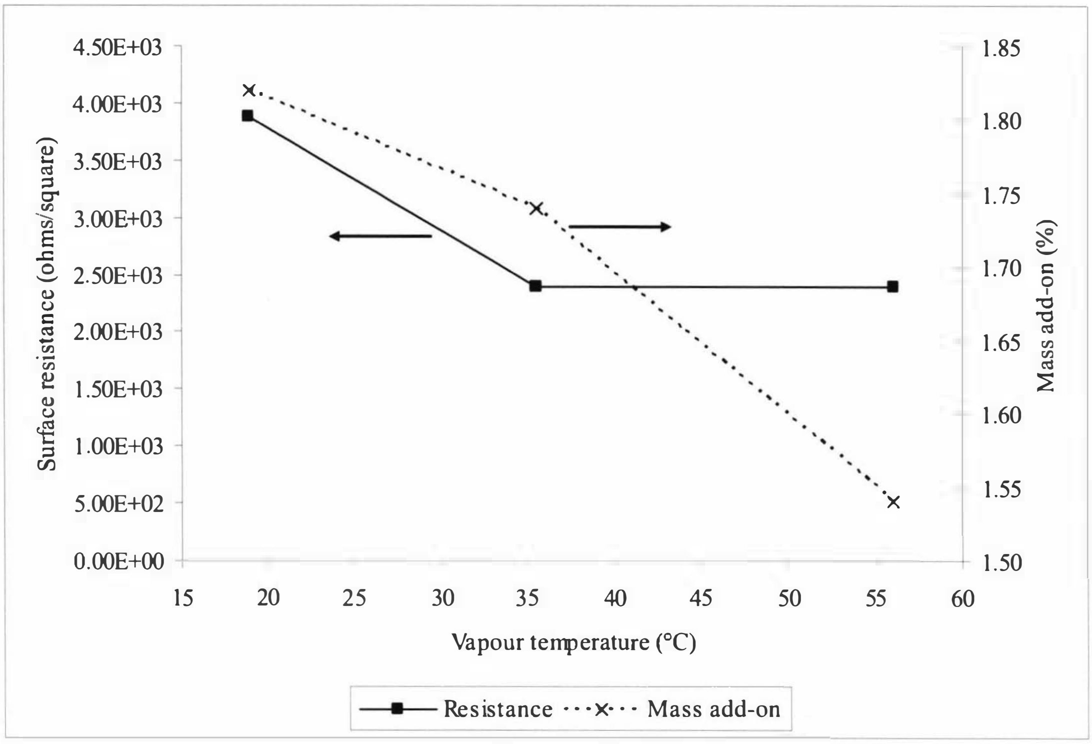


Figure 6.5. Mass add-on and surface resistance – elevated temperature (pyrrole).

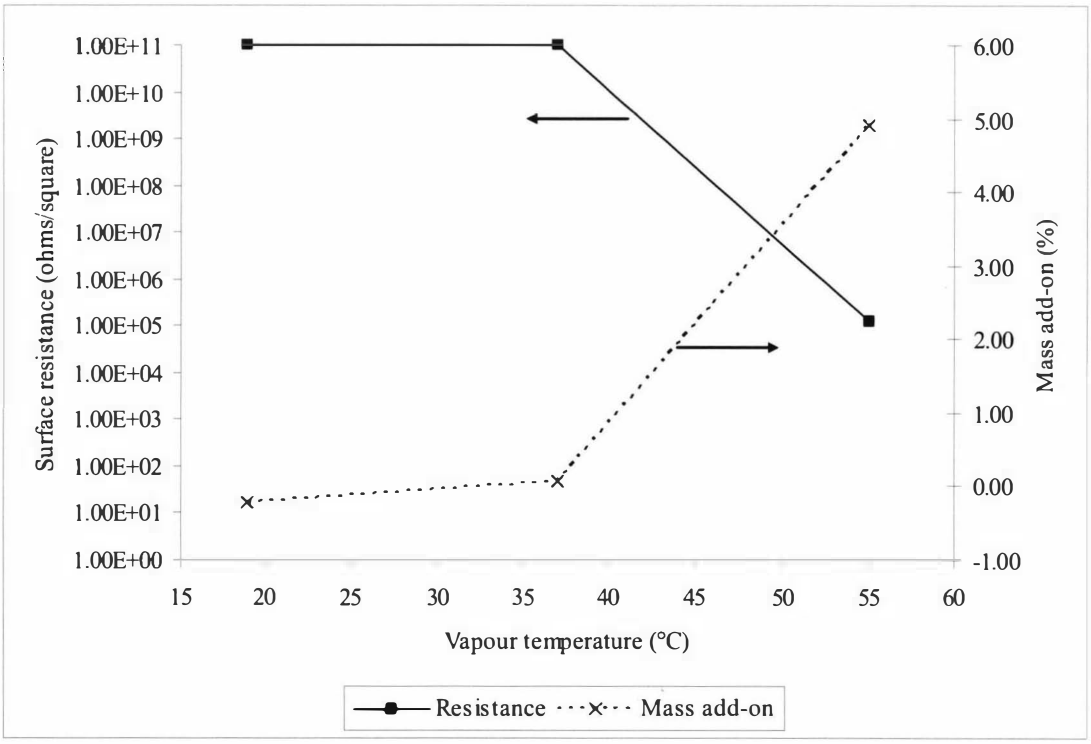


Figure 6.6. Mass add-on and surface resistance – elevated temperature (2,2'-bithiophene).

By contrast, EDOT responded very well to the increase in temperature across the range of temperatures used, with a steady decrease in resistance and a corresponding increase in mass add-on. However, the mass add-on at the highest temperature was very high (~17%), meaning that the mechanical properties of the fabric that relate to its drape and flexibility were likely to have been adversely affected.

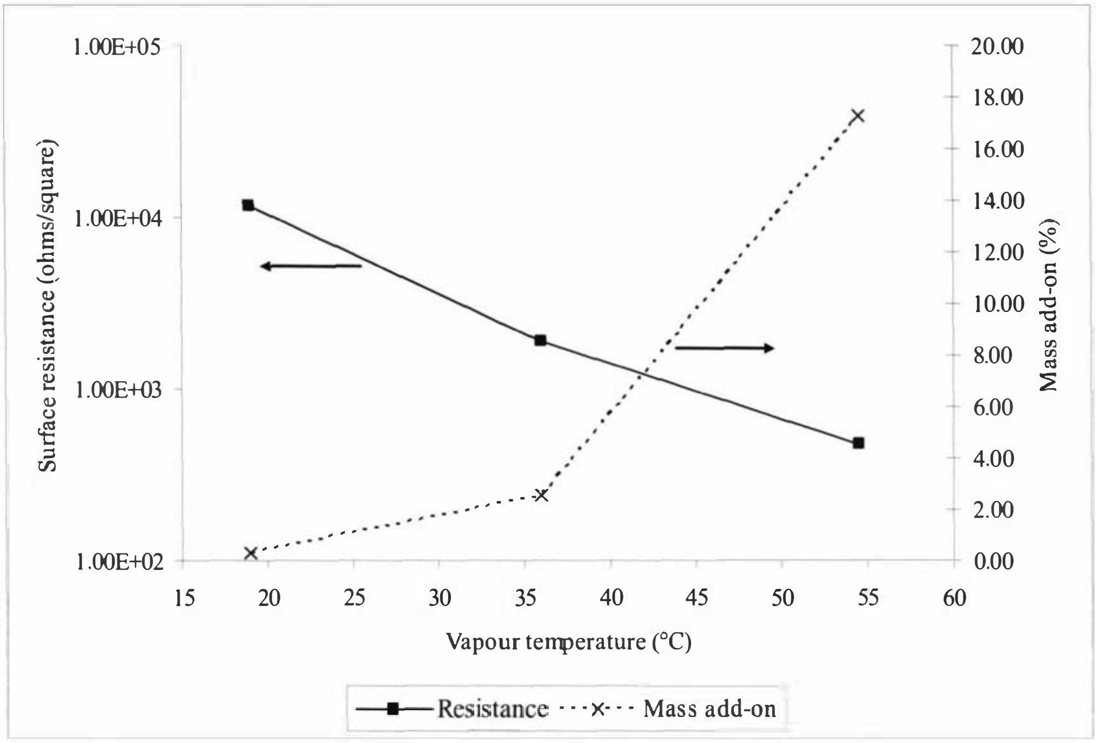


Figure 6.7. Mass add-on and surface resistance – elevated temperature (EDOT).

6.3.3 Summary and Conclusions.

It is possible to use an increase in temperature to improve the polymer deposition rate of thiophene-based ICP precursors. Poly(2,2'-bithiophene) was deposited on to a textile substrate with a surface resistance lower than that achieved previously, with a corresponding increase in mass add-on. The indications from Figure 6.6 are that it would be possible to improve the performance of bithiophene further by using an even higher temperature.

Poly(EDOT) was also prepared much more rapidly by increasing the temperature. However, at the highest temperature, the mass add-on was too high to be acceptable. At this temperature it may be appropriate to use a much shorter vapour exposure time.

There did not appear to be any advantage in increasing the temperature of vapour deposition of polypyrrole, as the reaction was already rapid, and the relatively reactive pyrrole may be susceptible to degradation, resulting in a possible deterioration in polymerisation performance.

6.4 Effect of Additional Dopant.

6.4.1 Background.

The one-step polymerisation technique from an aqueous system (discussed in Chapter 5) makes use of an additional dopant. Under normal conditions, when using an ionic salt (such a iron (III) chloride) as the oxidant, the dopant is the associated anion. However, due to chloride's relatively small size it is thought to be easily lost from the conductive polymer, resulting in a loss of conductivity. Large dopant anions such as aromatic sulphonates are often used, and sulphonic acids are usually the source of these. They also reportedly have the effect of increasing the composite conductivity, which was also observed in Section 6.1.1.2 when *p*-TSA was used.

It is appropriate to determine if the same effect (namely the increase in conductivity) can be demonstrated (or improved upon) by incorporating an alternative additional dopant into vapour-deposited ICPs. In this section, work relating to the use of 1,5-naphthalenedisulphonic acid (NDSA) as an additional dopant is reported, with the dopant being added to the oxidant solution at varying concentration levels. Of particular interest is whether the polymerisation behaviour of 2,2'-bithiophene can be improved by this approach, as it has proved difficult to achieve a reasonably conductive composite with this precursor.

6.4.2 Experimental Work.

The technique described in Section 4.4.2 was used, with a similar procedure to that given in Section 6.2. Polyester interlock (P INT) was the only substrate. A polymerisation temperature of 20°C was used for pyrrole and EDOT (for 30 minutes and 24 hours respectively), while 55°C was used for 2,2'-bithiophene (for 24 hours). This set-up allowed the effect of the additional dopant to be assessed under conditions that would result in moderately conductive polymer formation for all precursors, even if the dopant had no effect.

Polymerisation proceeded as observed previously for pyrrole and EDOT at room temperature, and bithiophene at elevated temperature. There was no obvious difference in either the rate of polymerisation or in the final appearance of the specimens that might have been attributable to the presence of the dopant. Pyrrole specimens were dark grey, EDOT dark blue, and bithiophene a reddish-brown. Measurements of surface resistance and polymer mass add-on were made in the usual way and are presented in Table 6.12 and in Figure 6.8.

Table 6.12. Mass add-on and surface resistance – additional dopant.

Precursor	Dopant concentration (mol/L)	Mass add-on (%)	Surface resistance (Ω/square)
Pyrrole	0	0.78 (0.11)	3.58 (0.31) x 10^3
	0.01	-0.45 (0.64)	7.70 (1.23) x 10^4
	0.05	0.11 (0.11)	7.78 (3.44) x 10^4
	0.10	0.42 (0.07)	4.48 (0.72) x 10^4
	0.20	-0.11 (0.79)	2.12 (0.64) x 10^5
2,2'-Bithiophene	0	3.34 (0.28)	3.00 (0.87) x 10^6
	0.01	7.82 (2.97)	7.45 (2.68) x 10^4
	0.05	8.33 (1.03)	1.15 (0.40) x 10^5
	0.10	3.29 (1.05)	2.82 (1.55) x 10^5
	0.20	4.87 (1.30)	2.35 (0.40) x 10^5
EDOT	0	2.66 (0.22)	1.37 (1.07) x 10^4
	0.01	3.86 (0.74)	4.03 (0.77) x 10^3
	0.05	4.11 (0.47)	8.45 (0.13) x 10^2
	0.10	2.02 (0.39)	2.45 (0.18) x 10^3
	0.20	1.80 (0.36)	3.85 (0.65) x 10^3

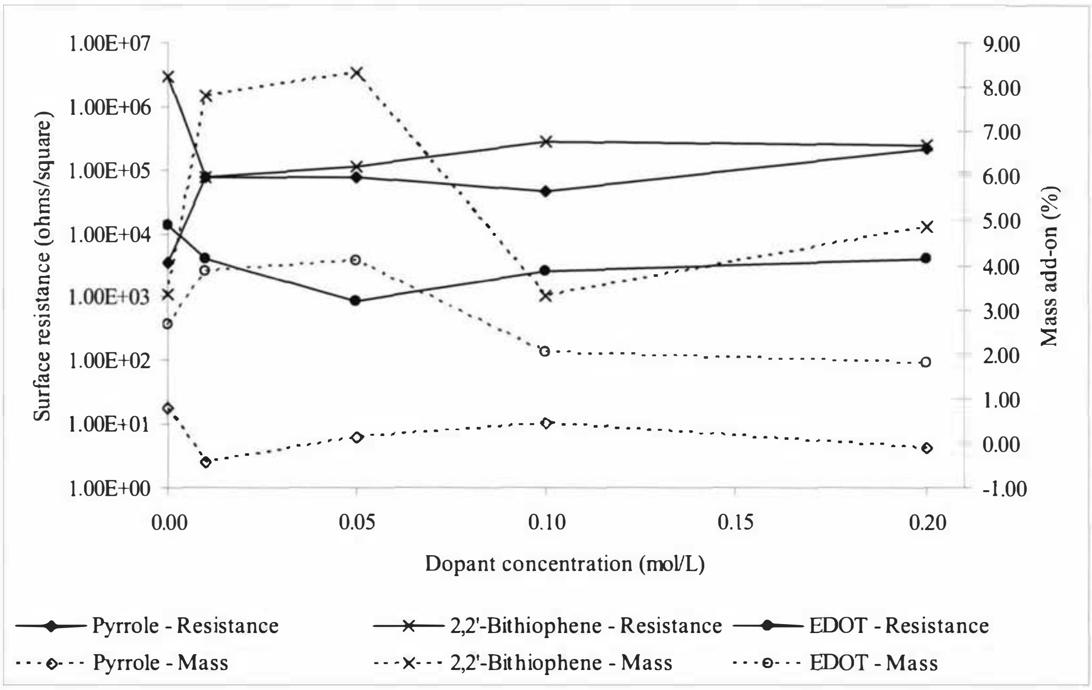


Figure 6.8. Mass add-on and surface resistance – additional dopant (three precursors).

In Figure 6.8, it is clear that behaviour was not consistent for all three precursors. The additional dopant had no beneficial effect on the surface resistance for pyrrole, with the lowest value being for the no-dopant situation. The mass add-on was also lower when NDSA was present. However, both bithiophene and EDOT showed improved performance with the additional NDSA. At low dopant levels, both had lower surface resistance than without NDSA, although as the NDSA concentration increased the resistance started to increase again. There was a fairly good correspondence between low resistance and high mass add-on, with the mass and resistance plots for bithiophene and EDOT in Figure 6.8 largely mirroring each other. The lowest resistance for EDOT occurred at NDSA concentration of 0.05 mol/L, while for bithiophene it was at 0.01 mol/L. In both cases the improvement (the reduction in surface resistance) compared to no NDSA was between one and two orders of magnitude. These concentration levels are remarkably low – only 5 and 1 % of the oxidant concentration respectively, but it is difficult to see how relevant this ratio might be, as it is not obvious how much oxidant was actually consumed during polymerisation. This seemingly low level of NDSA may, in fact, be sufficient to fully dope the conductive polymer with naphthalenedisulphonate in place of chloride, or it may only partly replace it. Either way, there is clearly no advantage in providing a large quantity of NDSA as it has a detrimental effect – perhaps by interfering with the oxidative polymerisation reaction in some way.

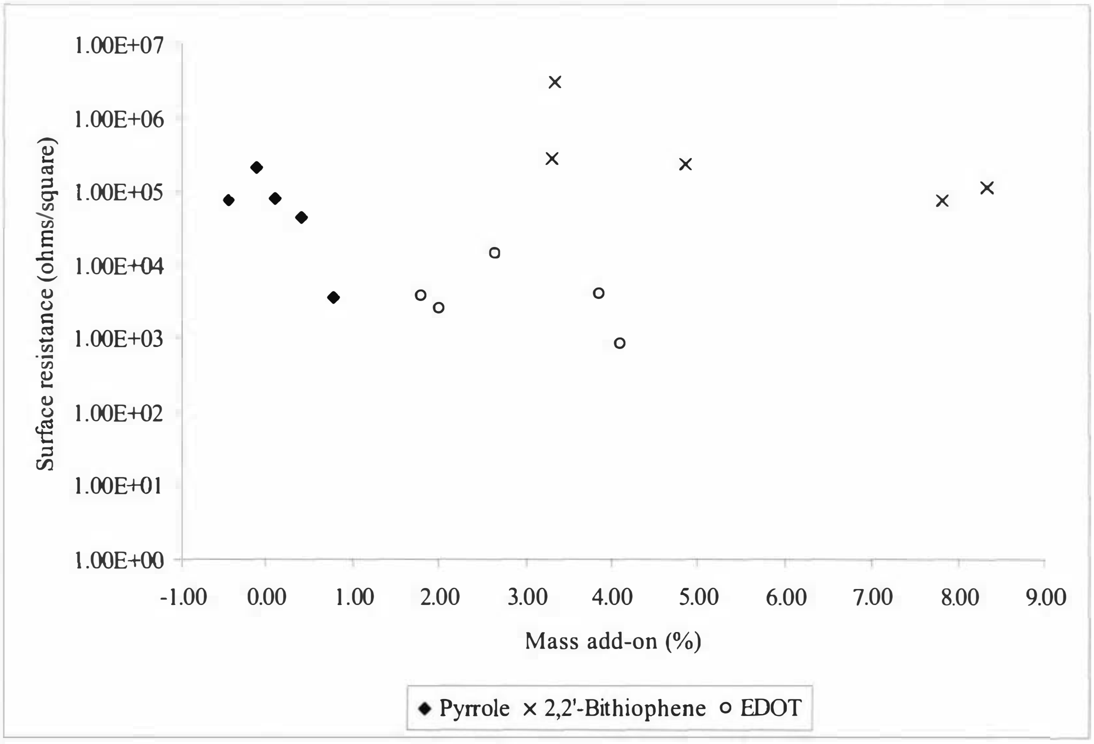


Figure 6.9. Surface resistance vs. mass add-on for three precursors with additional dopant (NDSA).

Unfortunately (for bithiophene in particular), the mass add-on at the lowest resistance was quite high (about 8%). If the same analysis of the efficiency of the conductive polymer deposition is carried out as was used in Section 6.2.2 (Figure 6.4), it is apparent that both EDOT and pyrrole have the same level of efficiency. This is shown in Figure 6.9, where the EDOT and pyrrole data points fall on approximately the same line towards the lower left of the plot, while the bithiophene data points are roughly on a line in the top right of the plot.

6.4.3 Summary and Conclusions.

The inclusion of an additional dopant was beneficial for the thiophene variants, but detrimental for pyrrole. Providing the appropriate concentration of dopant was, however, critical to achieving the reduction in resistance, with only a very low level of dopant required. Above this level, resistance increased and the mass add-on decreased. The behaviour of EDOT was again much better than 2,2'-bithiophene, with a lower resistance reached at a lower mass add-on.

6.5 Characterisation of Specimens.

6.5.1 Background.

A sequence of treatments was made to allow scanning electron microscopy to be carried out on specimens of particular interest from the previous sections. They were essentially recreated specimens from previous sections, prepared on slightly larger substrate specimens. All three precursors were used, and the influence of oxidant concentration and the presence of NDSA on coating morphology was examined. It was hoped that morphological differences would be observed between different specimens, and that these might relate to the measurable data of mass add-on (%) and conductivity. Of particular interest was the nature of the polymer deposition onto the fibres – whether it formed smooth or irregular coatings, and whether the polymer was surface-located or was found between fibres, in the fabric interstices.

6.5.2 Experimental Work.

The polymerisation conditions used were those found to be most effective for each precursor from the work reported previously in this chapter. The influence of an additional dopant on coating morphology was examined for all three precursors, at a level that was most likely to cause an improvement in electrical properties. Varying the mass add-on (by varying the oxidant concentration) was assessed for pyrrole only. The substrate was polyester interlock (P INT); the oxidant solution was iron (III) chloride in methanol; pyrrole and EDOT were polymerised at 20°C for 30 minutes at 24 hours respectively; 2,2'-bithiophene was polymerised at 55°C for 24 hours. Other parameters are summarised in Table 6.13, along with surface resistance and mass add-on measurements. A non-destructive version of the surface resistance test was used (so as to provide complete specimens for SEM imaging), so the surface resistance values recorded in Table 6.13 are not directly comparable with those reported elsewhere in this chapter.

Polymerisation proceeded as seen previously; the polypyrrole-coated specimens being various shades of grey, poly(2,2'-bithiophene) being reddish brown, and poly(EDOT) dark blue. Despite the difference in surface resistance test method, the results are generally consistent with those recorded elsewhere. The effect of the oxidant concentration and dopant on mass add-on and surface resistance was the same as when each specimen was created previously.

SEMs were recorded at least two magnifications (350 x and 1000 x) of all specimens. The operator was asked to record low magnification images that were representative of the whole, rather than unusual regions. An area of particular interest for each specimen is shown in the higher magnification images, provided as Figures 6.10 to 6.17. In most cases the specimens did not require gold coating prior to examination as they were already sufficiently conductive. Pyrrole at an oxidant concentration of 0.05 mol/L is the only exception to this.

Table 6.13. Mass add-on and approximate surface resistance – SEM specimens.

Precursor	Dopant concentration (mol/L)	Oxidant concentration (mol/L)	Mass add-on (%)	Surface resistance (Ω/square)
Pyrrole	0	1.00	0.96	8.50×10^{3}
	0	0.25	0.79	0.98×10^{5}
	0	0.05	0.13	$> 1 \times 10^{9}$
	0.05	1.00	0.15	8.57×10^{4}
2,2'-Bithiophene	0	1.00	3.04	3.70×10^{6}
	0.01	1.00	9.99	1.09×10^{5}
EDOT	0	1.00	3.47	1.30×10^{4}
	0.05	1.00	4.12	7.05×10^{2}

The effect of oxidant concentration on mass add-on can be observed in the first three sets of pyrrole images. In Figure 6.10 (1.00 mol/L) there are substantial areas of inter-fibre polymerisation, but a seemingly uniform coating of polymers on the fibre surface. In Figure 6.11 (0.25 mol/L) the fibre surface still appears generally smoothly coated, but there are now some quite large particles of loose polymer present in the structure (rather than filling the fabric interstices as they do with 1.00 mol/L). With the concentration reduced to 0.05 mol/L (Figure 6.12) the fibres have only a few small fragments of polymer apparent. These observations are consistent with a reduction in mass add-on. The only apparent morphological effect of adding NDSA to the pyrrole polymerisation situation is a reduction in inter-fibre polymerisation, which is consistent with the lower mass add-on that this specimen displays.

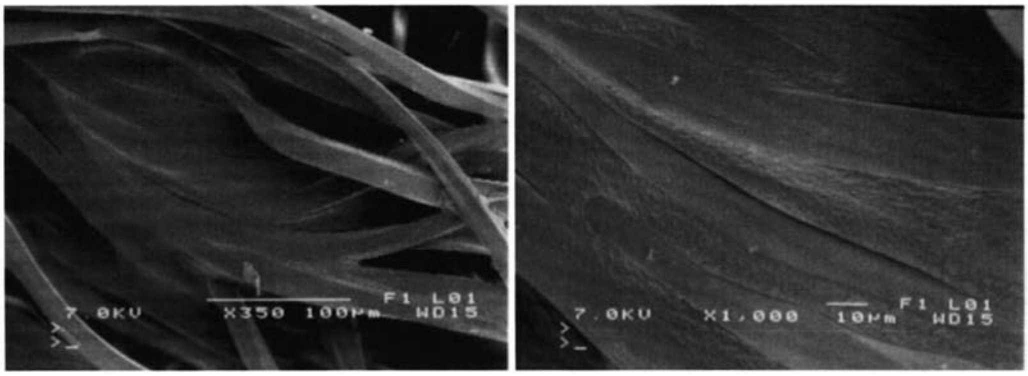


Figure 6.10. SEM images – pyrrole, 1.00 mol/L $FeCl_3.6H_2O$.

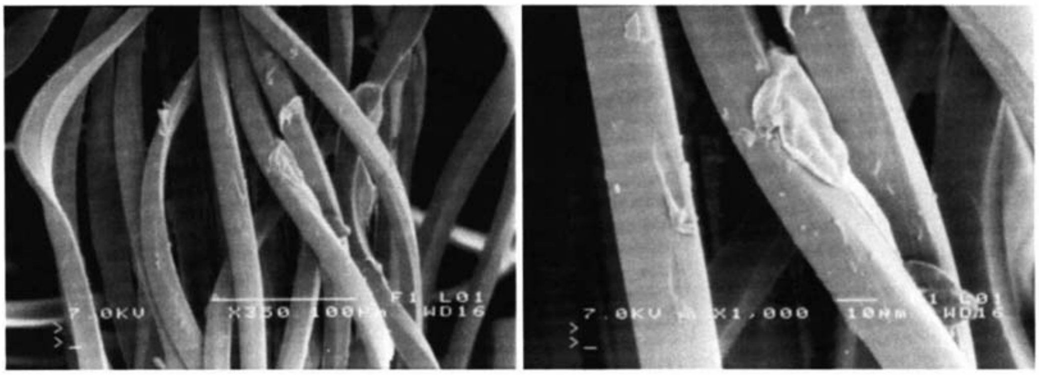


Figure 6.11. SEM images – pyrrole, 0.25 mol/L $FeCl_3.6H_2O$.

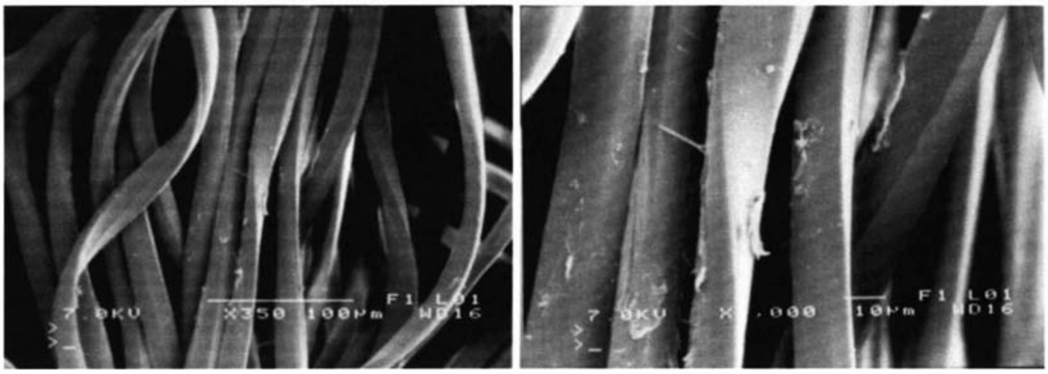


Figure 6.12. SEM images – pyrrole, 0.05 mol/L $FeCl_3.6H_2O$.

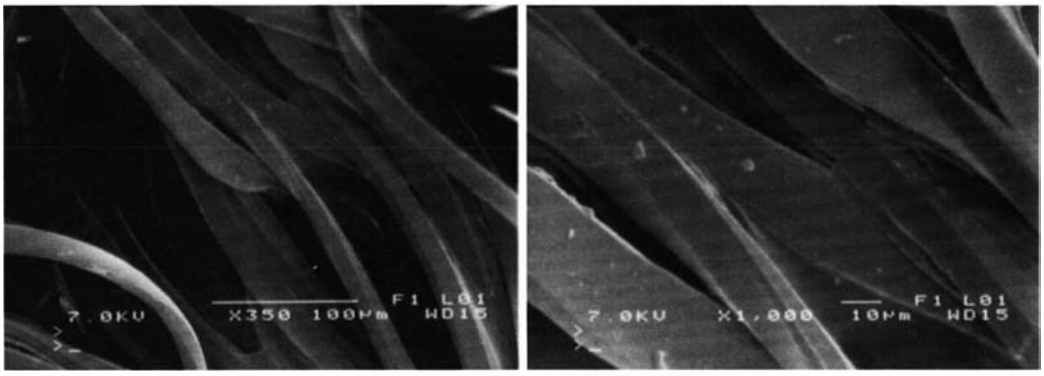


Figure 6.13. SEM images – pyrrole, 1.00 mol/L $FeCl_3.6H_2O$, 0.05 mol/L NDSA.

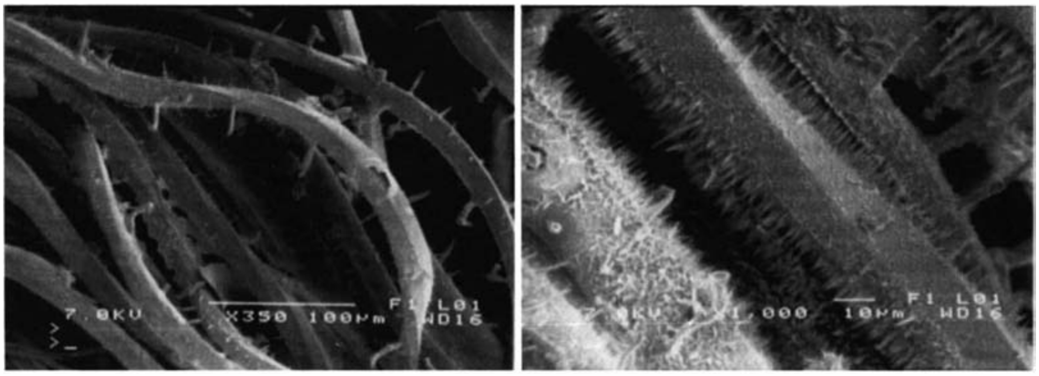


Figure 6.14. SEM images – 2,2'-bithiophene, 1.00 mol/L $FeCl_3.6H_2O$.

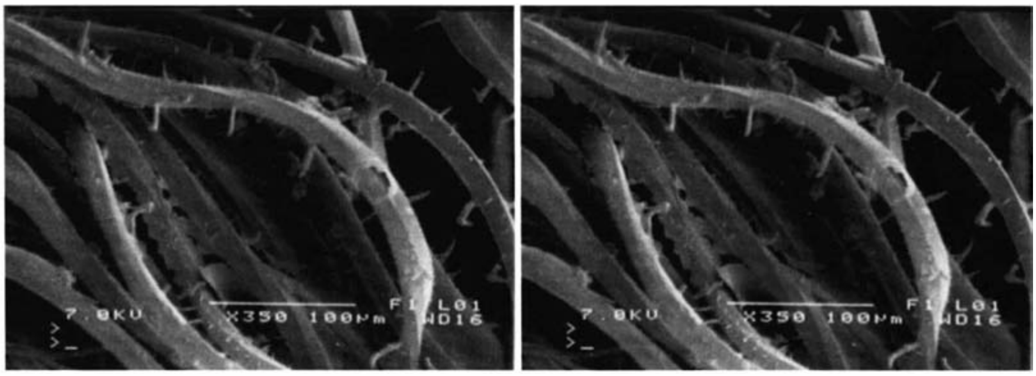


Figure 6.15. SEM images – 2,2'-bithiophene, 1.00 mol/L $FeCl_3.6H_2O$, 0.01 mol/L NDSA.

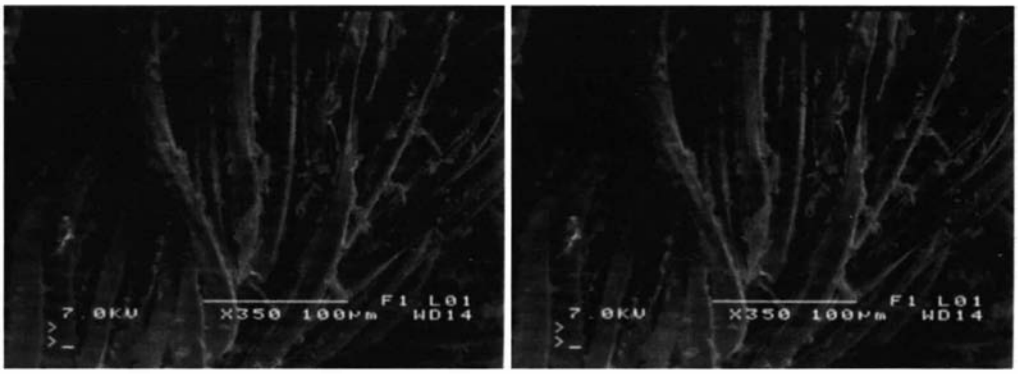


Figure 6.16. SEM images – EDOT, 1.00 mol/L $FeCl_3.6H_2O$.

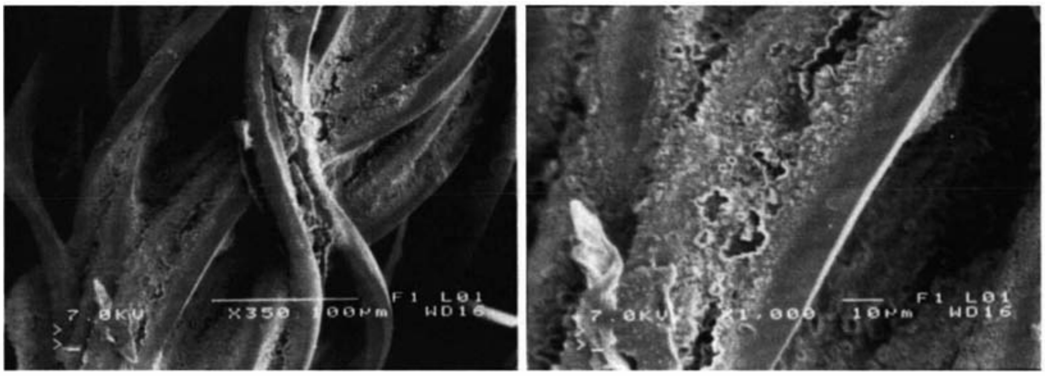


Figure 6.17. SEM images – EDOT, 1.00 mol/L $FeCl_3.6H_2O$, 0.05 mol/L NDSA.

The images of the bithiophene specimens are quite remarkable, with a growth of needle-like structures on the fibre surface (finer and denser on the specimen without NDSA). These look like crystalline structures, so may be re-crystallised iron (III) chloride, although this should be unlikely, given the extensive rinsing the specimens were given after treatment. Alternatively, they could be bithiophene that has condensed and crystallised as a solid on the fibre surfaces. This seems plausible as, being insoluble in water, it might not have been removed by rinsing. Another possibility is that it is the conductive polymer itself, although it is difficult to envisage a reason for its deposition in this way. Regardless, the specimen was moderately conductive, meaning that it is likely that underneath these structures there is a conductive polymer coating on the fibres. When NDSA was added, the increased mass add-on is reflected morphologically in an increase in large particles of loose polymer within the fibrous structure.

The peculiar needle-like structures are not apparent for EDOT. Instead there is a large amount of loose polymer apparent in the fibrous structure, some parts of which look like polymer that has formed on the fibre surface, but subsequently been dislodged. The mass add-on was not particularly high, so it is possible that a lower density polymer has been formed. This may certainly be the case when NDSA was added, as the deposited polymer looks almost 'bubbly' in texture.

6.5.3 Summary and Conclusions.

Generally, pyrrole appears to form smooth coatings on fibres when polymerised by a vapour deposition technique. By comparison, polymers from bithiophene and EDOT are less smooth; a property that may be due to the longer polymerisation time. Pyrrole strikes the oxidant-impregnated specimen and polymerises virtually instantaneously, whereas the process is much slower for EDOT and bithiophene. The morphological effect of a higher mass add-on (when induced by increased oxidant concentration) is an increase in the amount of loose polymer in the fabric interstices. It may also increase the coating thickness on the fibre surfaces, but it is difficult to verify this from these images.

In every case, NDSA changed the fibre morphology. For pyrrole it resulted in less polymer deposition, whereas for EDOT and bithiophene it changed the appearance of the polymer. For EDOT the polymer looks less dense with NDSA, with an irregular surface. This is inconsistent with the findings of Kuhn *et al.* [42], although their work was with polypyrrole deposited by the Milliken method. Kuhn *et al.* concluded that the presence of aromatic sulphonic acids gave a more compact polymer structure on the molecular level. If this is the case for vapour deposition of thiophene variants, it was not apparent from the SEM images.

6.6 Vapour Deposition Summary and Conclusions.

The key parameters that influence the vapour deposition of thiophene-based ICP precursors onto textile substrates have now been identified and their influence determined. Of most significance is the fact that thiophene-based precursors have been polymerised in this way, with surface resistance values that are comparable to (or lower than) those for pyrrole. This is (as far as can be ascertained) the first time that conductive poly(2,2'-bithiophene) and poly(3,4-ethylenedioxythiophene) have been *in situ* polymerised onto a textile substrate in this manner.

It is now possible to summarise the conditions (as far as they have been identified) that are optimal for the formation of conductive thiophene-based polymers on textile substrates. These are given in Table 6.14 (the dopant referred to is 1,5-naphthalenedisulphonic acid (NDSA)). There is an opportunity for these conditions to be further optimised in the future, for example by increasing the temperature at which 2,2'-bithiophene vapour deposition is carried out. Also, with 3,4-ethylenedioxythiophene (EDOT), there is the opportunity to balance temperature against duration, with a longer time at a lower temperature an alternative to a shorter time at a higher temperature.

Table 6.14. Optimum conditions for vapour deposition of thiophene-based conductive polymers onto textile substrates.

Parameter	3,4-Ethylenedioxythiophene	2,2'-Bithiophene
Oxidant	$FeCl_3.6H_2O$	$FeCl_3.6H_2O$
Oxidant solvent	Methanol	Methanol
Oxidant concentration	> 1 mol/L	> 1 mol/L
Temperature	Room temperature	> 50°C
Duration	> 8 hours	> 8 hours
Dopant concentration	~ 0.05 mol/L in oxidant solution	~ 0.01 mol/L in oxidant solution

Overall, polymers prepared with (EDOT) have consistently lower surface resistance at lower mass add-on levels than with bithiophene. In most situations where a reasonably low resistance was achieved with bithiophene, the mass add-on was greater than 5%. At this level and above it is likely that there will be a detrimental effect on the textile properties of flexibility and extensibility. Vapour deposition of EDOT onto textile substrates, either at low temperature for long times, or at elevated temperatures for shorter times, appears to be a viable option for the preparation of electrically conductive textile-ICP composites.

Chapter 7 Experimental Work – Two-Stage Impregnation.

7.1 Background.

7.1.1 Principle.

Park and Ruckenstein [48] described a two-stage technique in which a conductive polymer was deposited into the interstitial spaces of a porous substrate. They briefly explored the possibilities of carrying this process out on a textile substrate, with pyrrole and bithiophene ICP precursors, by the basic process described in Section 4.4.3. The principle is to thoroughly impregnate the substrate with the ICP precursor before adding the oxidant. Oxidative polymerisation occurs on the substrate surfaces during evaporation of the oxidant solution. It is possible to carry out the process the other way around – that is, oxidant impregnation followed by ICP precursor impregnation, but this is less appealing from a processing perspective. If precursor impregnation precedes oxidant, a bulk ICP precursor solution can be prepared, and if specimens are small, a series of them can be impregnated one after another in the same conditions (assuming that the dissolved precursor and the solvent are absorbed into the substrate to the same extent). As it is likely that some of the ICP precursor diffuses off the substrate when it is immersed in the oxidant solution, the latter ceases to have known chemical properties, and therefore cannot be re-used for multiple treatments. Since the oxidants used for this work are very much cheaper than the ICP precursors, it is sensible to sacrifice the oxidant solution in preference to the ICP precursor solution.

One fundamental limitation of this 'two-stage impregnation' approach is the tendency for the ICP precursor to separate from the substrate during the second (polymerisation) impregnation, and accumulate as polymer in solution. Minimising this is critical to being able to control the polymerisation process and make efficient use of the precursor. If the precursor migrates from the fibre surface into the solution, polymerisation may happen in solution rather than on the surface of the fibres. However, as Park and Ruckenstein describe [48], the polymerisation actually occurs on solvent evaporation after removal from the second solution. Therefore diffusion should only result in a loss of precursor (and hence a reduction in polymer), and not in polymerisation occurring in the solution. It is likely that careful selection of the two solvents (that used for the precursor impregnation and that used for the oxidant impregnation), and prevention of precursor diffusion by avoiding physical agitation of the solution should help to maximise the degree to which polymer formation is on the surface of the substrate.

Other parameters may influence the polymerisation process, including the concentration of precursor and oxidant. A higher level of precursor should lead to higher polymer mass add-on, and therefore lower surface resistance of the textile-ICP composite produced. Higher concentrations of the oxidant might result in more rapid and less well-ordered polymerisation (as well as less uniform deposition), and therefore a higher resistance composite. The conditions for solvent evaporation after precursor and oxidant impregnation may also be critical, and investigations into these are reported in subsequent sections of this chapter. Initially however, the process was trialled to determine whether it was feasible to use on a textile substrate, and to confirm that Park and Ruckenstein's technique could be replicated.

7.1.2 Initial Attempts.

A set of preliminary experiments was carried out with pyrrole, under the same conditions used in the literature [48]. The fabrics used were a cotton/elastane blend and a cotton/polyester blend. The experiments confirmed that conductive polypyrrole could be deposited onto a textile substrate by this technique, and that the best order in which to carry out the impregnations was precursor followed by oxidant (as discussed in the previous section), rather than oxidant followed by precursor. In the latter case, there was a tendency for the oxidant to diffuse off the substrate, and hence reduce the amount of polymer able to be formed on the surface of the fibres. In general, a higher concentration of oxidant in solution resulted in both a higher polymer mass add-on and lower resistance. Iron (III) chloride as the oxidant performed better than hydrogen peroxide or ammonium persulphate. The latter two were trialled with and without hydrochloric acid present (to provide a chloride counter-ion, as is the case for iron (III) chloride), but in all cases were less effective than iron (III) chloride.

The next step was to determine if thiophene-based precursors could be used to deposit conductive polymers onto a textile substrate. This was done using thiophene, 3-methylthiophene (3-MT), 2,2'-bithiophene and EDOT precursors, in acetonitrile at 1 g/10 mL, while the oxidant was iron (III) chloride in methanol or water at 1 mol/L. Both impregnations were for 10 minutes, and the drying times after impregnation were 30 minutes (precursor) and 240 minutes (oxidant).

The surface resistance and polymer mass add-on was measured both before and after rinsing the specimens with copious amounts of de-ionised water. This illustrated the need for thorough rinsing, as all specimens were quite conductive and had mass add-on of ~120% before this was carried out. This was mainly due to the absorbed oxidant (and possibly other unreacted materials or non-adhering polymer), as, after rinsing, only the bithiophene/methanol and EDOT/methanol combinations had any appreciable mass add-on (~2 and ~10 % respectively) and measurable resistance (of ~250 and ~10 kΩ/square respectively). The bithiophene/methanol combination appeared to have dark reddish polythiophene deposited onto it, while for EDOT dark blue poly(EDOT) was apparent. Thiophene and 3-MT specimens were unchanged in appearance. Clearly bithiophene and EDOT could be polymerised in this system, but the less reactive thiophene and 3-MT could not.

Another experiment indicated that the concentration of EDOT could be reduced with a commensurate reduction in mass add-on, but with no change to surface resistance. However, the rough measurement system used in these preliminary trials was unable to determine whether this was a significant difference.

These initial experiments confirmed that the two-stage impregnation system could be employed with textile substrates and thiophene-based precursors. The influence of various parameters is reported in more depth in the following sections.

7.2 Effect of ICP Precursor Type and Concentration.

7.2.1 Background.

Preliminary experiments demonstrated that a range of ICP precursors could be used to deposit conductive polymers onto a textile substrate. A more rigorous comparison of different precursors was required, to determine which perform the best in terms of low resistance, and (ideally) low mass add-on at that resistance level. Also, it would be useful to identify which precursor might be most suitable for larger-scale processing. This involved making an assessment of the extent to which polymer formation is limited to the surface of the textile, how much poorly-adhered polymer accumulates in the interstices of the fabric; and how much polymer forms in the oxidant solution (second impregnation).

There was an indication from one of the preliminary experiments that it might be possible to reduce the concentration of the precursor, with only a slight (if any) increase in surface resistance, and with a drop in mass add-on. At high mass add-on the fabric specimen is likely to feel stiffer, as the deposited polymer fills the interstices of the fabric and also increasingly 'glues together' yarns and fibres that would otherwise be able to move independently when the specimen is bent or stretched.

7.2.2 Effect of Precursor Type for a Range of Substrates.

A series of very different substrates was chosen, to determine if there was a consistently best-performing precursor when polymerised onto many fibre types and fabric constructions. This work was carried out before the standard fabrics described in Section 4.2 were obtained; but as a comparison of pre-cursors on diverse substrates was what was being assessed, directly comparable fabrics were not required. One specimen of each fabric was used, and it was only large enough to allow two measurements of surface resistance to be made.

The ICP precursors used were pyrrole, 2,2'-bithiophene and 3,4-ethylenedioxythiophene (EDOT). They were dissolved in acetonitrile at 1 mol/L (pyrrole and EDOT) and 0.5 mol/L (2,2'-bithiophene). The bithiophene solution was prepared at half the molar concentration of the EDOT and pyrrole solutions, because each bithiophene molecule is actually a dimer rather than a monomer, and contains two heterocyclic rings. Hence one mole of EDOT and 0.5 moles of bithiophene have the same number of thiophene rings. In most other work reported in this thesis, mass-based concentration (typically g/10 mL) was used to simplify this situation.

The oxidant solution was iron (III) chloride in methanol at 1 mol/L concentration, and the substrates were polyester-cotton rib (PC RIB), polyester interlock (P INT), nylon-elastane warp-knit (N WRP), and cotton (C WVE), polyester (P WVE) and wool (W WVE) woven fabrics. Impregnations were six and four minutes (precursor, then oxidant), while drying times were 10 minutes (after precursor impregnation) and overnight (after oxidant impregnation). These timings were chosen somewhat for convenience, but were long enough for each process (impregnation or drying) to be fully completed.

As can be seen from the results presented in Table 7.1, it was possible to form a conductive ICP coating on each of these widely varying substrates. EDOT resulted in the highest mass add-on for five of the six substrates used; ranging from nearly 30% for the nylon-elastane warp knit, to just 0.3% for the polyester woven fabric. It also had the lowest resistance for four of substrates. As expected from the preliminary experiments reported in Section 7.1, bithiophene had the highest resistance in all but one situation. Clearly the substrate had a large effect on polymer deposition, but the fabrics used here were too variable in structure and composition to allow determination of the exact influence of these properties.

Table 7.1. Mass add-on and surface resistance – three precursors.

Substrate	Mass add-on (%)			Surface resistance (Ω/square)		
	Pyrrole	Bithiophene	EDOT	Pyrrole	Bithiophene	EDOT
PC RIB	3.3	0.5	16.8	9.3×10^{2}	3.3×10^{9}	7.0×10^{3}
P INT	0.9	0.3	10.4	5.2×10^{3}	$> 1.0 \times 10^{11}$	1.5×10^{4}
N WRP	6.9	0.9	29.5	1.2×10^{3}	2.0×10^{10}	1.3×10^{2}
P WVE	1.1	0.6	0.3	1.0×10^{10}	1.3×10^{10}	6.0×10^{3}
C WVE	0.5	1.3	3.8	8.3×10^{9}	1.7×10^{9}	9.1×10^{4}
W WVE	1.7	2.5	4.6	2.8×10^{7}	3.0×10^{7}	1.9×10^{3}

Note: For P INT-bithiophene the electrical resistance exceeded the upper limit of the resistance meter used. Therefore the surface resistance is expressed as being greater than the meter's upper limit.

These results suggest that EDOT can be successfully polymerised by the two-stage impregnation technique, and while pyrrole can also be polymerised in this way, it appears to suit the less reactive EDOT better. EDOT had a higher mass add-on, suggesting that more of the precursor was being converted to polymer attached to the substrate. It was observed with pyrrole that the second solution (oxidant impregnation) darkened after the specimen was placed into it, which suggests that pyrrole was diffusing into the oxidant solution and being polymerised there, rather than on the surface of the fibres after removal. With both EDOT and bithiophene, the specimen only darkened after removal from the solution, and no darkening of the oxidant solution was observed.

The relationship between mass add-on and resistance is not straightforward. The correlation between the two parameters is weak, as demonstrated by the low correlation coefficients for each precursor: -0.503 (pyrrole), -0.518 (bithiophene) and -0.362 (EDOT). All are negative values, indicating that, in general, the lower the mass add-on, the higher the resistance (as would be expected). However, none are at all close to 1 or -1 (meaning that any correlation is weak), so it is not possible to draw a clear conclusion about the relationship between mass add-on and resistance based on these results.

7.2.3 Effect of Precursor Concentration for a Range of Substrates.

A series of experiments was carried out to directly examine the relationship between mass add-on and surface resistance. These experiments also allowed precursor concentration to be evaluated as a direct means of controlling the polymer mass add-on, as with more precursor available, more polymer should be formed. Because of the influence that substrate type had on both mass add-on and surface resistance in Section 7.2.2, a range of substrates was used in these experiments to verify if their results could be applied universally.

In this work, the concentration of ICP precursor was defined in terms of mass per unit volume of solvent, rather than moles per unit volume. The conversion from one to another can be easily made. This is also the convention used in some of the relevant literature [49,61], and it seems logical to use a mass-based expression of concentration when assessing the accumulation of polymer on the substrate as a mass percentage.

7.2.3.1 Effect of precursor concentration for three precursors on one substrate.

EDOT, pyrrole and 2,2'-bithiophene were again compared. Specimens were prepared from the polyester interlock fabric (P INT) used in the work reported in Section 7.2.2. Three replicates were prepared for each polymerisation variant. Although the performance of 2,2'-bithiophene on this substrate was poor previously, this fabric was used because it is easy to handle, remaining flat and stable during the treatment (many others have a tendency to curl up, which makes them difficult to handle and assess), and also because it was hoped that improvements might be observed with more experience in using the technique

The treatment conditions (except for precursor concentration, which is provided in Table 7.2) were identical to those used in Section 7.2.2, and polymer deposition followed the procedure described in Section 4.4.3. The precursor concentration values seem somewhat irregularly spread, as, when the experiment was designed, the concentrations were determined in mol/L then calculated back to g/10 mL. However, this is still a useful range of values.

The polymerisation proceeded as expected, the pyrrole specimens tending to darken in solution and the others darkening only after removal from the oxidant solution (during solvent evaporation). The specimens were darker at higher precursor concentrations, although this was less apparent for bithiophene. The bithiophene polymerisation looked more effective (darker, more uniform) on this occasion than previously. The reason for this is not clear. The results obtained for these specimens are given in Table 7.2 (standard deviation in parentheses) and are also plotted in Figure 7.1.

Table 7.2. Mass add-on and surface resistance – precursor concentration.

Precursor	Concentration (g/10 mL)	Mass add-on (%)	Surface resistance (Ω/square)
Pyrrole	0.671	2.74 (0.16)	3.62 (0.42) x 10^3
	0.503	2.06 (0.49)	6.18 (0.65) x 10^3
	0.336	1.35 (0.09)	8.62 (1.17) x 10^3
	0.168	0.56 (0.13)	1.98 (0.45) x 10^4
	0.067	0.15 (0.28)	9.08 (2.75) x 10^4
2,2'-bithiophene	0.831	3.89 (0.24)	9.07 (4.11) x 10^5
	0.416	2.42 (0.02)	8.53 (4.31) x 10^5
	0.166	1.33 (0.07)	4.87 (4.92) x 10^6
EDOT	1.422	11.22 (2.69)	4.65 (0.96) x 10^4
	0.711	4.24 (0.53)	3.07 (0.10) x 10^4
	0.142	1.06 (0.32)	1.06 (0.56) x 10^4

For all precursors, the mass add-on clearly increased with increasing precursor concentration. Surface resistance reduced with increasing precursor concentration, with the exception of EDOT, which exhibited the reverse behaviour. This is very unexpected, and requires further investigation, particularly to determine the point at which the behaviour ceases (obviously it cannot continue to zero precursor concentration). The correlation coefficients for the precursor concentration, mass add-on and surface resistance are provided in Table 7.3. These data further emphasise the result seen in Figure 7.1.

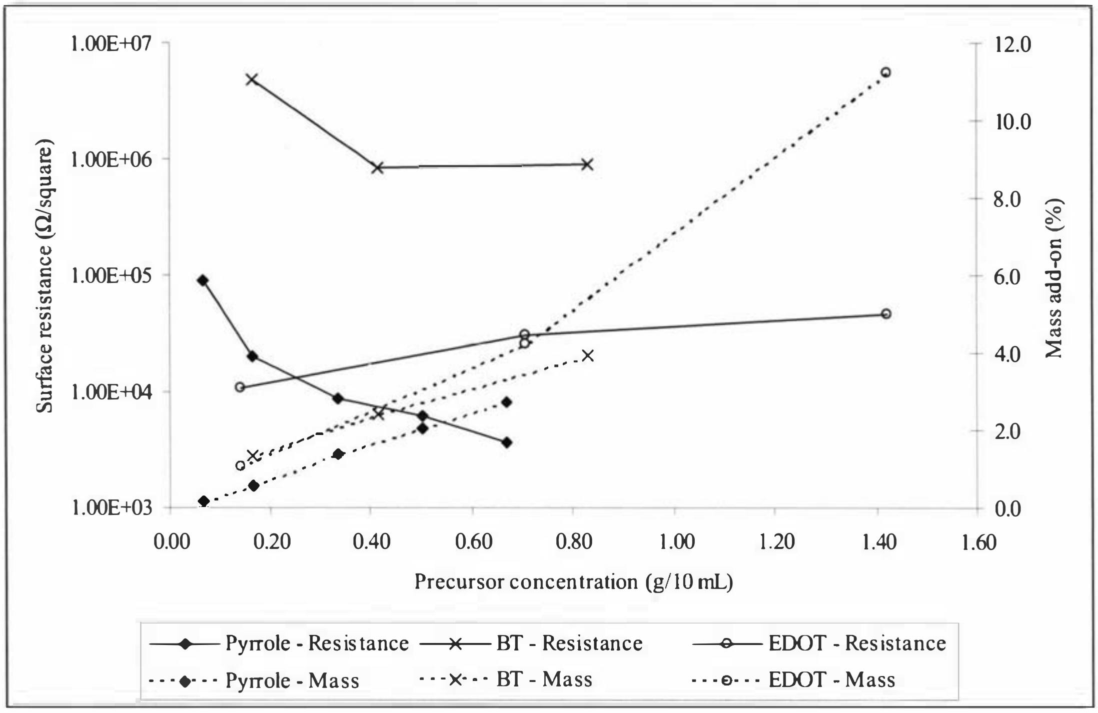


Figure 7.1. Mass add-on and surface resistance – precursor concentration (three precursors).

Table 7.3. Correlation coefficients.

Parameters	Precursor		
	Pyrrole	2,2'-bithiophene	EDOT
Precursor concentration / mass add-on	1.000	0.998	0.989
Precursor concentration / surface resistance	-0.753	-0.779	0.991
Mass add-on / surface resistance	-0.755	-0.813	0.961

7.2.3.2 Effect of precursor concentration for one precursor on three substrates.

A further experiment investigated the effect of reducing the EDOT concentration below that used in the previous section. Two additional substrates were added (a wool/elastane knit, WL, and one of the standard fabrics described in Section 4.2; the acrylic woven, O) to determine if the unexpected behaviour noted previously may have been associated with only the substrate used in the previous experiment (P INT). The treatment conditions (except for precursor concentration, which is provided in Table 7.4) were virtually identical to those used in Section 7.2.2, and polymer deposition followed the procedure described in Section 4.4.3. One slight change to the conditions was impregnation times of nine and four minutes, and drying times of four minutes and two hours. These were sufficient to achieve completion of the reaction, and the shorter times allowed a more efficient experimental procedure.

Polymerisation proceeded as expected: specimens darkened after removal from the oxidant solution, and lower precursor concentrations were associated with lighter colour. Images of the specimens were collected using a scanner, and are provided in Appendix 3. The specimens were large enough to allow surface resistance to be assessed as specified in Section 4.3. The average of the eight measurements is reported in Table 7.4, with standard deviations in parentheses.

Table 7.4. Mass add-on and surface resistance – precursor concentration (EDOT).

EDOT concentration (g/10 mL)	Mass add-on (%)			Surface resistance (Ω/square)		
	P INT	WL	O	P INT	WL	O
0.671	1.81	2.22	1.54	38.5 (22.2) x 10^3	11.6 (2.0) x 10^3	21.7 (7.4) x 10^3
0.336	0.74	1.32	0.80	20.8 (8.0) x 10^3	5.85 (1.57) x 10^3	11.5 (2.8) x 10^3
0.252	0.80	0.86	0.56	16.0 (4.4) x 10^3	5.09 (0.98) x 10^3	10.6 (2.5) x 10^3
0.168	0.34	0.40	0.25	31.4 (20.9) x 10^3	7.25 (1.56) x 10^3	30.7 (10.3) x 10^3
0.084	0.21	0.06	0.07	9.75 (8.07) x 10^4	2.42 (0.61) x 10^4	5.73 (3.97) x 10^5
0.034	-0.09	-0.03	-0.04	> 39.6 x 10^6	> 22.8 x 10^6	> 40 x 10^6

These results confirm the findings reported in Section 7.2.3.1. They also indicate the point at which the precursor concentration (and thus the mass add-on) became low enough for the surface resistance to increase again; best illustrated in Figure 7.2, where the results from Table 7.4 are plotted. Note that the 'greater than' values in Table 7.4 have been given a nominal maximum value. As this value is very much higher than any other result for each substrate, it does not compromise the clear trend indicated in Figure 7.2, where it appears that the optimum value for the precursor concentration was about 0.25 g/10 mL regardless of the substrate used. The mass add-on (in the range of 0.5 to 1.0 % at this precursor concentration) is unlikely to affect the fabric's handle properties (i.e. it will still feel similar to an untreated fabric). There is no advantage in increasing the mass add-on above this level, as there will not be any resulting decrease in electrical resistance. As observed in earlier trials, the correlation between mass add-on and surface resistance is poor (and negative): -0.534, -0.477 and -0.484 for P INT, WL and O respectively.

One possible explanation of this behaviour is that polymer formation at higher precursor concentrations is of a poor quality – possibly only short and/or highly branched chains. In lower concentration conditions the formation of polymer is more ordered. Eventually, as the precursor concentration drops below ~0.25 g/10 mL, the quantity of polymer deposited is insufficient to form conductive pathways through the composite, and the resistance increases again. This phenomenon is discussed in more detail in Section 8.2, for an alternative polymer deposition method.

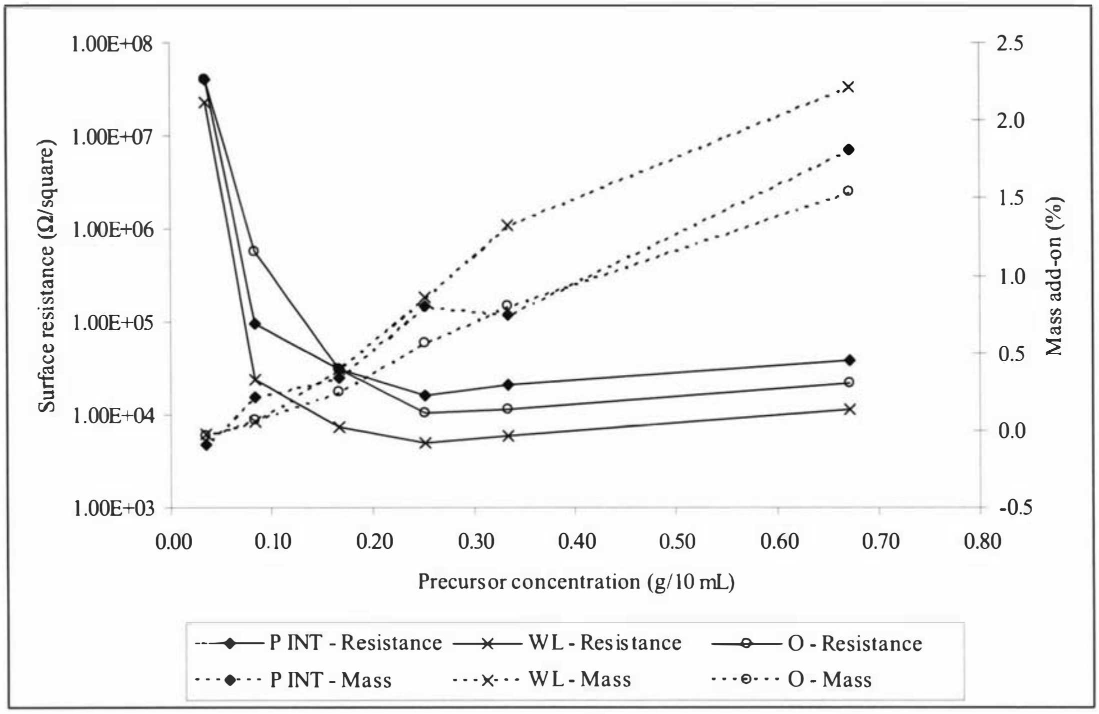


Figure 7.2. Mass add-on and surface resistance – precursor concentration (EDOT, three substrates).

7.2.4 Summary and Conclusions.

In conclusion, the thiophene derivative 3,4-ethylenedioxythiophene is very promising as a precursor for polymerisation by the two-stage impregnation technique. Its reactivity is sufficiently low to allow polymerisation to be well controlled (and to occur not in solution, but during subsequent solvent evaporation), but good enough to allow the deposition of fairly high add-on levels of conductive polymer. Pyrrole is probably better suited to being polymerised by the one-step method described in Section 5, while 2,2'-bithiophene can be polymerised by the two-stage technique, but higher resistance composites result.

An intriguing behaviour was noted for EDOT: as the concentration of precursor in the precursor solution was reduced, the surface resistance of the composite decreased while the mass add-on increased. This behaviour was further investigated, and an optimum concentration of approximately 0.25 g/10 mL (0.176 mol/L) has been identified. The same behaviour was not observed for pyrrole or 2,2'-bithiophene. Unfortunately, this optimum concentration was not determined until after a number of the other investigations in this chapter were carried out, so subsequent sections in this chapter use precursor concentration levels that are not optimal. However, their findings are still relevant to the performance of the two-stage impregnation polymerisation technique.

7.3 Effect of Drying Time After Precursor Impregnation.

7.3.1 Background.

Previous experiments utilising the two-stage impregnation method have used arbitrary post-precursor impregnation solvent evaporation times (referred to here as the 'drying time'), usually chosen to facilitate easy processing of multiple specimens in succession rather than for any specific functional reason. Because the solvent is usually very volatile compared to the precursor, it is likely that there is only precursor left on the fibre by the time it is placed into the oxidant solvent. During this evaporation time, as well as during the precursor solution impregnation that precedes it, the precursor is taken up by the fibre. The duration of the drying time probably influences the degree to which this occurs.

It isn't clear whether uptake is absorption of the precursor into the fibre itself, or simply adsorption onto the surface (this probably depends on the type of fibre being used, as some fibre types have hydrophilic surfaces and/or interiors, and others hydrophobic). For the work described in this section, two different substrates were used; one a naturally hydrophobic polyester woven fabric (P WVE), the other a polyester/cotton blend (PC RIB). The cotton content of the latter is naturally hydrophilic. The full set of standard fabrics (see Section 4.2) was not available when this work was carried out.

Another interesting issue is that 3,4-ethylenedioxythiophene (EDOT) is a liquid at room temperature, while 2,2'-bithiophene is a solid. This means that bithiophene may re-crystallise from the precursor solution onto the surface of the fibre as the solvent evaporates, which could in turn lead to an irregular polymer deposition if the crystallisation itself is irregular.

7.3.2 Experimental Work.

Only EDOT and 2,2'-bithiophene were included in this investigation, as pyrrole was less suitable for the two-stage impregnation technique. The conditions used for polymerisation were as described in Section 7.2.2, following the procedure given in Section 4.4.3. Precursor concentrations were 1 mol/L (EDOT) and 0.5 mol/L (2,2'-bithiophene). The post-precursor impregnation drying times are given in Table 7.5, alongside the mass add-on and surface resistance results. These results are interpreted most easily in graphical form, and are shown in Figures 7.3 (mass add-on) and 7.4 (surface resistance).

Table 7.5. Mass add-on and surface resistance – drying time.

Drying time (minutes)	Mass add-on (%)				Surface resistance (Ω/square)			
	EDOT		2,2'-Bithiophene		EDOT		2,2'-Bithiophene	
	P WVE	PC RIB	P WVE	PC RIB	P WVE	PC RIB	P WVE	PC RIB
0	0.56	8.54	0.83	3.64	9.00×10^2	2.00×10^3	2.38×10^9	1.45×10^6
4	1.69	9.14	2.18	3.56	7.40×10^2	2.10×10^3	6.06×10^7	1.40×10^6
10	2.54	8.97	1.93	5.71	2.50×10^4	1.60×10^3	1.32×10^8	4.00×10^5

From these results, it is clear that even with zero drying time after impregnation, sufficient precursor was taken up by the substrate to allow conductive polymer to be formed. This was also apparent from simple observation of the specimens – even at zero drying time, a darkening of the substrate (due to the deposited polymer) was apparent. Despite this, there are no combinations of precursor and substrate at which either the highest mass add-on or lowest resistance occurs with zero drying time. For PC RIB the differences are relatively small across all drying times (with the exception of mass add-on for 2,2'-bithiophene), suggesting that the drying time is not particularly important for this substrate. This may be because of its relatively absorbent nature, due to both its cotton component and the fabric's relatively porous structure. An absorbent structure is not only likely to take up more precursor (reflected in the relatively high mass add-on levels), but will take it up more rapidly.

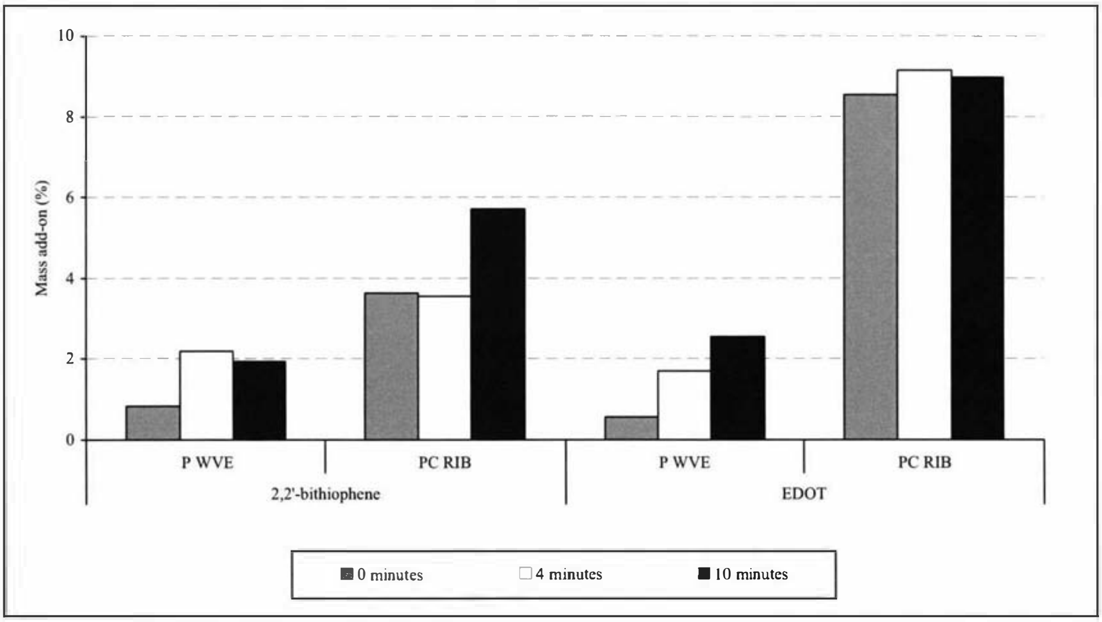


Figure 7.3. Mass add-on – drying time (two substrates, two precursors).

For the P WVE substrate there was an increased mass add-on with increasing drying time, suggesting that more precursor was actually taken up by this substrate during this extended time. For both precursors, the lowest resistance occurred with a drying time of four minutes. Given the lack of sensitivity of PC RIB to drying time, and the suitability of four minutes for P WVE, it seems that this duration would be a suitable value to use in future work.

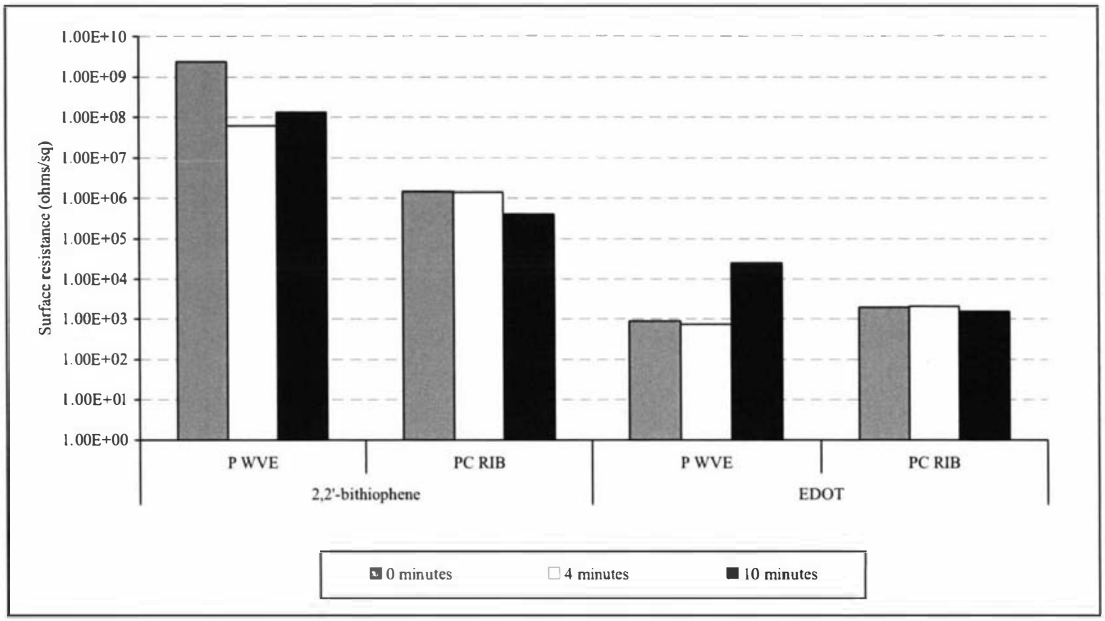


Figure 7.4. Surface resistance – drying time (two substrates, two precursors).

There was a generally poor (negative) correlation between mass add-on and surface resistance. The correlation coefficient was -0.34 across all specimens. There was no clear difference in behaviour between EDOT and 2,2’-bithiophene, except that EDOT provided a lower surface resistance (as expected and observed previously). There was no recrystallisation of 2,2'-bithiophene during solvent evaporation observed, and the deposition of poly(2,2’-bithiophene) was uniform.

7.4 Effect of Oxidant Concentration.

7.4.1 Background.

Because the preliminary experiments (discussed briefly in Section 7.1.2) and the literature indicated the suitability of iron (III) chloride as an oxidant for polymerisation of ICP precursors, it was decided to limit the investigation into oxidant-related properties to this species only. The critical parameter is oxidant concentration, particularly in light of the interesting behaviour noted for precursor concentration in Section 7.2. Therefore the main aim of this work was to determine the optimum concentration of oxidant to create a composite with low electrical resistance. The polymerisation of thiophene-based precursors takes place during the evaporation of the oxidant solvent, and presumably cannot continue after evaporation has finished, as the mobility of the oxidant species will be hindered in the absence of a solvent. Therefore it seems most likely that a higher oxidant concentration would allow polymerisation to proceed further in the available time. The influence of the type of solvent used for the oxidant is investigated in Section 7.5.

The fact that polymerisation occurs during evaporation suggests that it may be dependent on the oxidant becoming very highly concentrated on the surface of the fibres. This is another reason why it is likely that a high oxidant concentration would lead to a greater amount of ICP being deposited onto the substrate. However, we have seen that a high polymer mass add-on does not always correspond to a low composite resistance. It may be the case here (as it was for precursor concentration) that low concentration conditions lead to a better 'quality' deposition of ICP, possibly because the polymer formed under these conditions has a better molecular structure for conduction, such as a higher molecular weight (i.e. longer polymer chain length) and less chain branching.

7.4.2 Experimental Work.

The conditions of polymerisation were as described in Section 7.2.2, and followed the procedure given in Section 4.4.3. The substrate used was polyester interlock (P INT), and the precursors were 2,2'-bithiophene and EDOT at 0.5 and 1.0 mol/L respectively. Three fairly widely-spaced oxidant concentrations (given in Table 7.6) were used, in order to identify concentration levels at which unusual behaviour occurred (if necessary, those levels could be investigated in more detail subsequently).

Polymerisation proceeded as expected, with the specimens darkening to blue (EDOT) or reddish brown (bithiophene) during oxidant solvent evaporation. There was a noticeable trend of lighter colour at lower oxidant concentration for EDOT; less clearly so for bithiophene. This suggests that the quantity of conductive polymer deposited is less with lower oxidant concentrations. The mass add-on and surface resistance results for these specimens are shown in Table 7.6, and presented in graphical form in Figure 7.5.

Table 7.6. Mass add-on and surface resistance – oxidant concentration.

Oxidant concentration (mol/L)	Mass add-on (%)		Surface resistance (Ω/square)	
	EDOT	BT	EDOT	BT
0.1	7.41	0.90	> 1 x 10^{11}	2.82 x 10^{10}
0.5	7.93	1.80	4.50 x 10^{6}	4.39 x 10^{7}
1.0	9.65	2.52	3.80 x 10^{4}	2.88 x 10^{6}

Note: For EDOT/0.1 the electrical resistance exceeded the upper limit of the resistance meter used. Therefore the surface resistance is expressed as being greater than the meter's upper limit.

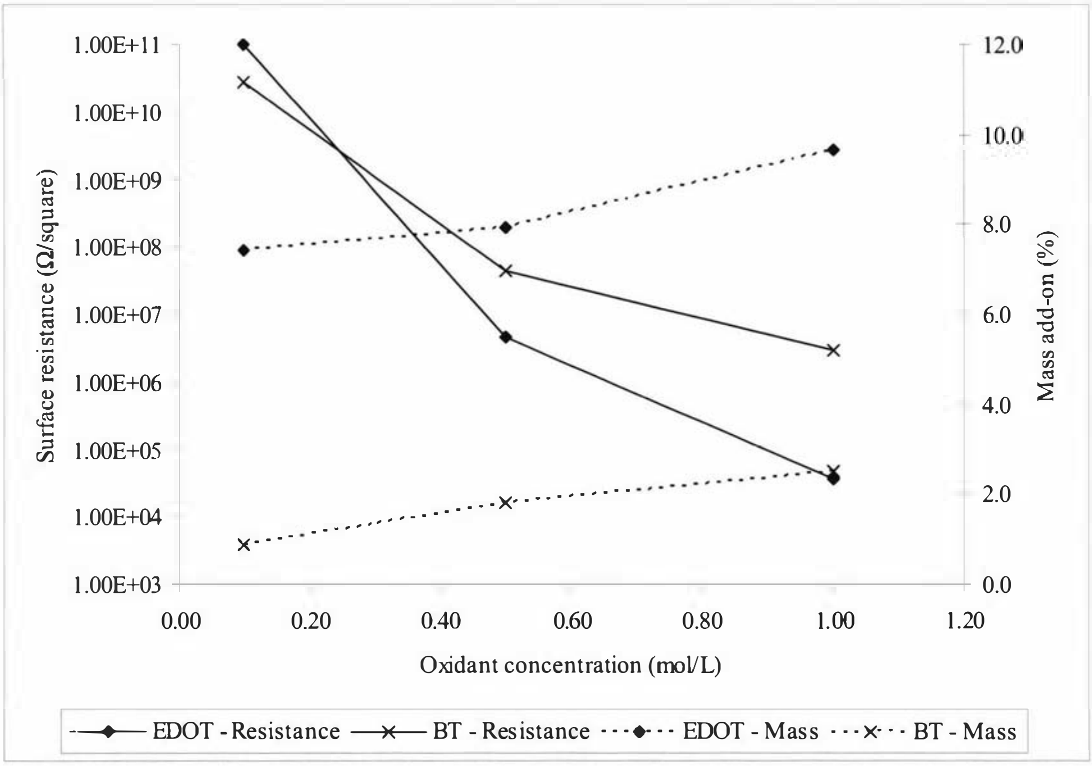


Figure 7.5. Mass add-on and surface resistance – oxidant concentration (two precursors).

The observation of a lighter colour at lower oxidant concentration was supported by the mass add-on data, with a fairly linear increase in add-on with increasing concentration, accompanied by a decrease in surface resistance. At very low oxidant concentration the composite was virtually non-conductive, with a very high resistance measured for bithiophene, and resistance exceeding measurable values for EDOT.

As expected, the correlation between surface resistance and mass add-on was quite good (and negative). The correlation coefficient for EDOT is -0.68, while that for bithiophene -0.90. In contrast to the behaviour seen for precursor concentration, the higher the mass add-on, the lower the surface resistance. This suggests that quality of conductive polymer deposition is not influenced by the oxidant concentration, and to reach low resistance at a particular precursor concentration it is necessary to get as high a mass add-on as possible (by using a high oxidant concentration).

There are limits to the concentration that is achievable before the oxidant solution is saturated. Maximum concentration is quite high in methanol (about 1 mol/L) compared to other organic solvents, presumably due to the relatively polar nature of the solvent. Higher concentrations are possible with water, but the preliminary experiments reported in Section 7.1.2 indicated that the performance of water in this method was poor (presumably due to the precursor's poor solubility in water). The influence of oxidant solvent is explored further in Section 7.5.

7.5 Effect of Oxidant Solvent Type.

7.5.1 Background.

The potential influence of the oxidant solvent on the polymerisation process was briefly discussed in the conclusion of Section 7.4. That parameter was more closely examined in work described this section, with regard to a variety of different types of solvents.

There are several ways in which oxidant solvent type may be important.

a. *Solubility of oxidant in solvent*: Although the oxidant solutions used were nominally prepared to a 1 mol/L concentration, there were several for which this was not possible. In reality, some of these solutions are effectively saturated with iron (III) chloride at concentrations lower than 1 mol/L. Therefore, the experimental work reported on here compares the performance of the oxidant solvents with as close to 1 mol/L iron (III) chloride dissolved in them as is possible at room temperature. Previous experiments have already clearly indicated the value of having a high concentration of oxidant.

b. *Interaction between oxidant solvent and precursor*: If, for example, water is used as the oxidant solvent, then limited interaction between the precursor (largely insoluble in water) and the oxidant (very soluble in water) might be expected. Conversely, if acetonitrile is used as the oxidant solvent, then the interaction could be very good. However this may be in turn limited by the lower solubility (and therefore dissociation) of iron (III) chloride in acetonitrile. The fundamental difference in solubility of precursor and oxidant (i.e. the precursors are soluble in organic solvents, while the oxidant is most soluble in water) presents some important issues for this polymerisation technique.

c. *Interaction between solvent and substrate*: The ‘wetting-out’ and penetration of water into a hydrophilic substrate (e.g. cotton) will be much better than into a hydrophobic one (e.g. polyester). Conversely, organic solvents are more readily taken-up by hydrophobic substrates than by hydrophilic ones.

7.5.2 Experimental Work.

The conditions used for polymerisation were the same as those described in Section 7.2.2, and followed the procedure given in Section 4.4.3. The oxidant solvents are given in Table 7.7; their concentration was 1.0 mol/L or saturated, whichever was lower. Precursors were 2,2’-bithiophene and EDOT, at 0.5 and 1.0 mol/L respectively. The substrates were polyester interlock (P INT) and cotton woven (C WVE) fabrics. The mass add-on and surface resistance results for all specimens are also provided in Table 7.7.

Table 7.7. Mass add-on and surface resistance – oxidant solvent.

Oxidant solvent	Mass add-on (%)				Surface resistance (Ω/square)			
	EDOT		2,2'-Bithiophene		EDOT		2,2'-Bithiophene	
	P INT	C WVE	P INT	C WVE	P INT	C WVE	P INT	C WVE
Water	44.37	8.51	21.08	4.00	1.18×10^{3}	1.51×10^{5}	1.75×10^{7}	1.40×10^{7}
Methanol	5.66	3.03	2.76	1.83	8.00×10^{3}	2.80×10^{4}	5.08×10^{5}	5.29×10^{7}
Acetonitrile	7.10	4.13	7.09	1.77	9.22×10^{2}	5.98×10^{2}	1.28×10^{4}	7.37×10^{6}
Ethanol	15.28	5.85	9.19	3.67	5.20×10^{4}	8.32×10^{5}	2.47×10^{4}	3.09×10^{6}
Acetone	11.00	4.70	5.35	2.79	$> 10^{11}$	2.34×10^{8}	1.13×10^{5}	3.62×10^{6}
Diethyl ether	13.69	3.09	10.00	2.17	2.23×10^{5}	2.24×10^{8}	5.27×10^{4}	9.27×10^{7}

Note: The value '$>10^{11}$' indicates that the surface resistance of this specimen (acetone/EDOT/P INT) exceeded the upper limit measurable on the resistance meter used.

There was a very wide range of mass add-on levels; from 1.77% to 44.37%. The surface resistance results also spanned a large range. These results are presented graphically in Figures 7.6 and 7.7. In interpreting this data it is important to note that the most desirable result is a low resistance with a low mass add-on. While some results certainly stand out (for example, the very high mass add-on values for water), it is probably best to simplify this data, and look at the rankings from lowest to highest of mass add-on and surface resistance for each of the four combinations of substrate and precursor. These are provided in Tables 7.8 and 7.9.

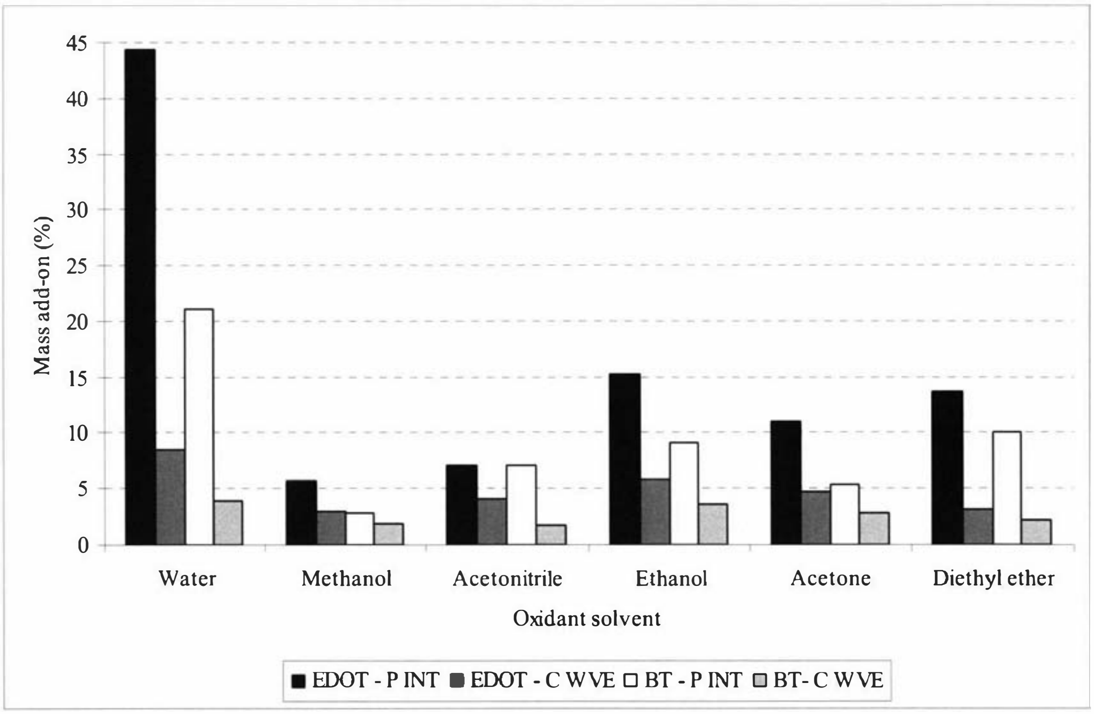


Figure 7.6. Mass add-on – oxidant solvent (two substrates, two precursors).

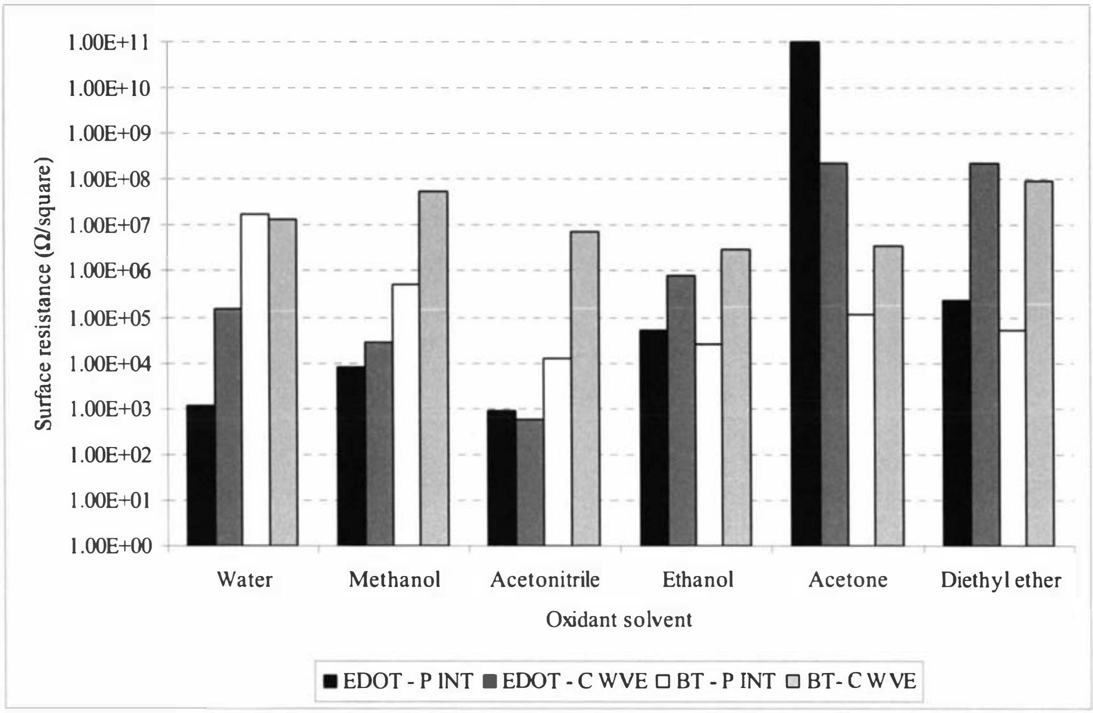


Figure 7.7. Surface resistance – oxidant solvent (two substrates, two precursors).

Table 7.8. Mass add-on ranking.

Precursor/ substrate	Lowest mass add-on					Highest mass add-on
EDOT/P INT	Methanol	Acetonitrile	Acetone	Ether	Ethanol	Water
EDOT/C WVE	Methanol	Ether	Acetonitrile	Acetone	Ethanol	Water
2,2'-Bithiophene/ P INT	Methanol	Acetone	Acetonitrile	Ethanol	Ether	Water
2,2'-Bithiophene/ C WVE	Acetonitrile	Methanol	Ether	Acetone	Ethanol	Water

Table 7.9. Surface resistance ranking.

Precursor/ substrate	Lowest surface resistance					Highest surface resistance
EDOT/P INT	Acetonitrile	Water	Methanol	Ethanol	Ether	Acetone
EDOT/C WVE	Acetonitrile	Methanol	Water	Ethanol	Ether	Acetone
2,2'-bithiophene/ P INT	Acetonitrile	Ethanol	Ether	Acetone	Methanol	Water
2,2'-bithiophene/ C WVE	Ethanol	Acetone	Acetonitrile	Water	Methanol	Ether

Taking both sets of rankings together, it becomes apparent that there were different optimum solvents for different precursor/substrate combinations. Acetonitrile generally performed well (probably due in part to the solubility of the precursor in it), but the disadvantage of this solvent (along with diethyl ether and acetone, although neither of these perform particularly well) is its high volatility and toxicity, meaning that less hazardous solvents (such as water and the alcohols) are preferable. On this basis (and with a focus on low mass add-on, so as to minimise the detrimental effect on fabric mechanical properties such as flexibility), methanol was the most suitable solvent for EDOT. Water was unsatisfactory because of its very high mass add-on (it was noted the specimens prepared with water were all noticeably stiffened by the polymer deposition). The best solvent for 2,2'-bithiophene was ethanol.

The consistently high mass add-on with water must be addressed, and was likely to be due to two factors. There is an extremely good dissociation of the iron and chloride ions in solution (resulting in a high oxidation potential), which should bring about a high level of polymerisation. Secondly, it is important to remember that polymerisation occurs during the oxidant solvent evaporation period. As water is non-volatile, there is a long time for this polymerisation to occur. In fact the dynamics of the situation are probably completely different to the organic solvents, because the evaporation period is so much longer (hours compared with minutes). Why this results in a higher mass add-on but not lower resistance is not clear. As already noted, the relationship between these two parameters is not readily apparent.

On the other hand, there was a consistently higher resistance and lower mass add-on for acetone and diethyl ether, probably because the oxidant solution is saturated at low concentration, resulting in weaker oxidative conditions. Also the high volatility of these solvents means that the polymerisation 'window' (during which the reagents are sufficiently mobile on the substrate surface to interact) is short.

7.5.3 Summary and Conclusions.

While the lowest resistance textile-ICP composites are produced when acetonitrile is used as the oxidant solvent, there are compelling reasons not to use it. Alternatives such as methanol and ethanol seem to perform acceptably well, and are both cheaper and safer to handle. Both of these factors must be considered if there is an intention in the future to scale up the preparation of conductive textile materials by this method. On the basis of the results given above, methanol is the most suitable oxidant solvent to use for polymerisation of 3,4-ethylenedioxythiophene, while ethanol is the most suitable to use for 2,2'-bithiophene. As the lower resistance of EDOT means that it is of greater interest, conditions that suit its polymerisation are most relevant. Therefore, in subsequent experiments where both precursors were used but only one variable (not oxidant solvent) was being tested, methanol is used.

7.6 Effect of Additional Dopants.

7.6.1 Background.

In chemically polymerised conductive polymers where an ionic salt (such as iron (III) chloride) is used as the oxidant, the counter-ion (such as Cl^-) acts as the dopant anion in the polymer, providing the mechanism for charge movement, and thus conductivity. In the Milliken polymerisation method used for pyrrole [9], an additional anion is added, usually in the form of an aromatic sulphonic acid. 1,5-Naphthalenedisulphonic acid (NDSA, providing the naphthalenedisulphonate (NDS) anion) is one of the preferred dopants in that system, so its use in the two-stage impregnation technique was investigated.

One reason to use these types of dopants is to improve durability of the ICP. As the NDS ion is large compared to the chloride ion provided by the oxidant, it should be less prone to migration out of the structure, and thus should maintain a higher level of conductivity over time. The presence of this type of dopant in the aqueous polymerisation system also increases conductivity for composites prepared by that system. For the two-stage impregnation system however, the addition of NDSA to the oxidant solution (the logical solution to combine it with, to ensure its involvement in polymerisation) may interfere with the polymerisation process itself, and hinder the formation of conductive textile-ICP composites.

Another unknown is the appropriate quantity of NDSA to add to the system. The Milliken method does not provide a useful guide, as the concentration of all the reagents is very low compared to the two-stage system. We also do not know how efficiently they may be incorporated into the polymer; in other words, whether it is necessary to supply a large excess in order to get any dopant integration, or if small amounts will be incorporated and interfere less with other aspects of the polymerisation process. Therefore to cover the wide range of potential doping levels, a wide range of dopant concentrations was used.

7.6.2 Experimental Work.

The basic conditions used for polymerisation were as described in Section 7.2.2, and followed the procedure given in Section 4.4.3 with one variation: the ICP precursor concentrations were lower than those typically used elsewhere (0.5 mol/L for EDOT; 0.25 mol/L for 2,2'bithiophene). This was for two reasons: firstly because the optimum level (as determined in Section 7.2) is less than those typically used in this work, and secondly because at the time of carrying out this experiment the available quantities of ICP precursors were limited (due to delivery delays from the supplier). The substrate was polyester interlock (P INT), and dopant concentrations were varied as noted in Table 7.10.

The polymerisation reaction for the four specimens with NDSA present in the oxidant solution appeared to be slightly slower (slower darkening of specimens after removal from solution), and their final colour not as dark as those prepared without NDSA. The EDOT specimens with NDSA also appeared to have a reddish hue to their dark blue colouration, although this disappeared on rinsing. Poly(2,2'-bithiophene) is reddish brown in colour, so if NDSA caused this hue on those specimens, it could not be detected. Finally, it was noted that the specimens with higher NDSA levels seemed quite stiff, although this also disappeared on rinsing. This may have been caused by a precipitate of excess NDSA, which is a powdery-white crystalline solid. The mass add-on and surface resistance results for all specimens are provided in Table 7.10, and graphically in Figure 7.8 (the resistance data relates to the left-hand axis, while the mass data relates to the right-hand axis).

Table 7.10. Mass add-on and surface resistance – additional dopant.

Dopant concentration (mol/L)	Mass add-on (%)		Surface resistance (Ω/square)	
	EDOT	2,2'-Bithiophene	EDOT	2,2'-Bithiophene
0	5.58	1.65	1.80×10^4	2.77×10^6
0.01	5.78	1.71	7.89×10^4	4.17×10^6
0.05	5.99	1.75	1.85×10^6	4.63×10^6
0.10	6.06	1.84	2.56×10^6	7.54×10^7
0.20	6.24	1.92	1.55×10^7	6.58×10^8

From Figure 7.8 it is immediately apparent that the additional dopant did not have a beneficial effect on surface resistance. The lowest surface resistance for both precursors was with no NDSA present. Because the scale for resistance is logarithmic, the increase in resistance with even the lowest level of NDSA added (0.01 mol/L) was substantial. For EDOT the increase was from 18.0 kΩ to 78.9 kΩ, while for 2,2'-bithiophene it was from 2.77 MΩ to 4.17 MΩ. Mass add-on showed a steady increase with increasing NDSA concentration, suggesting that the additional dopant was being trapped in the polymer in some way, but without having a beneficial effect on conductivity. In fact it appears to have interfered with the polymerisation process, resulting in increased surface resistance.

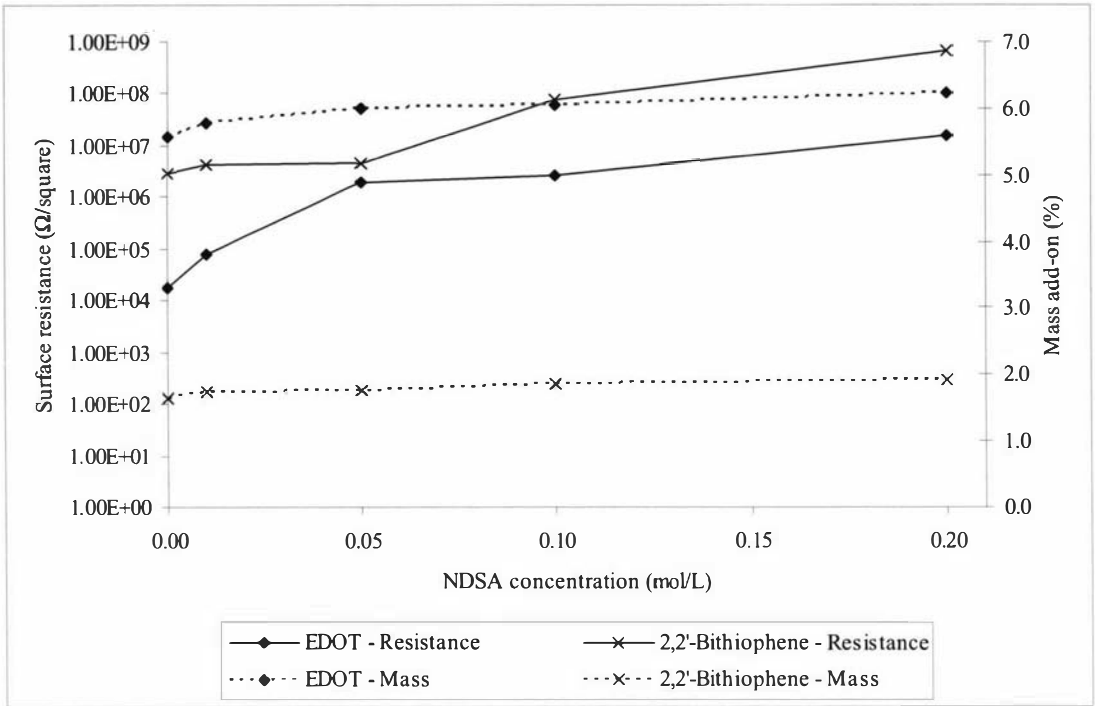


Figure 7.8. Mass add-on and surface resistance – additional dopant (NDSA, two precursors).

7.6.3 Summary and Conclusions.

Because it is important to achieve a low resistance at as low a mass add-on as possible (to retain the flexibility of the textile substrate), the use of an additional dopant is of little advantage, even if durability is improved. These results were not sufficiently encouraging to justify further investigation of the effect of additional dopant in the preparation of textile-ICP composites by the two-stage impregnation technique. Subsequent experiments using the two-stage technique did not use any dopants other than those provided by the oxidant counter-ion.

7.7 Effect of Post-Treatment Hold Time.

7.7.1 Background.

An interesting aspect of this method of polymerisation is that, for the thiophene-based precursors that have been used, polymerisation only seems to occur during the evaporation of the oxidant solvent (second impregnation). For this reason, changing the post-oxidant impregnation conditions may have an influence on the polymerisation process. The polymer mass add-on for water was much higher than for organic solvents (Section 7.5), and it may be that the polymerisation reaction should be considered completely differently for water, because of its relatively slow evaporation time.

A technique for slowing (or at least delaying) the solvent evaporation was investigated for methanol; chosen as it is the preferred oxidant solvent for polymerising 3,4-ethylenedioxythiophene (EDOT). This was evaluated by simply keeping the specimens in a sealed vessel after removing them from the oxidant solution. Two substrates were used; an absorbent cotton woven fabric (C WVE), and the non-absorbent polyester interlock (P INT). Given that the hold time should allow larger amounts of the oxidant solution to be absorbed, this difference in substrate absorbency may be significant.

It should be noted that the effect of holding the specimens in this way is not the same as simply leaving them in the oxidant solution for longer. In that case, the ICP precursor is able to diffuse off the specimen, as it is fully immersed in a solution. This is much less able to occur with a 'hold time', as the specimen is not immersed (although it is still 'wet').

7.7.2 Experimental Work.

The basic conditions used for polymerisation were as described in Section 7.2.2 and followed the procedure given in Section 4.4.3, except that the concentration of 2,2'-bithiophene used was the same as that of EDOT, as this experiment was carried out before it was decided that half the molar concentration of bithiophene was more appropriate. Hold times of zero, four and 16 hours were effected by placing the specimen in a covered 10 cm Petrie dish after removal from the oxidant solution.

For EDOT the specimens darkened slightly during the hold time; the polyester interlock fabric slightly more than the cotton weave. This implies that some polymerisation did occur during the hold time. There was no darkening of the bithiophene (BT) specimens. In both cases, polymerisation appeared to proceed as normal after the Petrie dishes were unsealed; the specimens darkening fairly rapidly as the methanol evaporated. The mass add-on and surface resistance results for all specimens are provided in Table 7.11, and presented graphically in Figures 7.9 and 7.10.

Table 7.11. Mass add-on and surface resistance – hold time.

Hold time (hours)	Mass add-on (%)				Surface resistance (Ω/square)			
	C WVE		P INT		C WVE		P INT	
	EDOT	BT	EDOT	BT	EDOT	BT	EDOT	BT
0	3.27	0.46	14.11	1.96	9.48×10^4	4.02×10^8	6.73×10^3	2.00×10^7
4	2.41	-0.11	10.84	2.17	5.73×10^8	1.02×10^9	2.50×10^4	2.05×10^7
16	2.18	0.84	16.38	3.90	4.17×10^8	3.36×10^8	1.52×10^4	5.05×10^5

From these data it is apparent that the hold time has not generally been beneficial. On both EDOT substrates, the lowest resistance occurred at zero hold time. For C WVE / BT a four-hour hold time was inferior to zero hold time, and the 16-hour hold time only marginally better. Only for P INT / BT did the longest hold time result in a clearly lower resistance. The four-hour hold time was not beneficial to resistance in any circumstance. Hold time also had no consistent effect on mass add-on; for C WVE / EDOT there was a consistent decrease in mass add-on with increasing hold time, while for P INT / BT there was a consistent increase. For the other two specimens, the mass add-on at 16 hours was higher than with no hold time, but lower with only four hours.

It was expected that longer hold times – during which the polymerisation agents were available to be absorbed by the substrate – would lead to higher mass add-on levels. However this was certainly not the case for the four-hour hold time, which showed consistently lower mass add-on than zero hold time. The result for C WVE / BT shows that it is possible for composite mass to reduce, even with the deposition of polymer, implying that while polymer is deposited, the substrate can also be degraded by the reagents used. It is therefore likely that the actual polymer deposition on the 16-hour specimens was higher than that indicated by the mass add-on value, as some of the substrate's original mass has been lost (a reasonable assumption, as the conditions of polymerisation are strongly oxidative with a low pH). Even the relatively inert polymers used for textile materials will be partially degraded under exposure to these conditions for a prolonged period.

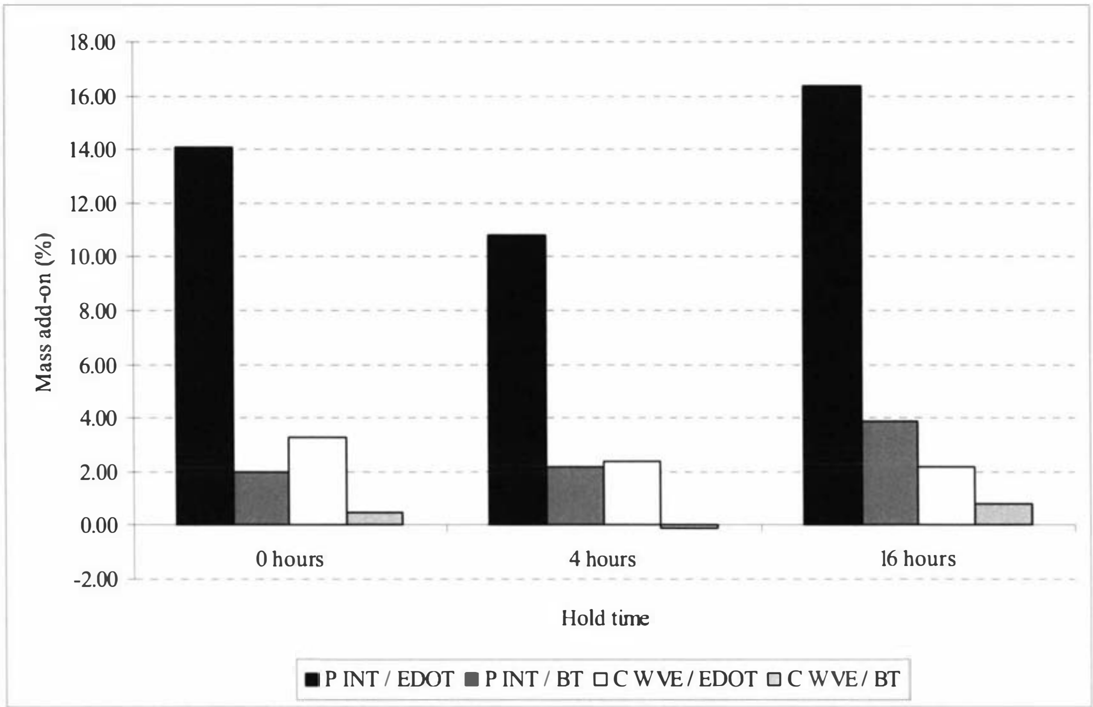


Figure 7.9. Mass add-on – post-treatment hold time (two substrates, two precursors).

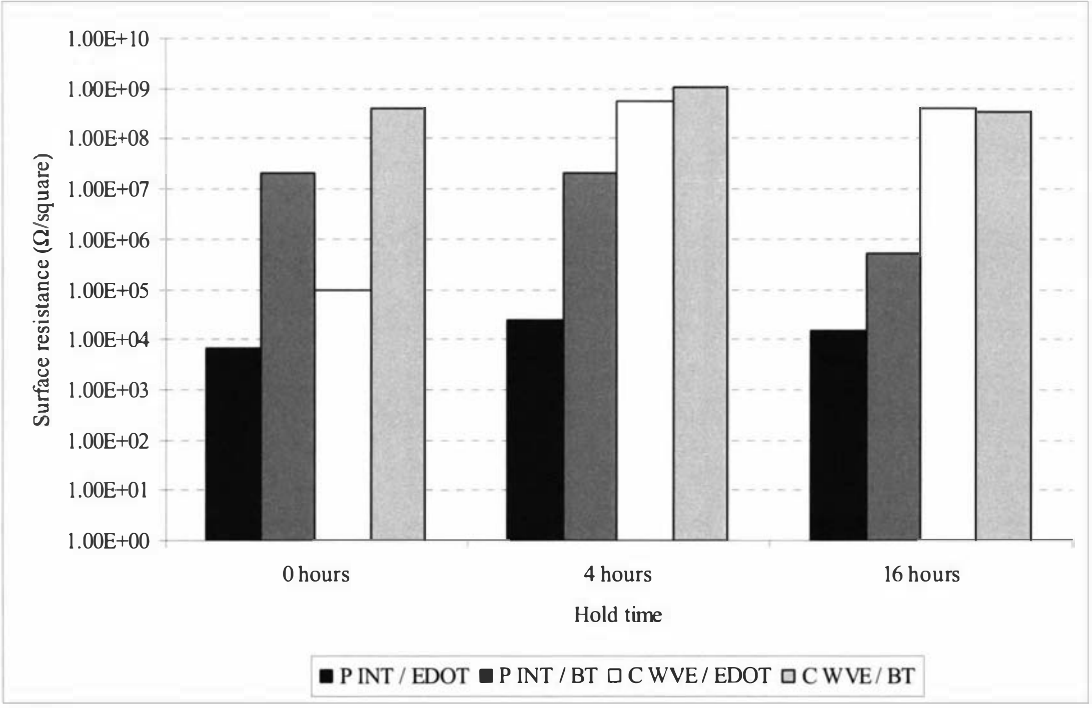


Figure 7.10. Surface resistance – post-treatment hold time (two substrates, two precursors).

As has been observed in other situations, an increase in mass add-on does not necessarily correspond to lower resistance. For the EDOT specimens, slowing polymerisation has not resulted in a more conductive polymer deposition, despite expectations. In fact, in both cases (although mass add-on is higher in one case and lower in the other) the resistance after 16-

hour hold time was higher than that with zero hold time. For bithiophene it appeared that, although polymerisation was apparently prevented by the restricted evaporation, the resistance was lower with the long hold time. The lowest resistance in both cases was with a 16-hour hold time (despite being higher with a four-hour hold time).

7.7.3 Summary and Conclusions.

While there may be benefits in placing the specimens in an environment where evaporation is slowed or restricted (particularly for the polymerisation of bithiophene), there is no overwhelming advantage. In fact, as there is evidence to suggest that the polymerisation solutions can degrade the substrate material, it seems sensible to reject this approach except where bithiophene is the precursor, and then only after determining that the damage to the underlying substrate is acceptable. As EDOT was proving to be of greater interest in this work, the post-oxidant impregnation hold time was not employed further.

7.8 Characterisation of Specimens.

7.8.1 Background.

A sequence of treatments was carried out to prepare specimens of interest for examination by scanning electron microscopy. These specimens were recreated versions of those already described in previous sections, and involved 3,4-ethylenedioxythiophene (EDOT) and 2,2'-bithiophene polymerised at different precursor concentrations, with different oxidant solvents, with and without an additional dopant (1,5-naphthalenedisulphonic acid, NDSA). The surface morphology of the conductive fibres should be visible under SEM, and it was of particular interest how the deposited polymer adhered to the fibres; whether it formed a cohesive coating around the fibres, or was merely amorphous polymer lodged in the fabric interstices.

7.8.2 Experimental Work.

The basic conditions used for polymerisation were as described in Section 7.2.2 and followed the procedure given in Section 4.4.3. Five specimens were prepared using EDOT and 2,2'-bithiophene with the variations given in Table 7.12, with a polyester interlock (P INT) substrate.

Table 7.12. Treatment variations.

Parameter	Treatment number				
	i.	ii.	iii.	iv.	v.
Precursor concentration (g/10 mL)	0.671	0.134	0.671	0.671	0.671
Oxidant solvent	Methanol	Methanol	Water	Acetonitrile	Methanol
Dopant (NDSA) concentration (mol/L)	0	0	0	0	0.05

Surface resistance and mass add-on measurements were made to verify the result previously noted for these combinations. The specimens were left intact (for provision to the SEM laboratory), so resistance measurements were made by a non-destructive approximation to the standard method given in Section 4.3. The specimens were larger than those treated previously, meaning that the vessels used for treatment and the quantities of reagents were larger. These factors mean that the results could differ slightly from those observed elsewhere, but the relationship between different specimens should be the same (i.e. the effect of changing precursor concentrations should hold regardless of the specimen size, and so on). These results are given in Table 7.13.

Table 7.13. Approximate surface resistance and mass add-on values – SEM specimens.

Sample code[1]	Brief description[2]	Surface resistance (Ω/square)	Mass add-on (%)
BT(i)	BT/0.671/CH_3OH/no dopant	5.3 x 10^3	2.9
BT(ii)	BT/0.134/CH_3OH/no dopant	3.2 x 10^7	1.2
BT(iii)	BT/0.671/H_2O/no dopant	1.8 x 10^5	16.1
BT(iv)	BT/0.671/CH_3CN/no dopant	1.4 x 10^4	7.0
BT(v)	BT/0.671/CH_3OH/0.05	2.7 x 10^6	2.9
EDOT(i)	EDOT/0.671/CH_3OH/no dopant	9.3 x 10^3	4.4
EDOT(ii)	EDOT/0.134/CH_3OH/no dopant	1.9 x 10^3	0.9
EDOT(iii)	EDOT/0.671/H_2O/no dopant	4.0 x 10^3	12.5
EDOT(iv)	EDOT/0.671/CH_3CN/no dopant	8.2 x 10^2	4.4
EDOT(v)	EDOT/0.671/CH_3OH/0.05	6.1 x10^4	4.2

Notes:

1. The code uses BT for 2,2'-bithiophene and EDOT for 3,4-ethylenedioxythiophene. The number in parentheses corresponds to that given in Table 7.12.
2. The format for the brief description is precursor / precursor concentration (g/10 mL) / oxidant solvent / dopant (NDSA) concentration (mol/L).

All specimens polymerised as expected. The results given in Table 7.13 are largely consistent with those obtained earlier for the equivalent specimens, taking into account the different surface resistance measurement technique used here. The effect of the different variables was the same on these specimens as reported in previous sections.

There can be a tendency, when taking SEM images, to identify and record only unusual regions on the specimen. For this work, the operator was asked to provide an image that is representative of the specimen as a whole. These images of the specimens described in Table 7.12 are provided in Figures 7.11 to 7.19 (with the exception of BT(iii), which was inadvertently excluded). No specimens were gold-coated prior to examination, as in most cases the conductive polymer coating was sufficiently conductive for a clear image to be obtained. SEM images at 350x and 1000x magnification are provided for each specimen.

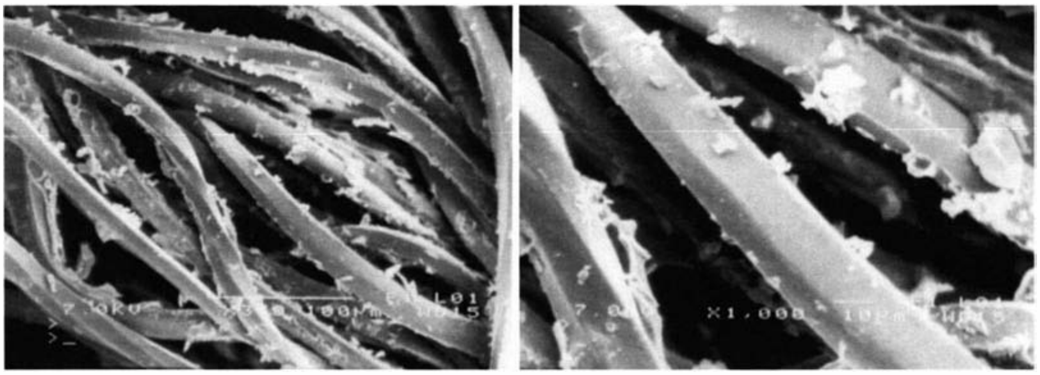


Figure 7.11. SEM images of BT(i).

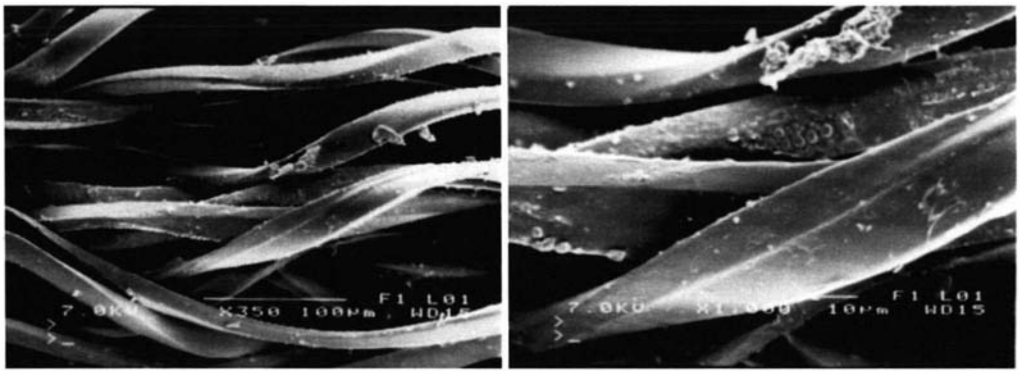


Figure 7.12. SEM images of BT(ii).

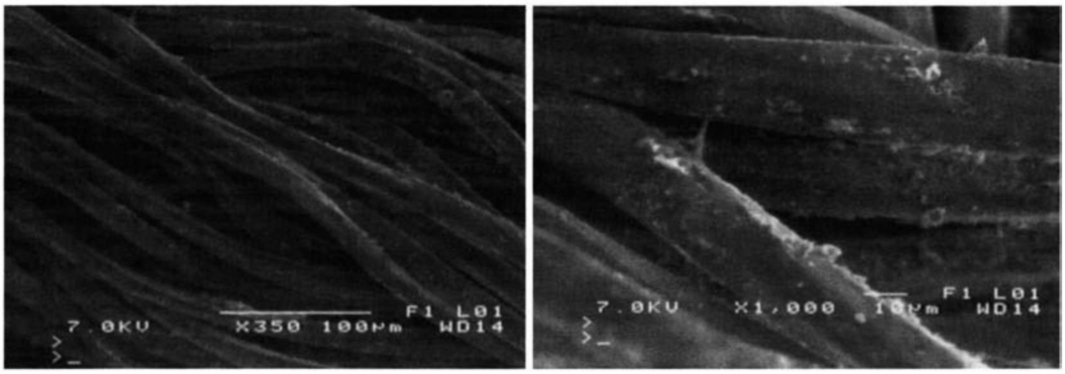


Figure 7.13. SEM images of BT(iv).

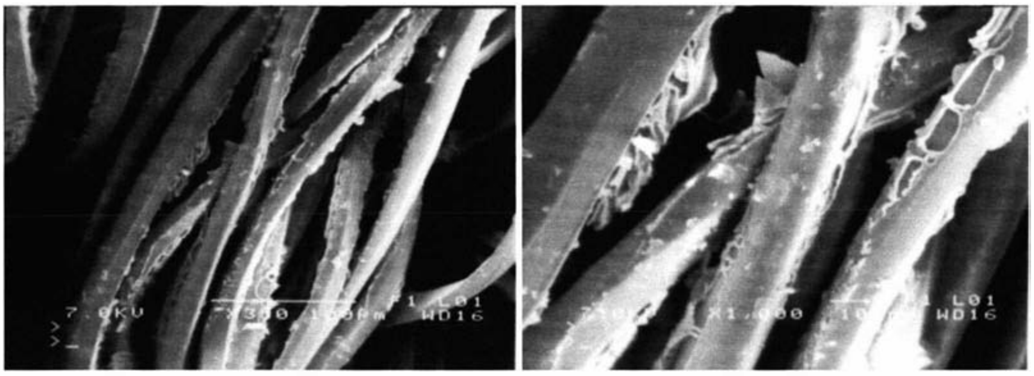


Figure 7.14. SEM images of BT(v).

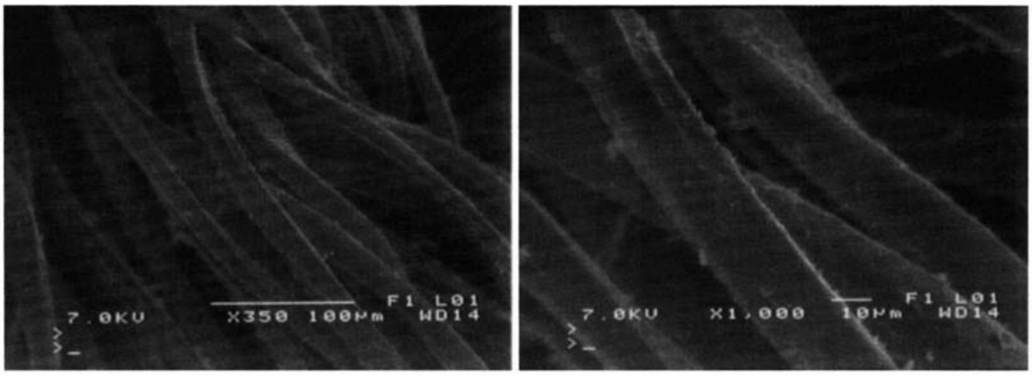


Figure 7.15. SEM images of EDOT(i).

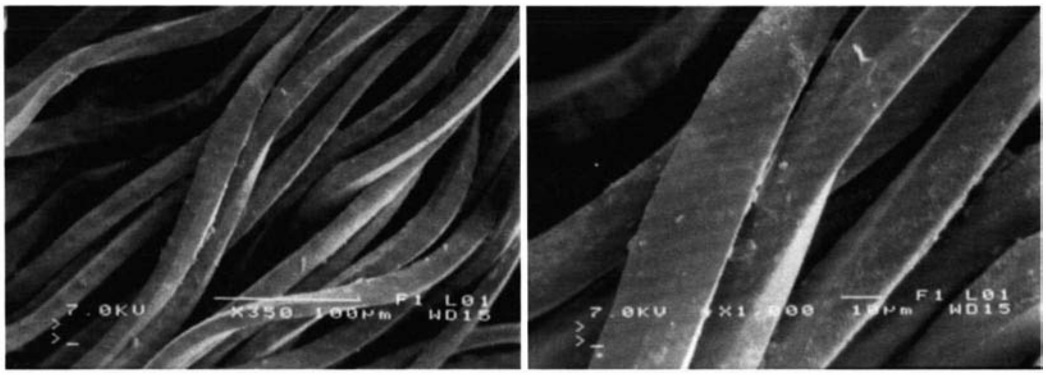


Figure 7.16. SEM images of EDOT(ii).

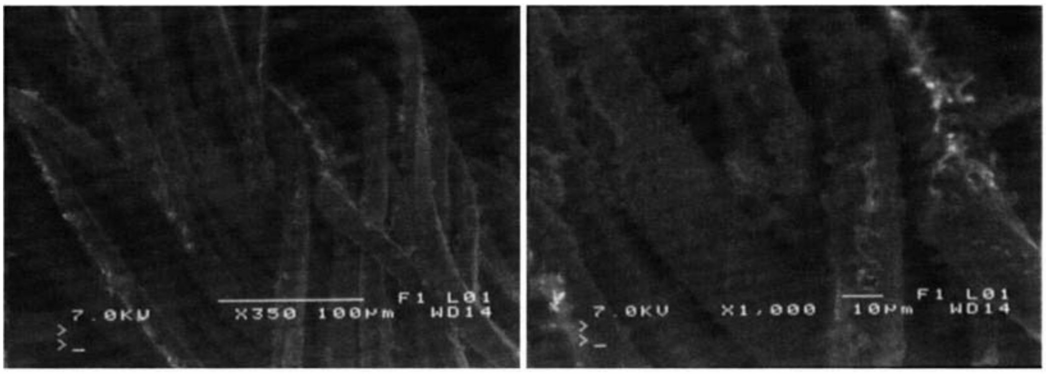


Figure 7.17. SEM images of EDOT(iii).

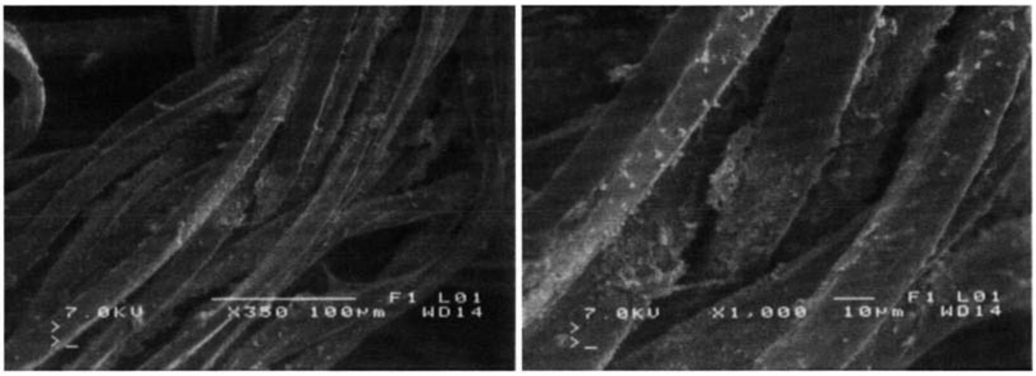


Figure 7.18. SEM images of EDOT(iv).

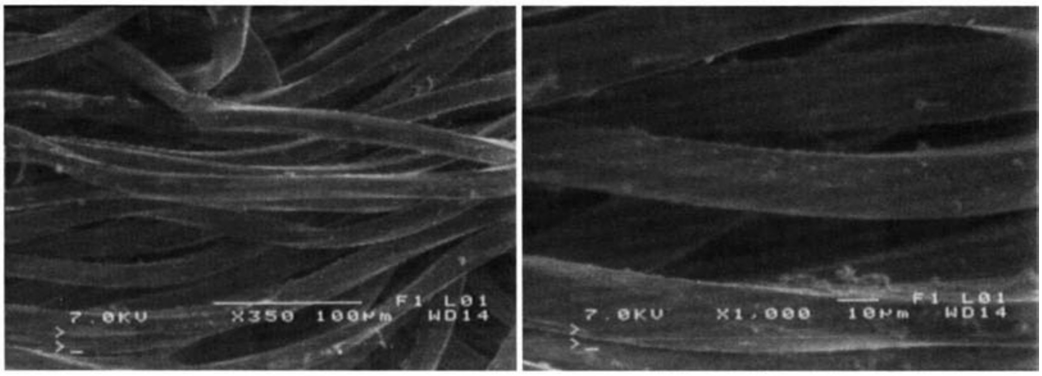


Figure 7.19. SEM images of EDOT(v).

Considering first the (i) specimens in each case; the fibre surfaces were mostly smooth with some loose particles adhering, presumably of the conductive polymer. It seems likely that the smooth surface of the fibre was also conductive (i.e. that the ICP has coated the fibres), as they are clearly visible in the SEM (textile fibres are usually impossible to obtain clear images of without first applying a conductive coating). The loose particles suggest that not all polymerisation was confined to the surface of the fibres, which is not surprising given that the conditions of polymerisation do not confine the precursor to the fibre surface. There is no apparent inter-fibre polymer 'bridging', which is encouraging, as this would 'glue together' fibres, reducing the flexibility and extensibility of the fabric.

The effect of precursor concentration on fibre surface morphology can be assessed by comparing the (i) and (ii) specimens. Clearly the reduction in precursor concentration had an effect on the amount of loose polymer present. Given that the mass add-on also reduced, it seems that a substantial proportion of the mass add-on may have been the loosely adhering polymer particles. For EDOT, removing these does not increase resistance – in fact the resistance decreases at this concentration, as was reported in Section 7.2. Poly(EDOT) must form relatively uniform conductive coatings on the fibres that do not benefit from the presence of loose polymer, whereas the less conductive poly(2,2'-bithiophene) coating seems to benefit from the presence of these particles (although it must be noted that it showed the same behaviour as a function of precursor concentration as EDOT, but at concentration levels higher than those used here).

The effect of oxidant solvent can be seen for EDOT specimen (iii). This is similar in appearance to (i), except there was an increased amount of the loosely adhering polymer present. This is somewhat surprising, as it suggests that EDOT migrated away from the fibre surfaces when immersed in an oxidant solvent that it was <u>insoluble</u> in (water) to a greater extent than when immersed in an oxidant solvent it was soluble in (methanol). Perhaps the level of diffusion in methanol is sufficient for the loose polymer formed to be so loosely adhered to the fibre that it is lost in rinsing, whereas for water it lodges in the interstices in the fabric. Certainly this higher level of loose polymer is reflected in the mass add-on (higher for water than for methanol).

Acetonitrile as the oxidant solvent was assessed in the (iv) specimens. The EDOT specimen looked very similar to when water was used, with more loose polymer particles. Presumably the underlying polymer coating is of a better quality in acetonitrile than in methanol, as the surface resistance is lower without a substantial increase in mass add-on. For bithiophene there was an increase in mass add-on and a reduction in resistance, and a large amount of polymer visibly present, adhering to the fibres and loose in the fabric structure. The quantity of polymer present was such that a region of inter-fibre polymerisation is apparent in the top left hand corner of the higher magnification image.

Finally, the effect of the additional dopant can be seen in the images of the (v) specimens. For bithiophene, the polymer coating itself now seemed to be slightly loose on the fibre surface, with cracks and peeling visible, especially in the higher magnification image. The mass add-on was similar to that of the (i) specimen, which suggests that the presence of NDSA did interfere with the polymer deposition (and resulted in a higher resistance). By contrast, the EDOT specimens appeared very similar both with and without dopant, despite the increase in resistance caused by the NDSA.

7.8.3 Summary and Conclusions.

Useful information has been obtained from observing the surface morphology of the fibres via SEM images. However, while the influence of the different parameters on the morphology can be observed, it is difficult in many cases to relate this to the surface resistance behaviour. Mass add-on seems to be clearly reflected in these images, in that high mass add-on levels are associated with larger amounts of loosely adhering polymer lodged in the fabric interstices.

One clear conclusion is that the process is a somewhat inefficient use of ICP precursor, as large amounts of polymer form away from the fibre surfaces. Some of this remains in the fabric structure as amorphous particles, but (presumably) also a substantial amount of precursor is lost completely into the oxidant solution.

7.9 Two-Stage Impregnation Summary and Conclusions.

The influence of a range of parameters has been determined for the two-stage impregnation technique for deposition of conductive polymers onto textile substrates. Both poly(3,4-ethylenedioxythiophene) and poly(2,2'-bithiophene) in their conductive forms have been deposited onto a range of substrates, with the former generally having a much lower surface resistance than the latter. It should be noted that pyrrole can also be polymerised by this technique, but seems better suited to the one-step Milliken technique (described in Section 2.2.1 and experimentally verified in Chapter 5). The preferred conditions for poly(3,4-ethylenedioxythiophene and poly(2,2'-bithiophene) deposition by two-stage impregnation are summarised in Table 7.14. It should be noted that these are not necessarily the conditions that give the lowest surface resistance, as mass add-on and ease of use of the materials involved have also been taken into account.

Table 7.14. Preferred conditions for two-stage impregnation deposition of thiophene-based conductive polymers onto textile substrates.

Parameter	3,4-Ethylenedioxythiophene	2,2'-Bithiophene
Precursor solvent	CH_3CN	CH_3CN
Precursor concentration	0.25 g/10 mL	~0.4 g/10 mL
Precursor impregnation time	~4 minutes	~4 minutes
Precursor drying time	~4 minutes	~4 minutes
Oxidant	$FeCl_3.6H_2O$	$FeCl_3.6H_2O$
Oxidant solvent	CH_3OH	CH_3CH_2OH
Oxidant impregnation time	~4 minutes	~4 minutes
Oxidant drying time	> 2 hours	> 2 hours
Dopant concentration	None	None

The technique is quite useful, as it is not complex and produces moderately conductive composites. The fact that low precursor concentrations provide the composites with the lowest resistance (at a corresponding low mass add-on) is a very useful outcome, as it suggests an obvious way of increasing the efficiency of the process. However, the SEM images in Section 7.8 (as well as observations during specimen rinsing) show a tendency towards considerable loose, amorphous polymerisation, which indicates that much of the polymerisation is occurring elsewhere than on the fibre surfaces.

It was decided to test a set of conditions that would be expected take the above phenomenon to an extreme level. A two stage-impregnation was carried out for three specimens of polyester interlock, using 3,4-ethylenedioxythiophene. For the first, the oxidant impregnation was carried out with no movement of the solution or specimen. For the second, a gentle swirling of the solution (and specimen) was carried out, while for the third, the solution and specimen were vigorously agitated by shaking. The expectation was that increasing agitation would decrease the amount of polymer deposited, and the surface resistance would increase. The results of this trial are given in Table 7.15.

Table 7.15. Effect of agitation of the solution during oxidant impregnation.

Level of agitation	Mass add-on (%)	Surface resistance (Ω/square)
No agitation	3.38	3.06×10^5
Gentle swirling	3.10	3.76×10^5
Vigorous shaking	2.92	3.09×10^5

Surprisingly, it seems that agitation of the oxidant solution had no effect. In the 'vigorous shaking' situation, the actual conditions of polymerisation are a single solution containing both precursor and oxidant. All aspects of the process (including polymerisation occurring during solvent evaporation) were as observed previously. This result clearly indicates the possibility of using an alternative 'single-dip' technique, and investigations into this novel approach are the focus of Chapter 8 of this work.

Chapter 8 Experimental Work – Single Dip Technique.

8.1 Initial Investigation.

It was noted in the conclusion to Chapter 7 that the effect of vigorous agitation during the second impregnation created a situation where the specimen was simply being thoroughly soaked with a solution containing dissolved oxidant and precursor. After removal from the solution, polymerisation proceeded as usual, with the specimen darkening as the solvent evaporated. The electrical properties and mass add-on were not substantially different from the true two-stage impregnation method, and there did not appear to be any polymerisation in the solution itself during the impregnation time. A simplified version of the two-stage impregnation technique for polymer deposition may be viable.

The proposed 'single dip' technique is as follows:

- Prepare a solution having an optimal concentration of both oxidant and precursor dissolved in an appropriate solvent; concentrations and solvent to be determined.
- Place the specimen into the solution for an optimal time, with agitation to ensure penetration of the reagents into the textile substrate; impregnation time to be determined.
- Remove the specimen from the solution and allow polymerisation to occur during solvent evaporation, as for the two-stage method.

All post-deposition methodologies remain the same as with other techniques. The procedure is described more fully in Section 4.4.4.

An initial experiment was carried out as an assessment of the feasibility of this technique, and to identify key parameters for further investigation. For this experiment, three specimens of each of three fabrics having very different properties were used: polyester interlock (P INT), wool/elastane knit (WL) and standard acrylic woven (O).

Three polymerisation solutions were prepared by taking approximately 0.25 g of EDOT and adding 10 mL of a 1 mol/L iron (III) chloride solution. The solutions were prepared with three different solvents: methanol, water and acetonitrile. One specimen of each fabric was treated in each solution. The precursor and oxidant concentrations used were the optimum concentrations derived from the two-stage method. Three different fabric specimens were treated in each solution, in the order: P INT, O, WL. The wool/elastane specimen was treated last as it was most likely to absorb (and hence deplete) the polymerisation solution. The solution (with specimen) was agitated periodically for four minutes, then the specimen was removed and placed flat under a fume hood to allow solvent evaporation. The two organic solvents were given two hours, and water four hours, to evaporate. The specimens were turned periodically to prevent 'pooling' of the solution on either face of the fabric. After solvent evaporation, the specimens were rinsed, dried, and conditioned in the usual manner. All specimens darkened to some degree, indicating ICP deposition. During the rinsing process it was observed that the acetonitrile specimens had loose polymer in the rinse water (i.e. polymer that had not adhered to the fibre surfaces). These nine specimens are shown in Appendix 3 (8.1).

The solutions prepared using organic solvents resulted in fairly uniform ICP deposition, while water resulted in poor and/or uneven deposition. Surface resistance and mass add-on results are provided in Table 8.1. The standard deviation of surface resistance is given in parentheses.

Table 8.1. Mass add-on and surface resistance – initial trials.

Substrate/Solvent	Mass add-on (%)	Surface resistance (Ω/square)
P INT / CH_3OH	10.31	30.96 (12.02) x 10^3
P INT / H_2O	86.88	52.53 (61.84) x 10^3
P INT / CH_3CN	8.93	10.27 (8.18) x 10^3
O / CH_3OH	7.32	19.18 (7.33) x 10^3
O / H_2O	0.79	1.395 (1.336) x 10^6
O / CH_3CN	7.53	7.38 (3.02) x 10^3
WL / CH_3OH	9.13	58.21 (19.31) x 10^3
WL / H_2O	2.11	> 40 x 10^6
WL / CH_3CN	6.47	21.21 (11.16) x 10^3

It is clear that electrically conductive composites can be produced by this technique. Water was the least suitable of the solvents, while acetonitrile gave consistently the lowest resistance, and a lower mass add-on than methanol. However, the toxicity of this solvent makes it undesirable. The mass add-on values were high compared with the two-stage method, but it isn't clear how the precursor concentration used in this case relates to that used for the two-stage method. The effective precursor concentration was almost certainly much higher here.

This experiment demonstrated that the single dip method could be used to create viable textile-ICP composites. Subsequent sections of this chapter report the effect of various parameters on composite properties.

8.2 Effect of Precursor Concentration.

8.2.1 Background.

The concentration of precursor in the polymerisation solution is likely to be an important parameter in determining the polymer mass add-on and surface resistance. For the two-stage impregnation method, it was found that increasing the precursor concentration increased the mass add-on, but this did not result in lower resistance. In fact, the lowest resistance was achieved at a relatively low precursor concentration. Above and below this concentration, the resistance was higher. This implied that polymer deposited at higher precursor concentrations has a less conductive physical or chemical structure. It is likely that similar behaviour will be observed here, given that the single dip method is essentially an evolution of the two-stage method.

It should be noted that the precursor concentration at which the composite surface resistance reached a minimum for the two-stage method is difficult to relate to the precursor concentration used here. For the two-stage method, the concentration is that of the precursor solution into which the specimen is dipped before being dried and then placed into oxidant. The amount of precursor retained by the specimen and the volume of the oxidant solution could be used to calculate the equivalent single-dip concentration, but the former was not known. Also the impregnation method is quite different for the single dip technique; using vigorous agitation, while the two-stage method uses a minimum of agitation to prevent the precursor diffusing into the solution and away from the specimen.

8.2.2 Preliminary Investigation.

A single substrate was initially used to determine the effect of precursor concentration across a wide range of values. The polyester interlock fabric was chosen for its ease of handling during preparation and polymer deposition. Six 10 mL polymerisation solutions were prepared as described in Section 4.4.4, with nominal and actual concentrations of EDOT as detailed in Table 8.2.

The EDOT amount measured out for the lowest concentration here was roughly equal to one drop from a 1 mL disposable pipette, and was, therefore, virtually the minimum concentration that could be prepared with this set-up. To prepare lower concentration polymerisation solutions it would be necessary to use larger volumes of oxidant solution. The deviation of actual concentration of EDOT from the nominal values was not important, provided they were known accurately and covered the range of interest.

Table 8.2. Polymerisation solution details – precursor concentration (EDOT).

Specimen ID	Nominal EDOT concentration (g/10 mL)	Actual EDOT concentration (g/10 mL)
1	0.25	0.248
2	0.20	0.197
3	0.15	0.159
4	0.10	0.113
5	0.06	0.079
6	0.03	0.028

Polymer deposition was carried out as described in Section 4.4.4. The six specimens are shown in Appendix 3 (8.2.2), and were dark and uniform in coloration, with the lowest precursor concentration slightly lighter than the others; probably indicative of a lower mass add-on. The specimens were measured for polymer mass add-on and surface resistance by the usual techniques. These results are provided in Table 8.3 (standard deviation of surface resistance given in parentheses). The effect of precursor concentration is perhaps best illustrated graphically, as shown in Figure 8.1, where the most obvious feature is the non-linear form of the relationship between precursor concentration and surface resistance. The mass add-on increased linearly with precursor concentration, meaning that the correlation between mass add-on and surface resistance was poor ($r = 0.65$). Precursor concentration was directly proportional to mass add-on, so increasing the precursor concentration increased the amount of polymer deposited, but not in a form that was as electrically conductive as that produced at lower concentrations.

Table 8.3. Mass add-on and surface resistance – precursor concentration (EDOT).

Specimen ID	EDOT concentration (g/10 mL)	Surface resistance (Ω/square)	Mass add-on (%)
1	0.248	69.53 (23.96) x 10^3	9.13
2	0.197	82.33 (34.00) x 10^3	6.84
3	0.159	103.06 (48.28) x 10^3	5.52
4	0.113	89.53 (26.47) x 10^3	3.57
5	0.079	45.96 (13.86) x 10^3	2.55
6	0.028	9.96 (1.32) x 10^3	0.91

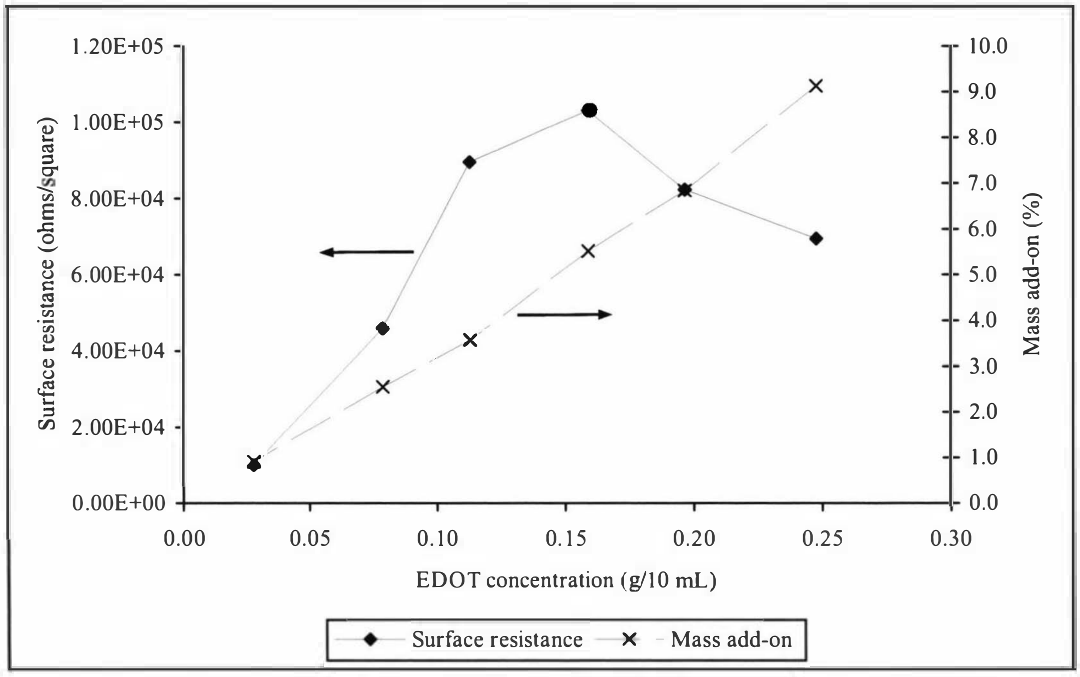


Figure 8.1. Mass add-on and surface resistance – precursor concentration (EDOT).

The low precursor concentration behaviour (< 0.15 g/10 mL) must be examined in more detail to determine the point at which surface resistance reaches a minimum. The high concentration behaviour (> 0.15 g/10 mL) is of less interest, because although the resistance dropped, the mass add-on and resistance were both well above those occurring at low concentrations. Higher mass add-on made the fabric stiff, and used more of the relatively expensive precursor to no useful effect.

8.2.3 Behaviour at Low Precursor Concentration on Three Substrates.

Three different substrates were chosen for an investigation into the low concentration behaviour. The polyester interlock fabric (P INT) used in the preliminary trial was included, plus the standard acrylic woven fabric (O) and the wool/elastane knit (WL). These covered such a wide range of fibre types and structures that any behaviour different for a particular fibre or type of fabric should be detected. Six specimens were prepared from each fabric, one to be treated at each of the precursor concentrations given in Table 8.4 (larger volumes were necessary to prepare the low precursor concentration solutions).

As before, the exact concentration levels were not important; merely a good spread of values across the range of interest was needed. Only six solutions were used, with three specimens treated successively in each. The order of treatment was P INT, then O, then WL. Indications from previous experiments were that several specimens could be treated in each solution without deterioration in composite properties (discussed in more detail in Section 8.8.5). The wool/elastane fabric specimens were treated last because of the higher absorbency of the wool. The polymer deposition procedure was as described in Section 4.4.4.

Table 8.4. Polymerisation solution details – lower precursor concentration (EDOT).

Specimen ID	Nominal EDOT concentration (g/10 mL)	Actual EDOT concentration (g/10 mL)	Preparation*
1	0.100	0.0968	3 drops in 10 mL
2	0.067	0.0616	2 drops in 10 mL
3	0.033	0.0367	1 drop in 10 mL
4	0.017	0.0250	1 drop in 20 mL
5	0.010	0.0103	1 drop in 30 mL
6	0.007	0.0090	1 drop in 40 mL

* Drops of EDOT from 1 mL plastic disposable pipette in volume of oxidant solution.

Polymerisation proceeded as usual, with the specimens darkening gradually during evaporation. Polymerisation on WL appeared to be slower than on the other two fabrics. After rinsing, the WL specimens appeared more heavily coated, being darker in colour than the others. The treated specimens are shown in Appendix 3 (8.2.3). Surface resistance and mass add-on data are provided in Table 8.5, with standard deviation of surface resistance in parentheses.

The surface resistance and mass add-on data are each plotted as a function of precursor concentration in Figures 8.2 and 8.3 respectively. From Figure 8.2 it is clear that there was a minimum surface resistance value for each of the three substrates at approximately the same precursor concentration (between 0.02 and 0.04 g/10 mL). Below this concentration the resistance rapidly increased, presumably as the polymer loading diminished to a level where there were significant discontinuities in the polymer coating. Above this concentration the resistance also increased, but more gradually. It is possible that the quality of polymer deposition improved as the precursor concentration decreased, but eventually there was simply too little ICP present (only ~0.2-0.3% add-on) to provide good conductive pathways through the textile-poly(EDOT) composite. Polymer mass add-on was directly proportional to precursor concentration, and as Figure 8.3 indicates, followed a very similar pattern for all three substrates.

Table 8.5. Mass add-on and surface resistance – lower precursor concentration (EDOT, three substrates).

Substrate	EDOT concentration (g/10 mL)	Surface resistance (Ω/square)	Mass add-on (%)
P INT	0.0968	25.88 (7.28) x 10^3	3.06
	0.0616	13.48 (3.42) x 10^3	2.35
	0.0367	7.63 (2.44) x 10^3	1.47
	0.0250	8.47 (2.84) x 10^3	0.95
	0.0103	17.52 (9.69) x 10^3	0.40
	0.0090	20.09 (10.05) x 10^3	0.30
O	0.0968	12.43 (4.31) x 10^3	2.51
	0.0616	6.42 (1.24) x 10^3	1.58
	0.0367	4.66 (0.91) x 10^3	0.91
	0.0250	4.25 (0.75) x 10^3	0.58
	0.0103	11.37 (3.95) x 10^3	0.18
	0.0090	10.03 (1.90) x 10^3	0.21
WL	0.0968	5.09 (1.74) x 10^3	3.33
	0.0616	2.93 (0.80) x 10^3	2.08
	0.0367	2.44 (0.72) x 10^3	1.25
	0.0250	3.94 (0.85) x 10^3	0.74
	0.0103	8.93 (2.09) x10^3	0.21
	0.0090	14.90 (4.68) x 10^3	0.16

8.2.4 Summary and Conclusions.

The most conductive composite was prepared when using a low precursor concentration (and thus a low polymer loading), and the optimum level was similar for all three substrates. As the optimum level was somewhere between 0.02 and 0.04 g/10 mL, it is reasonable to take 0.03 g/10 mL as a default precursor concentration to use in other experiments. It may be possible to optimise it further for specific substrates (as would be useful for large-scale production), but for research purposes, the value of 0.03 g/10 mL is appropriate.

With the single-dip technique, polymerisation conditions that favour high levels of polymer deposition do not necessarily produce composites with low surface resistance. Other researchers have found that conditions favouring slow polymer formation (such as reducing the temperature) can lead to better electrical properties of the ICP [9], but in this work there was no observable difference in the rate of polymerisation with different precursor concentrations. It is unlikely that the precursor concentration would substantially effect the rate of polymerisation, as the oxidant (which initiates the process) is in such excess. In the polymerisation conditions used in Section 8.2.3 for example, there is 15 to 150 times more oxidant than precursor (in mole terms).

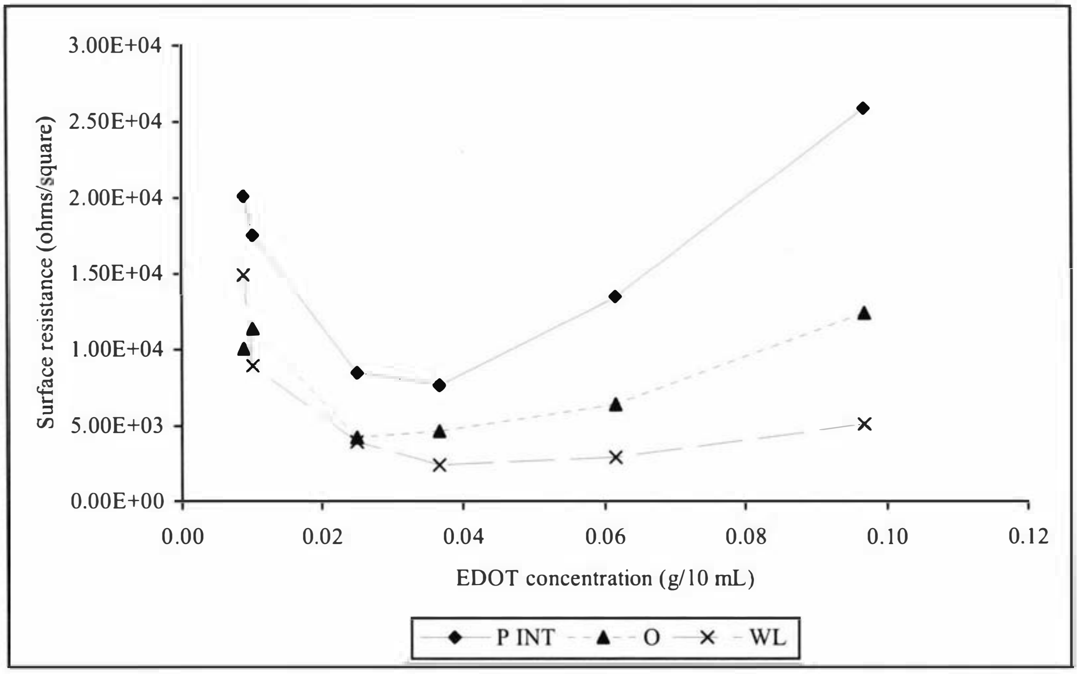


Figure 8.2. Surface resistance – lower precursor concentration (EDOT, three substrates).

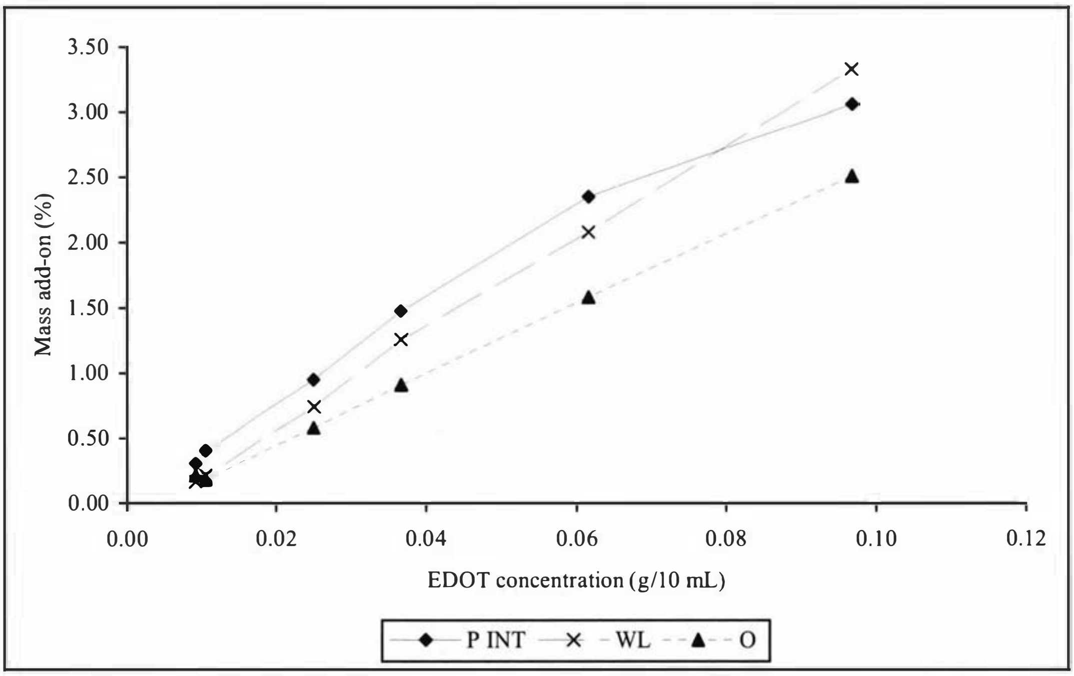


Figure 8.3. Mass add-on – lower precursor concentration (EDOT, three substrates).

Clearly, some feature of low precursor concentration conditions favours formation of lower resistance poly(EDOT). Low availability of precursor may encourage linear polymer chain formation with a minimum of branching, and this better-ordered arrangement would be more conductive. Another possibility is chemical groups in the substrate providing a ‘template’ for polymer deposition, which also results in more ordered polymer formation, whereas when this layer builds up (with higher mass add-on) the template effect is lost. Because the resistance is measured via contact with the surface of the fibres, the electronic properties of the outermost portion of the deposited polymer have a major influence on the surface resistance of the composite. This may be the key to the unexpected behaviour observed here.

8.3 Effect of Oxidant Concentration.

8.3.1 Background.

In Section 8.2, the effect of precursor concentration on the mass add-on and surface resistance of textile-poly(EDOT) composites was described. Equally important is the influence of the oxidant concentration, as it is this that initiates polymerisation, and provides the dopant anion to make the conductive form of the ICP. Intuitively, it seems likely that the higher the oxidant concentration, the faster polymerisation will proceed. This may not necessarily lead to better electrical properties, as polymer deposition may be less controlled and molecular structures in the polymer chain could be less linear and therefore less conductive. Conversely, higher oxidant concentrations provide a greater number of dopant anions, and thus may lead to higher levels of doping in the ICP.

To investigate the effect of oxidant concentration, experiments were carried out for two oxidants (iron (III) chloride and iron (III) perchlorate) where the concentration of the oxidant in the polymerisation solution was varied,. The perchlorate salt was included because of a literature reference indicating its superiority over chloride [26]. The precursor concentration was held at the optimum level as determined in Section 8.2, and only one solvent was used. For the perchlorate version, both EDOT and 2,2'-bithiophene were used, whereas only EDOT was used with chloride.

8.3.2 Iron (III) Chloride Concentration.

For this investigation, the polyester interlock fabric was used. Six polymerisation solutions were prepared as detailed in Table 8.6.

Table 8.6. Polymerisation solutions – oxidant concentration (iron (III) chloride).

Specimen ID	Oxidant concentration (mol/L)	Amount of EDOT (g)	Volume of solution (mL)
1	1.00	0.0300	10.0
2	0.75	0.0302	10.1
3	0.50	0.0307	10.2
4	0.25	0.0269	9.0
5	0.10	0.0301	10.0
6	0.05	0.0333	11.1

Polymerisation was carried out as described in Section 4.4.4, and was apparent at all oxidant concentrations (indicated by darkening of the specimens), although at lower concentrations the specimens appeared to darken more slowly. The rinsed and dried specimens are shown in Appendix 3 (8.3.2). At lower concentrations the specimens are lighter in colour, suggesting lower polymer mass add-on. This is confirmed by the data in Table 8.7 (also presented graphically in Figure 8.4, with a log scale used for surface resistance).

There was a consistent increase in mass add-on with oxidant concentration, apart from a small fluctuation at very low concentration. In turn, there was a consistent decrease in resistance with increasing concentration. Unlike the situation with the precursor concentration (Section 8.2), there is a negative correlation between mass add-on and precursor concentration (the correlation coefficient, r = -0.653). The resistance curve in Figure 8.4 flattens out at high oxidant concentrations, so it is unlikely that there would be any great benefit in using concentrations higher then 1 mol/L. The solubility of iron (III) chloride in methanol is not much higher than 1 mol/L, and this could also preclude the use of higher concentrations.

Table 8.7. Mass add-on and surface resistance – oxidant concentration (iron (III) chloride).

Oxidant concentration (mol/L)	Polymer mass add-on (%)	Surface resistance (Ω/square)
1.00	1.05	8.88 (3.33) x 10^3
0.75	0.99	12.96 (4.24) x 10^3
0.50	0.69	91.54 (33.54) x 10^3
0.25	0.51	1.40 (0.39) x 10^6
0.10	0.41	> 36.9 (6.8) x 10^6 (1)
0.05	0.47	> 40 x 10^6 (2)

Notes:

1. Six of the eight readings exceeded the maximum measurable resistance for the ohmmeter used. The value given is the average of the two readings that could be made. The true mean value is in excess of this.
2. All eight of the readings exceeded the maximum measurable resistance for the ohmmeter used.

As demonstrated for precursor concentration, a higher mass add-on does not necessarily result in lower resistance. Here, therefore, lower resistance observed at high mass add-on may not simply be due to the larger amount of ICP, but also because the higher oxidant concentration favours formation of a more conductive form of poly(EDOT). One way this could occur is by causing a higher level of doping (that is, a larger number of chloride ions incorporated into the polymer), leading to better charge transport through the ICP.

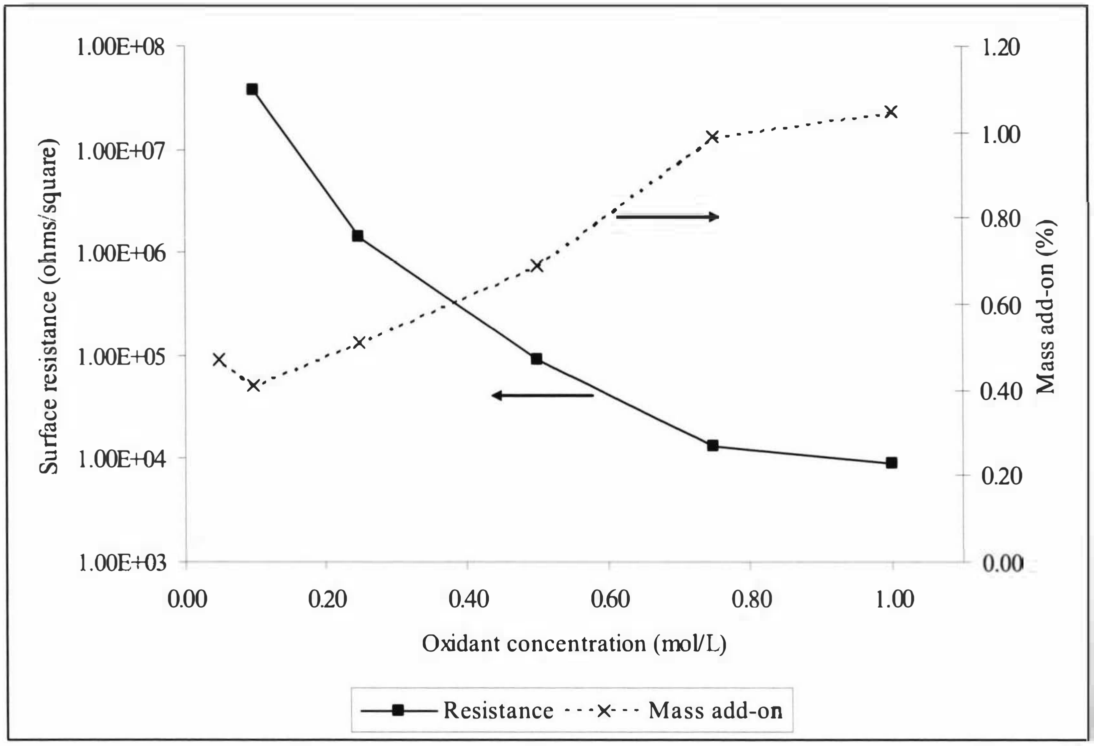


Figure 8.4. Mass add-on and surface resistance – oxidant concentration (iron (III) chloride).

8.3.3 Iron (III) Perchlorate Concentration.

Experiments reported later in this chapter (Section 8.4) indicated that iron (III) perchlorate could produce textile-poly(EDOT) composites with a lower resistance than iron (III) chloride, and that it was possible to prepare conductive textile-poly(2,2'-bithiophene) composites using this oxidant. The purpose of the work reported in this section was to determine the influence of the concentration of iron (III) perchlorate in the polymerisation solution on the mass add-on and surface resistance of textile-poly(EDOT) and textile-poly(2,2'-bithiophene) composites.

Six polymerisation solutions were prepared as detailed in Table 8.8. Because of the higher solubility of iron (III) perchlorate than iron (III) chloride in methanol, the range of oxidant concentrations is slightly different to that used for iron (III) chloride. Polymerisation was carried as described in Section 4.4.4. At higher concentrations the specimens darkened (polymerised) more rapidly, but all specimens ultimately became uniformly dark. The three highest oxidant concentrations with EDOT appeared to have some loose particles of polymer present on their surface, and these solutions appeared to have some solids present in solution – presumably polymer that had formed in the polymerisation solution.

Table 8.8. Polymerisation solutions – oxidant concentration (iron (III) perchlorate).

Specimen ID	Oxidant concentration (mol/L)	EDOT		2,2'-Bithiophene	
		Amount (g)	Solution volume (mL)	Amount (g)	Solution volume (mL)
1	1.50	0.0322	10.7	0.0275	9.2
2	1.25	0.0317	10.6	0.0295	9.8
3	1.00	0.0295	9.8	0.0312	10.4
4	0.75	0.0308	10.3	0.0298	9.9
5	0.50	0.0311	10.4	0.0316	10.5
6	0.25	0.0347	11.6	0.0297	9.9

The specimens are shown after rinsing and drying in Appendix 3 (8.3.3). The loose polymer observed for EDOT specimens 1, 2 and 3 was removed in rinsing. Their mass add-on and surface resistance values are provided in Table 8.9.

Table 8.9. Mass add-on and surface resistance – oxidant concentration (iron (III) perchlorate).

	EDOT		2,2'-Bithiophene	
Oxidant concentration (mol/L)	Surface resistance (Ω/square)	Mass add-on (%)	Surface resistance (Ω/square)	Mass add-on (%)
1.50	1.415 (0.279) x 10^3	1.03	30.01 (4.91) x 10^6	0.66
1.25	1.001 (0.096) x 10^3	1.43	2.601 (0.337) x 10^6	0.84
1.00	8.450 (0.623) x 10^2	1.31	847.1 (88.2) x 10^3	1.11
0.75	7.104 (0.941) x 10^2	1.19	304.0 (72.3) x 10^3	1.11
0.50	8.343 (0.865) x 10^2	1.37	304.0 (83.9) x 10^3	1.07
0.25	1.400 (0.230) x 10^3	1.00	921.6 (400.1) x 10^3	0.70

To better observe the relationship between oxidant concentration and the two key parameters (mass add-on and surface resistance), these results were plotted in Figures 8.5 (EDOT) and 8.6 (2,2'-bithiophene). In Figure 8.6 it was necessary to plot surface resistance on a log scale.

The simple relationships observed for iron (III) chloride for both mass add-on and surface resistance (Figure 8.4) were not apparent for iron (III) perchlorate. There was a similar pattern for both precursors, with mass add-on fluctuating but tending to be higher at mid-range oxidant concentrations. Resistance reached a minimum value at mid-range concentrations.

This implies a negative correlation between mass add-on and surface resistance, and the calculated correlation coefficients are r_{EDOT} = -0.727 and $r_{2,2'\text{-Bithiophene}}$ = -0.629. This level of correlation is consistent with the iron (III) chloride results.

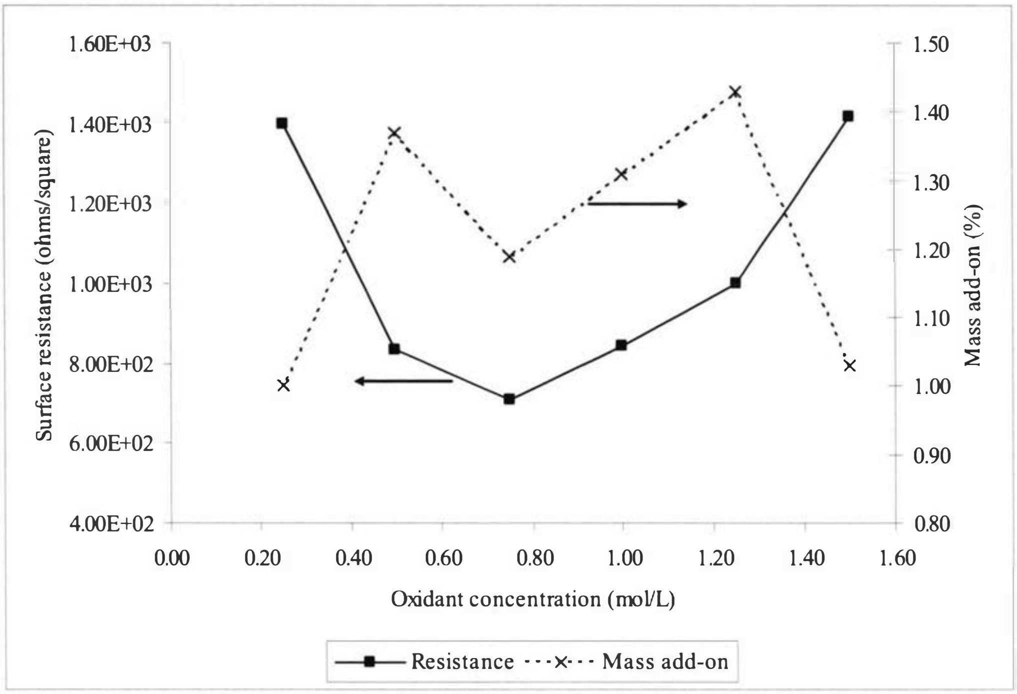


Figure 8.5. Mass add-on and surface resistance – oxidant concentration (iron (III) perchlorate, EDOT).

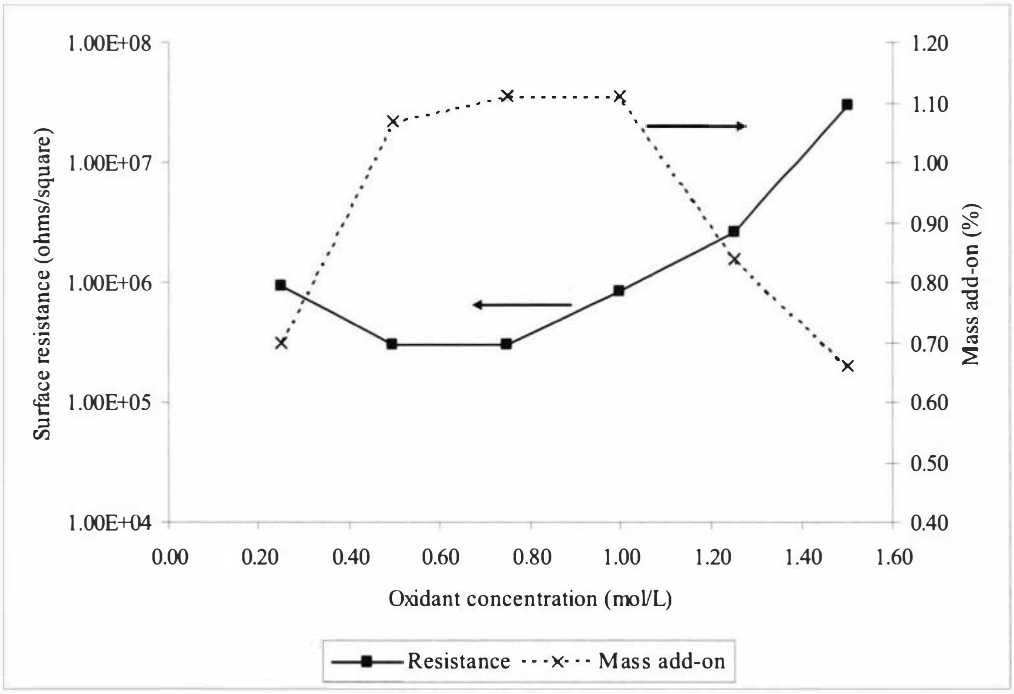


Figure 8.6. Mass add-on and surface resistance – oxidant concentration (iron (III) perchlorate, 2,2'-bithiophene).

An explanation for the unexpected shape of these curves may be related to the observed presence of polymer in solution at high oxidant concentrations. This suggests that at higher concentrations using iron (III) perchlorate, some polymerisation occurred in the solution (which it did not at lower concentrations, or with iron (III) chloride). The result was that reagents were consumed before the solvent evaporation phase, reducing their availability for surface deposition. As a result, at these high concentrations less polymer was deposited onto the fabric, and this is consistent with higher surface resistance.

8.3.4 Summary and Conclusions.

When iron (III) chloride is used as the oxidant, the concentration should be as high as possible, to yield a higher mass add-on and a lower surface resistance. Here, a concentration of 1 mol/L was used in methanol, which is close to saturation at room temperature. By contrast, the apparently stronger oxidising conditions provided by iron (III) perchlorate mean that there is a maximum oxidant concentration above which wasteful polymerisation occurs in solution, rather than on the fibre surfaces in the subsequent solvent evaporation. With methanol as the solvent and using either EDOT or 2,2'-bithiophene, this concentration appears to be about 0.75 mol/L.

It is a little difficult to understand why a high polymer mass add-on correlates well with surface resistance when oxidant concentration is varied and precursor concentration is fixed, but does not when precursor concentration varies at a fixed oxidant concentration. Possible reasons for the latter have been discussed in Section 8.2. One reason for the former could be that not only is a high oxidant concentration required to initiate polymerisation, but it may also be required to fully dope the ICP. The conditions of polymerisation may be such that doping is very inefficient, and a great excess of dopant anions are required to result in a fully doped (and hence more conductive) ICP.

The optimum oxidant concentration for polymerisation using iron (III) chloride is 1 mol/L (in methanol). Other than in special circumstances, this was the default concentration that was used in the remainder of this work. For iron (III) perchlorate, the optimum seems to be about 0.75 mol/L in methanol, and this should be used to minimise surface resistance. However, in most of the work that follows, 1 mol/L was used, as a more direct comparison with iron (III) chloride was required.

8.4 Effect of Oxidant Counter-Ion.

8.4.1 Background

In most of the research described in this thesis, polymerisation was initiated by an oxidising agent in the form of an iron (III) salt; typically iron (III) chloride hexahydrate ($FeCl_3.6H_2O$). The advantage of metal salts (such as iron chloride), over other types of oxidants (such as hydrogen peroxide (H_2O_2) or ammonium persulphate ($(NH_4)_2S_2O_8$)), is their provision of an anionic species to act as a dopant in the conducting polymer. Polymers formed using iron chloride as the oxidant are assumed to be doped with the chloride anion. Alternative iron (III) salts could also be employed, and would introduce alternative dopant species. Note that iron (III) salts are preferred in this work because of the relatively high oxidation potential of the $Fe^{3+} \rightarrow Fe^{2+}$ transformation. The standard electrode potential of the $Fe^{3+} + e^- \rightarrow Fe^{2+}$ reaction is 0.77 V, compared (for example) with the standard of electrode potential of the $Cu^{2+} + e^- \rightarrow Cu^+$ reaction, which is only 0.17 V [155].

One limitation on the use of many iron (III) salts is their solubility in the solvent used for the polymerisation solution. Experience has shown that iron (III) chloride hexahydrate is soluble to at least 1 mol/L in methanol (the solvent most often used in this work), and at lower concentrations polymer formation is hindered (see Section 8.3). Therefore oxidants with poor solubility are unlikely to be good candidates for chemical polymerisation. A preliminary investigation identified several iron (III) salts that were soluble to at least 0.5 mol/L in methanol, and rejected others (for example, iron (III) sulphate hydrate) with low solubility. These salts were compared in experiments described in this section.

The interaction between solvent and oxidant is discussed in Section 8.5. In non-aqueous systems, iron (III) chloride is thought to be poorly dissociated [3], and the same is likely to be true of the other iron (III) salts used in this work. A lack of dissociation leads to both a reduced oxidising effect from Fe^{3+} and a reduced availability of dopant anions. The compatibility of oxidant and solvent must also be considered. Care must be taken when preparing solutions of strong oxidisers in organic solvents, as violent reactions can occur. Preliminary tests with very small quantities of reagents confirmed that none of the combinations of oxidant and solvent used in this work behave hazardously.

8.4.2 Effect of Oxidant Counter-Ion for Two Precursors.

8.4.2.1 Experimental Design and Method.

In this experiment, three iron (III) salts were used to polymerise EDOT and 2,2'-bithiophene onto the polyester interlock fabric. The polymerisation solutions are detailed in Table 8.10.

Table 8.10. Polymerisation solution details – oxidant counter-ion.

Specimen ID	Precursor	Oxidant
EDOT 1	EDOT	$FeCl_3.6H_2O$
EDOT 2	EDOT	$Fe(ClO_4)_3.xH_2O$
EDOT 3	EDOT	$Fe(p\text{-}TS)_3.6H_2O$
BT 1	2,2'-Bithiophene	$FeCl_3.6H_2O$
BT 2	2,2'-Bithiophene	$Fe(ClO_4)_3.xH_2O$
BT 3	2,2'-Bithiophene	$Fe(p\text{-}TS)_3.6H_2O$

The anion '*p*-TS' is *para*-toluenesulphonate, shown in Figure 8.7. It is of particular interest, because aromatic sulphonate anions have been identified by several researchers [9,19,27] as providing higher conductivity and better environmental stability than simple ions such as chloride. This is thought to be a result of their reduced mobility compared to chloride, due to low volatility and large size; the latter generating steric hindrance to its migration out of the polymer. There could also be aromatic ring interactions between the aromatic dopant and heterocyclic precursor.

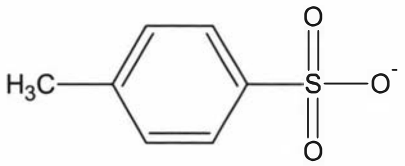


Figure 8.7. *p*-Toluenesulphonate.

Iron (III) perchlorate is known to be a strong, potentially hazardous oxidiser, so is of interest in comparison with the milder oxidative conditions of iron (III) chloride. It also offers an alternative counter-ion – perchlorate – that is very much larger than chloride, and should therefore resist migration out of the polymer, although to a lesser extent than *p*-TS. For these reasons, both of the two new oxidants would be expected to produce composites with lower surface resistance, and better durability of resistance over time.

Oxidant solutions were prepared to 0.5 mol/L concentration in methanol, as iron (III) *p*-TS hexahydrate was not soluble to 1 mol/L. In Section 8.3 it was demonstrated that moderately conductive composites could be prepared at this reduced oxidant concentration using iron (III) chloride hexahydrate, albeit with a surface resistance higher than in most other experiments. Polymerisation was carried out as described in Section 4.4.4.

8.4.2.2 Results and Discussion.

These six specimens are shown in Appendix 3 (8.4.2). The EDOT composites were all fairly uniform in colour, and mid-to-dark grey-blue. The perchlorate specimen was the darkest; probably indicating higher polymer mass add-on. The 2,2'-bithiophene specimens ranged from pale orange or red to dark brown. The lighter colours may have indicated incomplete oxidation of the polymer, suggesting a less conductive, non-fully doped polymer. As was the case for EDOT, the darkest specimen was from perchlorate. The surface resistance and mass add-on for these six specimens are presented in Table 8.11. The standard deviation of surface resistance is given in parentheses.

Table 8.11. Mass add-on and surface resistance – oxidant counter-ion (two precursors).

Precursor/Counter-ion	**Mass add-on (%)**	**Surface resistance (Ω/square)**
EDOT/Cl^-	0.80	70.8 (18.6) x 10^3
EDOT/ClO_4^-	1.17	1.33 (0.48) x 10^3
EDOT/*p*-TS^-	0.57	439 (164) x 10^3
2,2'-Bithiophene/Cl^-	0.17	> 40 x 10^6
2,2'-Bithiophene/ClO_4^-	0.79	631 (362) x 10^3
2,2'-Bithiophene/*p*-TS^-	0.04	> 40 x 10^6

Perchlorate behaved largely as predicted; for EDOT the composite has a resistance lower than that of chloride. This could be due to an increased amount of polymer being deposited under these more aggressive oxidation conditions, or due to the polymer itself being more conductive when doped with perchlorate. The mass add-on for perchlorate is greater than for chloride, but could simply reflect the incorporation of the heavier dopant anion, rather than a greater number of heterocyclic units having been deposited. Assuming that both chloride- and perchlorate-doped poly(EDOT) have a dopant ratio of one dopant anion to three heterocycle units, the molecular weight of perchlorate-doped poly(EDOT) is 14% greater than that of chloride-doped. Therefore if this was the only factor providing a higher mass add-on for the perchlorate-doped polymer, mass add-on for it should be 0.91%. It was found to be 1.17%, so this mechanism may not be a complete explanation for the situation (as illustrated by the error analysis in Section 4.3.1, the maximum error in these mass add-on values is less than 10%. Therefore with differences between the mass add-on for the three counter-ions being greater than 10%, we can be reasonably confident that these are not measurement errors).

Another possibility is that when polymerised by iron (III) perchlorate, the resultant polymer is more fully oxidised (therefore more fully doped and hence heavier) than when polymerised by iron (III) chloride. The stronger conditions of oxidation with perchlorate may also be able to yield more polymer from the available precursor. Also notable is that the poly(2,2'-bithiophene) composite produced using perchlorate was by far the most conductive of this type produced in this work.

The behaviour of *para*-toluenesulphonate is somewhat disappointing, as its resistance (for EDOT) is an order of magnitude higher than that of chloride. The mass add-on is also relatively low. The resistance of the poly(2,2'-bithiophene) composite prepared using *p*-TS was too high to be measurable on the ohmmeter used for these measurements. However one advantage of *p*-TS may be stability of resistance over time, as the bulky anion should be less prone to migration out of the polymer.

8.4.2.3 Ageing Behaviour.

The ageing behaviour of the four conductive composites prepared in this experiment was assessed by periodically re-measuring their surface resistance over a period of several months. During this they were kept in a standard conditioned room (65% relative humidity and 20°C). Because they started at different resistance levels, these measurements have been converted into relative resistance (R′) values by dividing the resistance at each stage by that specimen's initial resistance. The progression of R′ over a six-month period is illustrated in Figure 8.8, where the most striking feature is the particularly poor ageing behaviour of the poly(2,2'-bithiophene) composite, which reached nearly 41 times its initial resistance after six months. By contrast, *p*-TS-doped poly(EDOT) reached approximately six times its initial value, chloride-doped 3.5 times and perchlorate-doped 1.4 times their initial values. The predicted good performance of *p*-TS-doped poly(EDOT) did not eventuate, although perchlorate was clearly superior to chloride. Perchlorate-doped poly(EDOT) not only had the lowest resistance, it also had the best durability over time.

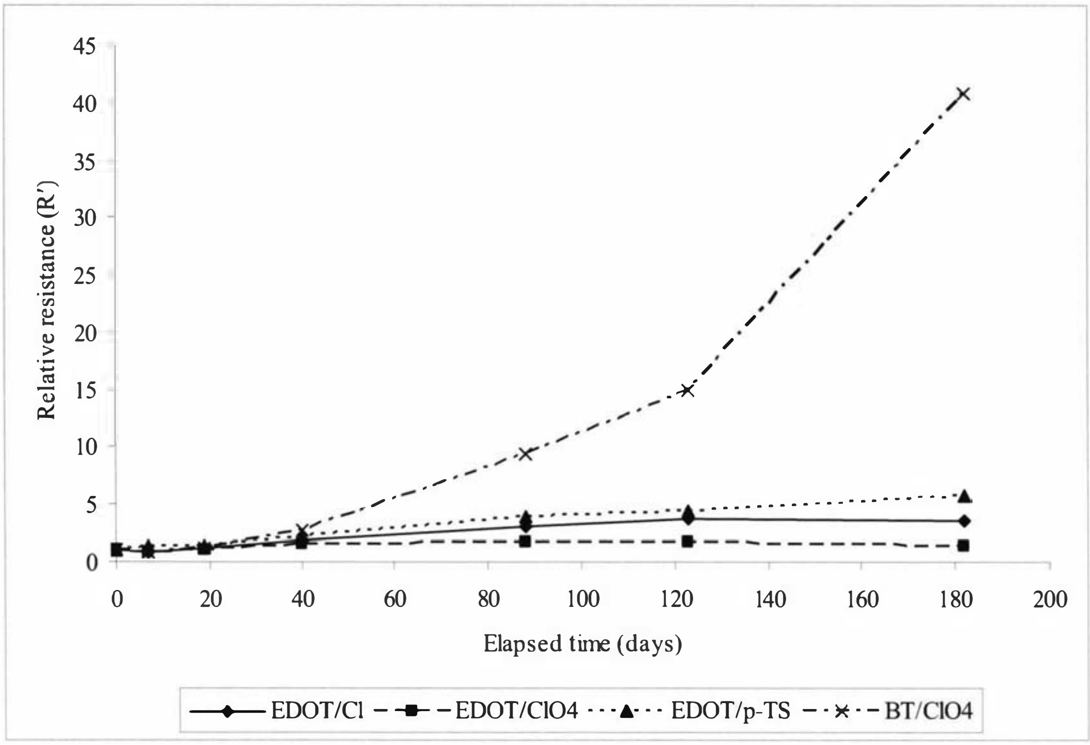


Figure 8.8. Progression of R′ with ageing of specimens with different dopant anions.

8.4.3 Effect of Oxidant Counter-Ion for Three Substrates.

8.4.3.1 Experimental Design and Method.

In this experiment, four iron (III) salts were used to polymerise 3,4-ethylenedioxythiophene (EDOT). The previous experiment examined the behaviour of different oxidants on just one substrate, whereas in this work the polymer is deposited onto specimens of the polypropylene, polyester and wool standard fabrics. Specimen details and experimental details are presented in Table 8.12.

The iron (III) salt of *para*-toluenesulphonate was omitted, due to its poor performance in the previously-reported experiment. The anhydrous form of iron (III) chloride was included for comparison with the hexahydrate, allowing the polymer treatment process to initially proceed in low water conditions. However, as the solvent evaporation (and therefore, the polymerisation) occurs in ambient conditions, the hygroscopic iron (III) chloride that was impregnated into the fabric has ample opportunity to absorb water from the environment and became hydrated before polymerisation is complete. Another iron (III) salt that was unavailable for the previous experiment, iron (III) nitrate, was also included here. The nitrate ion is also larger than chloride, and should therefore be better trapped in the conductive polymer.

Table 8.12. Specimen identification and polymerisation solutions – oxidant counter-ion.

Specimen ID	Substrate	Oxidant
P1	Polypropylene	$FeCl_3.6H_2O$
P2	Polypropylene	$FeCl_3$ (anhydrous)
P3	Polypropylene	$Fe(ClO_4)_3.xH_2O$
P4	Polypropylene	$Fe(NO_3)_3.9H_2O$
D1	Polyester	$FeCl_3.6H_2O$
D2	Polyester	$FeCl_3$ (anhydrous)
D3	Polyester	$Fe(ClO_4)_3.xH_2O$
D4	Polyester	$Fe(NO_3)_3.9H_2O$
W1	Wool	$FeCl_3.6H_2O$
W2	Wool	$FeCl_3$ (anhydrous)
W3	Wool	$Fe(ClO_4)_3.xH_2O$
W4	Wool	$Fe(NO_3)_3.9H_2O$

A preliminary trial found the solubility of iron (III) nitrate in methanol was less than the preferred concentration of 1 mol/L, so all four oxidants were prepared to 0.5 mol/L. The iron (III) chloride solutions were both brownish yellow, the solution prepared from the anhydrous salt slightly cloudy, while the hydrated salt solution was clear. The anhydrous iron (III) chloride also reacted somewhat vigorously when dissolved in methanol. Both the iron (III) perchlorate and nitrate solutions were a clear, reddish-orange. Polymerisation was carried out as described in Section 4.4.4, except that the solvent evaporation time was reduced to 30 minutes. Work reported later in this thesis (Section 8.8.3) indicated this was sufficient.

8.4.3.2 Results and Discussion.

Polymerisation proceeded as expected for all the oxidants, with the specimens darkening fairly rapidly after removal from the solution. Specimens were bright yellow on removal from iron (III) chloride hexahydrate solutions, dull yellow from anhydrous iron (III) chloride, and pale yellow from iron (III) perchlorate and nitrate. After rinsing, the specimens were mid-grey-blue from both iron (III) chloride solutions, darker blue from iron (III) perchlorate and pale blue from iron (III) nitrate. On the basis that depth of colour indicates polymer loading, it seemed likely that the mass add-on from perchlorate would be higher than that from nitrate. The twelve fabric specimens are illustrated in Appendix 3 (8.4.3).

Most specimens were uniformly coated with polymer. Several had small areas which appeared less well coated, and as these were generally at a corner of the specimen were probably due to handling (forceps were used to remove them from the polymerisation solutions). These areas were easily avoided during testing of the surface resistance. However, the wool specimen treated using iron (III) chloride hexahydrate was very poorly coated along one edge, possibly due to poor immersion in the polymerisation solution. This section of fabric was excluded from resistance testing, resulting in a reduced number of measurements. The mass add-on and surface resistance data are shown in Table 8.13. The standard deviation of resistance is given in parentheses.

Table 8.13. Mass add-on and surface resistance – oxidant counter-ion (three substrates).

Substrate	Counter-ion	Mass add-on	Surface resistance (Ω/square)
Polypropylene	Chloride	0.34%	4.27 (11.7) x 10^9
Polyester	Chloride	0.53%	7.93 (1.60) x 10^3
Wool	Chloride	0.97%	6.46 (5.12) x10^4
Polypropylene	Chloride (anhyd.)	0.43%	8.33 (15.4) x 10^9
Polyester	Chloride (anhyd.)	0.58%	1.24 (0.60) x 10^4
Wool	Chloride (anhyd.)	1.19%	1.40 (0.66) x 10^4
Polypropylene	Perchlorate	0.66%	8.45 (5.48) x 10^3
Polyester	Perchlorate	0.76%	4.55 (0.83) x 10^2
Wool	Perchlorate	2.51%	8.25 (3.37) x 10^3
Polypropylene	Nitrate	0.32%	6.71 (3.78) x 10^4
Polyester	Nitrate	0.40%	1.70 (0.45) x 10^3
Wool	Nitrate	1.13%	5.84 (10.9) x 10^6

Considering each comparable pair of oxidants in turn:

Iron (III) chloride hexahydrate and iron (III) chloride (anhydrous) – there was marginally higher mass add-on for each substrate prepared with the anhydrous form, although the differences were small and probably within the range of random errors. For polypropylene, the resistances were very high for both oxidants, and quite variable. It is impossible to draw any conclusions on the basis of this data, except that conductive polymer coating on polypropylene was unsuccessful under these conditions. On polyester, the composite formed using anhydrous iron chloride had a higher resistance, while on wool it had lower resistance. In both cases the differences were not large. Analysis indicated they were statistically significant for polyester (one-tailed), but not for wool (see Appendix 4, 8.4.3). Overall, it appears that there is no advantage to the use of anhydrous iron (III) chloride, probably because the polymer deposition system presents numerous opportunities for the oxidant to become hydrated before polymerisation is complete.

Iron (III) chloride and iron (III) perchlorate (both hydrated) – in all cases the mass add-on was greater with perchlorate; especially so for wool. Again the surface resistance of polypropylene was variable, but lower for perchlorate. Similarly, the resistances of polyester and wool were an order of magnitude lower with perchlorate. This is consistent with the results shown in Table 8.11, and Section 8.3.

Iron (III) chloride and iron (III) nitrate (both hydrated) – mass add-on was similar for nitrate and chloride. The surface resistance of both polypropylene and polyester was lower with nitrate, but very much higher for wool. For the synthetics the same conclusions can be drawn as for perchlorate: namely that the oxidation conditions are stronger and the polymer is more fully doped. Also the larger nitrate ion may be less prone to loss during post-deposition rinsing than chloride. For wool, however, the performance of nitrate was much worse than chloride. It is difficult to see why this would be the case, but it highlights the capacity for the substrate to influence the electronic properties of the composite. The chemical complexity of the wool substrate must have a significant effect on the behaviour of the reagents. Perhaps the nitrate ions were more readily absorbed into wool than chloride ions, and subsequently there was an unavailability of dopant for incorporation into the polymer. This did not appear to be the case with perchlorate.

Iron (III) perchlorate and iron (III) nitrate – polymerisation using nitrate resulted in lower mass add-on than perchlorate for all substrates. The surface resistance was higher for all substrates with nitrate.

Overall, it seems that there is no advantage to using anhydrous iron (III) chloride in place of the hexahydrate. Exclusion of water from the system is impossible with the technique employed. Iron (III) perchlorate and iron (III) nitrate performed better than chloride, with the exception of nitrate on wool. Their bulky anions are presumably better trapped in the polymer during polymerisation than chloride. They are also stronger oxidisers than iron (III) chloride, so a more fully oxidised (doped) polymer probably eventuates. Nitrate did not perform quite as well as perchlorate, but has the advantage of being a less hazardous reagent to work with.

8.4.4 Summary and Conclusions.

The outstanding oxidant counter-ion is perchlorate. Iron (III) perchlorate produces textile-composites from poly(2,2'-bithiophene) and poly(EDOT) that have lower surface resistance than those produced using either iron (III) chloride (hydrated or anhydrous), *para*-toluenesulphonate or nitrate. Iron (III) nitrate also looks promising, as it was superior to iron (III) chloride, and would be safer to use then the perchlorate salt. *Para*-toluenesulphonate was disappointing, as it did not produce particularly low resistance or have the expected good durability. In fact perchlorate provided the most stable resistance over time, as well as being the most conductive. There was no advantage to the use of an anhydrous iron salt.

8.5 Effect of Solvent Used in Polymerisation Solution.

8.5.1 Background.

The solvent used in a single dip polymerisation system will have an influence on all three of the other components of the system. The interaction of solvent with the precursor, oxidant and substrate will almost certainly influence the ICP deposition process.

Perhaps the most complex interaction is that between the solvent and the oxidant. For any oxidant there will be a maximum solubility, which will differ from solvent to solvent. In Section 8.3 it was shown that with iron (III) chloride, the higher the oxidant concentration, the better the formation of ICP, and in most experimental work a concentration of 1 mol/L in methanol has been employed. This concentration of oxidant will not be possible in all solvents, in that the solubility of iron (III) chloride in most organic solvents will be less than that in methanol. In water or in mixed water-organic solvents it will probably be higher.

The exact nature of the oxidant-solvent system is complex. For water it is well understood, and there is taken to be complete dissociation of Fe^{3+} and Cl^{-}. However this is not the case for other (organic) solvents. Armes [3] recognised this issue also, and stated that "…iron (III) chloride is highly associated in non-aqueous media, and it is possible that the dissociative equilibria processes are such that the activity of the oxidant is reduced". The standard redox potential for $Fe^{3+} \rightarrow Fe^{2+}$ is 0.77 V [155], but this is for aqueous systems. Redox potentials in solvents other than water are not readily available, but given the less-dissociated nature of ionic salts in non-aqueous solvents, they are likely to be substantially lower. Therefore, more effective polymerisation should occur from water than from other solvents. The single dip system, however, works because polymerisation does not commence until the specimen has been removed from the polymerisation solution. This means that polymer formation is confined to fibre surfaces, rather than occurring in the polymerisation solution (which would result in amorphous polymer powder being produced). More powerful oxidant solutions (such as more strongly dissociated solutions) may trigger polymerisation in solution, to the detriment of subsequent surface-located polymerisation.

The solubility of the precursor also is an important factor in the polymerisation system. For the precursor to be evenly distributed throughout the porous textile substrate, it needs to be fully soluble in the solvent used for the polymerisation solution. While pyrrole is slightly soluble in water, both EDOT and bithiophene are unlikely to be at all soluble. EDOT (liquid at room temperature) can form a fine dispersion in water with vigorous agitation, but this would still result in a more uneven polymer coating than if it was soluble. Bithiophene (solid at room temperature) cannot be distributed onto the substrate from water by any means. In organic solvents, all of these precursors have good solubility, and in these systems they would be well distributed through the fabric specimen.

Another issue is the interaction of the solvent with the substrate. Some fibre types (notably wool and polypropylene) have surfaces that are very difficult to wet with water. If a droplet of water is placed on the surface of fabrics made from these fibres (with no other finishes present), it will not readily soak in or spread. In comparison, the water droplet would rapidly be absorbed on cotton. This behaviour translates into the situation where fabrics are immersed in water. Wool, for example, tends to be unevenly impregnated in aqueous solutions, in the absence of wetting agents. By contrast, all fibre types used in this work are readily impregnated with organic solvents. Thus it is likely that polymer coatings on many substrates will be more uniform from organic solvents than from water.

Finally, the rate of evaporation of the solvent will also have some influence on the polymerisation process. Very volatile solvents could allow polymerisation to occur rapidly, while less volatile solvents may encourage it to proceed more slowly. In several investigations [9,69,82], faster conditions of polymerisation (such as at elevated temperatures) resulted in a less conductive ICP being formed. A very slow polymerisation however, could be detrimental to the substrate through prolonged exposure to strongly oxidising conditions. This would be manifested as a degraded specimen, perhaps with substantial loss of mass. The reagents themselves could also deteriorate during the evaporation time, as they are exposed to ambient conditions during this period. Faster polymerisation would also be preferred for any commercial-scale process based on this technique.

8.5.2 Effect of Solvent for EDOT with Iron (III) Chloride.

In this experiment, the process of single-dip polymerisation was examined for polymerisation solutions differing only in the solvent used. Water, a range of organic solvents, and a mixed organic/water solution was employed.

8.5.2.1 Experimental Design and Methodology.

The polyester interlock fabric was selected for this work. Polymerisation solutions were prepared as described in Section 4.4.4, using an oxidant solution of 0.5 mol/L iron (III) chloride hexahydrate. The solvents in Table 8.14 were used. The boiling point data are given as an indication of the volatility of each solvent, and relative polarity as an indication of how dissociated iron (III) chloride may be in that solvent.

Table 8.14. Solvents used for single dip polymerisation.

ID #	Solvent	Formula	Boiling Point (°C) [155]	Relative Polarity [160]
1	Methanol	CH_3OH	64.5	0.762
2	Ethanol	CH_3CH_2OH	78.3	0.654
3	Propan-1-ol	$CH_3CH_2CH_2OH$	97.2	0.617
4	De-ionised water	H_2O	100	1
5	De-ionised water / methanol	---	---	---
6	Acetonitrile	CH_3CN	81.6	0.460

The oxidant concentration (lower than the optimum of 1 mol/L) was chosen to ensure that the oxidant was fully soluble in all solvents, and a fair comparison could be made between them. Methanol – widely used in this work – was compared with higher molecular weight alcohols with lower volatility. Acetonitrile was included as an alternative high-volatility solvent to methanol, and water was included for completeness. The mixed water/methanol solvent was chosen to overcome the insolubility of EDOT in water. Very volatile non-polar solvents such as acetone or di-ethyl ether were rejected, as iron (III) chloride is unlikely to be soluble in them to a sufficient degree (as discussed in Section 7.5).

Polymerisation was carried out as described in Section 4.4.4, with the solvent allowed to evaporate under a fume hood for 30 minutes, or until 10 minutes after the specimens had become uniformly dark, which ever was the longer time. The time taken for the specimen to become uniformly dark was recorded as an indication of the rate of polymerisation.

Polymerisation proceeded for each of the solvents as described below. Scanned images of the six specimens plus an untreated control are provided in Appendix 3 (8.5.2).

1. Methanol: The specimen was bright yellow on removal from the polymerisation solution. It became uniformly dark after approximately 15 minutes solvent evaporation, and was rinsed after 30 minutes. There was no loose polymer powder observed during rinsing or on the absorbent paper. After treatment the specimen was a uniform mid-blue colour.
2. Ethanol: As for methanol, except that the specimen became uniformly dark approximately 26 minutes after removal from the polymerisation solution. It was rinsed

after 36 minutes, and there was no loose polymer observed during rinsing or on the absorbent paper. The specimen appeared similar to the methanol specimen.

3. Propan-1-ol: As for methanol, except that the specimen became uniformly dark after approximately 55 minutes of solvent evaporation, and was rinsed after 65 minutes. The specimen was mid-blue with darker edges. No loose polymer was observed during rinsing, but a very small amount appeared to have come from the edges of the specimen after pressing against absorbent paper.
4. Water: EDOT was observed to be a fine dispersion (after agitation) in this solvent, whereas for all other solutions it was fully dissolved. The specimen was a bluish yellow on removal from the polymerisation solution, possibly indicating partial polymerisation during impregnation. The specimen was dry 120 minutes after removal from the solvent, but not uniformly dark. It did not change further after a further 30 minutes, so was rinsed after 150 minutes. The specimen was very pale blue with dark blue blotches. No loose polymer was observed during rinsing or on the absorbent paper.
5. Water/Methanol: As for water, except that the EDOT appeared to be dissolved in this solvent mixture. The specimen was pale yellow on removal from the polymerisation solution. It was rinsed after 150 minutes, but was not uniformly coloured at this time. No loose polymer was observed during the rinse or on the absorbent paper. The specimen was unevenly coloured, with small dark blue spots.
6. Acetonitrile: The specimen was dull yellow on removal from the polymerisation solution and darkened rapidly, becoming uniformly dark approximately 14 minutes after removal. It was rinsed after 30 minutes, and a small amount of loose polymer was observed on the absorbent paper, but none during rinsing. The specimen was dark blue with darker edges.

8.5.2.2 Results and Discussion.

The mass add-on and surface resistance for each of the specimens is presented in Table 8.15, with the standard deviation of surface resistance given in parentheses. As was the case in Section 8.3, it was possible to produce conductive specimens with this below-optimum oxidant concentration. The lowest resistance was from ethanol, followed by acetonitrile, with methanol and propan-1-ol approximately equal. This seems to imply that the slightly slower polymerisation time for ethanol encourages the formation of a more conductive polymer. The low resistance for acetonitrile is harder to explain, as the polymerisation was fast, and the oxidant would be expected to be highly associated in this relatively non-polar solvent. Perhaps the interaction with the textile substrate is improved with acetonitrile; observations from earlier experiments with the two-stage impregnation technique suggested that acetonitrile solutions were very readily absorbed into a textile substrate. The solubility of

EDOT is likely to be greater in acetonitrile than in the other solvents used here, so this may also lead to better impregnation of the precursor, and subsequently a better distribution of conductive poly(EDOT) through the substrate.

Table 8.15. Mass add-on and surface resistance – six polymerisation solvents.

Solvent	Mass add-on (%)	Surface resistance (Ω/square)
Methanol	0.64	23.8 (7.9) x 10^3
Ethanol	1.04	4.98 (1.13) x 10^3
Propan-1-ol	1.03	22.5 (6.6) x 10^3
De-ionised water	0.94	> 12.1 (10.1) x 10^9
De-ionised water / methanol	0.33	> 17.6 (6.9) x 10^9
Acetonitrile	1.10	5.37 (2.21) x 10^3

The slow polymerisation of EDOT from propan-1-ol probably compensated (to some extent) for the higher degree of association for the oxidant in this solvent. As a result, it had a surface resistance approximately equal to the more polar methanol (in which iron (III) chloride will be more dissociated), with its more rapid polymerisation. The poor solubility of EDOT in water probably contributed to the obvious unevenness of the polymer coating with this solvent, and the mixed solvent has not overcome this problem to any degree. EDOT may be present largely in the organic phase of this mixture, with iron (III) chloride present largely in the aqueous phase. In this situation, the interaction of precursor and oxidant would be poor and polymerisation hindered.

Given the particularly hazardous nature of acetonitrile, the best solvent appears to be ethanol. However, in a scaled up version of the process that would be used should this technique be commercially employed, the faster polymerisation rate from methanol may still be preferable. Iron (III) chloride will probably have a higher solubility in methanol, meaning that a similar level of resistance can be reached to that with ethanol, albeit with a greater concentration of oxidant.

8.5.3 Comparison of Methanol and Ethanol for EDOT with Three Iron (III) Salts and Three Substrates.

This work was essentially an extension of the previous section, bearing in mind the advantages of other iron (III) salts, particularly perchlorate and nitrate (Section 8.4). These salts were compared for three substrates (polypropylene, polyester and wool standard fabrics) using ethanol and methanol.

8.5.3.1 Experimental Design and Methodology.

Polymerisation conditions were the same as used in Section 8.5.2, except that the oxidant concentration was increased to 0.8 mol/L. This is the maximum concentration at which the three oxidants could all be prepared in the two solvents employed here, as it is close to the saturation concentration of iron (III) nitrate in methanol at room temperature. Specimen and polymerisation solution details are provided in Table 8.16.

Only six solutions were prepared (each of the oxidants in each of the solvents), with the three specimens treated successively in each solution. Results reported in Section 8.8.4 indicated that up to six specimens of this size could be treated in ~10 mL of polymerisation solution before any deterioration in the results was observed. To ensure that depletion of the solution would not be an issue, the wool specimens were always the last to be treated (they were also the most likely to be degraded by the oxidant and leave contaminants in the solution). The order of treatment was polypropylene, followed by polyester, then wool.

8.5.3.2 Results and Discussion.

Polymerisation proceeded as expected, with all of the specimens darkening rapidly. Specimens prepared using iron (III) perchlorate seemed to darken more rapidly that those prepared from iron (III) nitrate or chloride. The specimens, shown in Appendix 3 (8.5.3), were all dark to mid-grey blue after rinsing, and no loose polymer was observed in the rinse water, indicating that the polymer formed had good adhesion to the fibre surfaces. The image in Appendix 3 also shows specimens of P INT treated using iron (III) chloride (prepared at the same time for another purpose). Polymer mass add-on and composite surface resistance are provided in Table 8.16, with the standard deviation of the surface resistance in parentheses. Surface resistance is also presented graphically in Figure 8.9.

The influence of substrate and oxidant counter-ion has been assessed in detail elsewhere, and these results serve to confirm those previous results. The main interest is in the comparison of ethanol and methanol across this diverse range of substrates and oxidants. There was no clear effect on mass add-on, with seven of the nine substrate/oxidant combinations yielding higher mass add-on for methanol than for ethanol. Only for wool did one solvent (methanol) provide a higher mass add-on for all oxidants. However the differences were small.

Table 8.16. Mass add-on and surface resistance – two polymerisation solvents (three oxidants, three substrates).

Substrate	Oxidant	Solvent	Polymer mass add-on (%)	Surface resistance (Ω/square)
Polypropylene	$FeCl_3.6H_2O$	Methanol	0.63	1.94 (1.03) x 10^4
Polypropylene	$Fe(ClO_4)_3.xH_2O$	Methanol	0.81	1.14 (0.47) x 10^3
Polypropylene	$Fe(NO_3)_3.9H_2O$	Methanol	0.63	2.50 (0.73) x 10^3
Polyester	$FeCl_3.6H_2O$	Methanol	0.77	2.60 (071) x 10^3
Polyester	$Fe(ClO_4)_3.xH_2O$	Methanol	0.89	3.04 (0.54) x 10^3
Polyester	$Fe(NO_3)_3.9H_2O$	Methanol	0.81	5.53 (0.77) x 10^2
Wool	$FeCl_3.6H_2O$	Methanol	0.99	6.56 (3.36) x 10^3
Wool	$Fe(ClO_4)_3.xH_2O$	Methanol	1.84	1.22 (0.35) x 10^2
Wool	$Fe(NO_3)_3.9H_2O$	Methanol	1.10	7.01 (2.13) x 10^3
Polypropylene	$FeCl_3.6H_2O$	Ethanol	0.65	9.80 (4.97) x 10^4
Polypropylene	$Fe(ClO_4)_3.xH_2O$	Ethanol	0.74	5.18 (0.78) x 10^2
Polypropylene	$Fe(NO_3)_3.9H_2O$	Ethanol	0.59	3.37 (1.77) x 10^3
Polyester	$FeCl_3.6H_2O$	Ethanol	0.88	4.36 (1.45) x 10^3
Polyester	$Fe(ClO_4)_3.xH_2O$	Ethanol	0.96	2.48 (0.46) x 10^2
Polyester	$Fe(NO_3)_3.9H_2O$	Ethanol	0.67	4.53 (0.63) x 10^2
Wool	$FeCl_3.6H_2O$	Ethanol	0.59	1.83 (0.81) x 10^4
Wool	$Fe(ClO_4)_3.xH_2O$	Ethanol	1.26	9.98 (2.05) x 10^2
Wool	$Fe(NO_3)_3.9H_2O$	Ethanol	1.06	2.75 (0.32) x 10^2

At first glance, Figure 8.9 also seems to be devoid of any pattern. There did not appear to be any clear relationship between substrate and solvent providing the lowest resistance; polypropylene favoured methanol by two to one, while polyester and wool favoured ethanol by the same margin. However there are some interesting features when the results are observed in terms of oxidant. For iron (III) chloride, methanol yielded composites with lower resistance; a contrary result to that observed in the previous experiment. This may be explained by the higher concentration used here, in that it is likely that the better solubility of iron (III) chloride in methanol (as a more polar solvent than ethanol) became more advantageous as the oxidant concentration increased, with the better dissociation of the oxidant in the solvent outweighing the improvement caused by the reduced rate of polymerisation for ethanol.

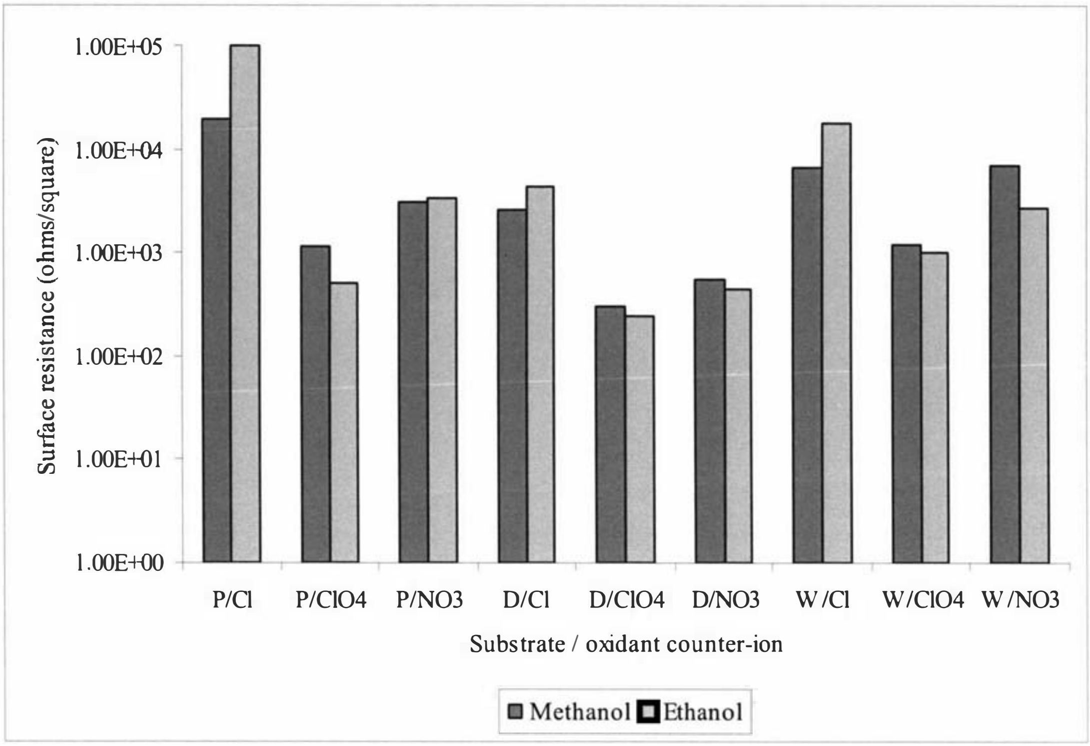


Figure 8.9. Surface resistance – two polymerisation solvents (three oxidants, three substrates).

With iron (III) perchlorate, ethanol yielded composites with lower resistance. This may have been because iron (III) perchlorate appeared to be more soluble than iron (III) chloride in all solvents used so far. There was good dissociation of the oxidant at this concentration in ethanol, so the slower evaporation of ethanol became an advantage in terms of creating a better-ordered deposition of poly(EDOT). For iron (III) nitrate there did not appear to be any advantage for either solvent; for two of the substrates, ethanol yielded composites with lower resistance, while for the other, methanol was favoured.

8.5.4 Summary and Conclusions.

An examination of six solvents indicated that ethanol and acetonitrile may perform better as solvents for the one-step ICP deposition method than methanol. This may in the case of ethanol be because the lower volatility of the solvent results in slower polymerisation, and hence a better-ordered polymer deposition, resulting in lower electrical resistance. The reasons for the superiority of acetonitrile are harder to explain. The oxidant (iron (III) chloride) should be less well dissociated in this solvent (because it is a less polar solvent), and polymerisation occurred rapidly because of the higher volatility. Yet the resistance was lower from acetonitrile than from methanol. Perhaps the better solubility of the precursor in acetonitrile (even though only a very low solubility is required) results in better penetration and distribution of the precursor through the textile substrate.

When alternative oxidants were used (iron (III) perchlorate and nitrate), and a direct comparison of methanol and ethanol was made at a higher (preferred) oxidant concentration, ethanol was not consistently superior. Note that the performance of iron (III) perchlorate in acetonitrile was not assessed for safety reasons, as acetonitrile is incompatible with strong oxidisers. With iron (III) perchlorate, ethanol yielded composites with lower surface resistance, while there was no clear difference for iron (III) nitrate. However, on this occasion with iron (III) chloride, methanol produced composites with a lower resistance, contrary to the results from the first experiment.

It seems likely that solvent behaviour varies in importance, depending on the oxidant and its concentration. A high oxidant concentration is generally preferred, and the more polar solvents generally allow a high concentration to be achieved. A slower evaporation may allow more ordered polymer deposition. Good solubility of the precursor in the solvent, and good penetration of the solvent into the substrate are also necessary. While ethanol or acetonitrile performed well at low oxidant concentrations with iron (III) chloride, at the preferred higher concentration, methanol was better with iron (III) chloride, and ethanol slightly better with iron (III) perchlorate. As methanol was used successfully throughout the work so far, it seemed sensible to continue with it, but to be aware that improvements may be possible with ethanol.

8.6 Effect of Additional Dopant.

8.6.1 Background.

In the work described so far in this chapter, the polymers produced have been doped with the oxidant counter-ion (for example, those prepared using iron (III) chloride are doped with chloride anions). Alternative counter-ions were studied in a previous section (8.4), including an aromatic dopant, *p*-toluenesulphonate, which did not appear to offer any advantages over the other simple ions being used. Nevertheless aromatic sulphonates are popular dopants for conductive polymers, with 1,5-naphthalenedisulphonate (NDS) in particular being preferred by a number of researchers [9,19,27]. No suitable metal salts of this anion are available to use as combined oxidant and dopant, so to dope with NDS it is necessary to add it to the polymerisation solution. NDS is available as a di-sodium salt or as 1,5-naphthalenedisulphonic acid (NDSA), also known as Armstrong's acid. Molecular structures of these compounds are shown in Figure 8.10. Both are solid at room temperature, and are white powders. They are very soluble in water, and sufficiently soluble in methanol to be used in this work.

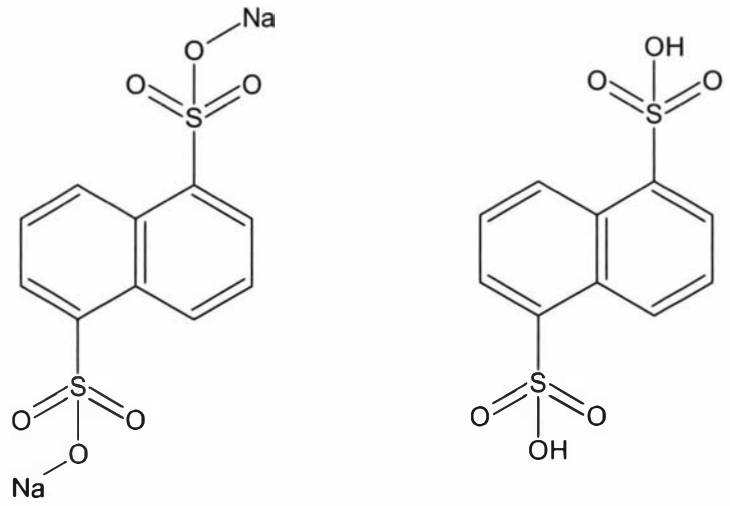


Figure 8.10. NDS (di-sodium salt, left) and NDSA (Armstrong's acid, right).

It is not certain the NDS anion will be incorporated into the polymer during polymerisation with this approach. It is likely that it will compete for incorporation into the polymer with the oxidant anion (chloride or perchlorate), and possible that the resultant polymer will be partially doped with chloride and partially doped with NDS. Unfortunately NDS does not contain any elements that are not also present in the two precursors used in this work: 3,4-ethylenedioxythiophene (EDOT) and 2,2'-bithiophene (BT). As a result, it would be difficult to use elemental analysis to determine exactly what form the doping is taking in the resultant polymer. However, any significant differences in behaviour between textile-ICP composites prepared with and without NDS would be indicative of a different doping configuration.

Various researchers have determined what the likely 'dopant-to-monomer ratio' is in the conductive polymer. For polypyrrole, a ratio of one dopant ion to four pyrrole rings was suggested by Armes [3], although more recently the accepted ratio seems to be one dopant ion to three pyrrole rings [68]. These ratios were taken into consideration in determining the range of dopant concentrations to employ here (ratios above and below 1:3). It is possible that a greater availability of dopant would be required in to achieve the 1:3 ratio in the polymer. A preliminary check was made that both forms of NDS used here were soluble in methanol, but one limitation may be their solubility in an oxidant solution that is already near-saturated $FeCl_3.6H_2O$ / CH_3OH.

8.6.2 Doping Poly(EDOT) and Poly(2,2'-Bithiophene) with the Di-Sodium Salt of NDS.

This approach was employed initially due to availability of di-sodium 1,5-naphthalenedisulphonate. Specimens prepared for 3,4-ethylenedioxythiophene and 2,2'-bithiophene using four different NDS levels were compared with one prepared with no NDS. The poly(EDOT) was prepared using iron (III) chloride hexahydrate as the oxidant, while poly(2,2'-bithiophene) was prepared using iron (III) perchlorate hydrate. Both oxidants were used at 1.0 mol/L concentration.

Table 8.17 details the precursor, oxidant and NDS combinations for each polymer solution. That the actual dopant concentration differs from the nominal concentration is of no real consequence, as the intention was simply to have specimens prepared across the range of concentrations. The mole ratio of NDS to precursor was calculated from the exact quantity of precursor in each solution and the actual mass of dopant added.

Five specimens of polyester interlock fabric were prepared for each precursor. They were treated as described in Section 4.4.4. The poly(EDOT) specimens were all uniformly coated and dark blue; the poly(2,2'-bithiophene) specimens were all uniformly coated and dark brown. Images of all specimens are shown in Appendix 3 (8.6.2). The surface resistance and mass add-on of these specimens is illustrated in Figures 8.11 and 8.12 respectively.

Table 8.17. Polymerisation solution details – di-sodium 1,5-naphthalenedisulphonate.

Specimen ID	Oxidant	Nominal NDS concentration (mol/L)	Actual NDS concentration (mol/L)	Mole ratio NDS : precursor
EDOT 1	$FeCl_3.6H_2O$	0	0	0
EDOT 2	$FeCl_3.6H_2O$	0.01	0.0083	1 : 2.54
EDOT 3	$FeCl_3.6H_2O$	0.05	0.0528	2.50 : 1
EDOT 4	$FeCl_3.6H_2O$	0.10	0.0860	4.07 : 1
EDOT 5	$FeCl_3.6H_2O$	0.20	0.1674	7.91 : 1
BT 1	$Fe(ClO_4)_3.H_2O$	0	0	0
BT 2	$Fe(ClO_4)_3.H_2O$	0.01	0.0105	1 : 4.02*
BT 3	$Fe(ClO_4)_3.H_2O$	0.05	0.0563	1.33 : 1*
BT 4	$Fe(ClO_4)_3.H_2O$	0.10	0.1040	2.46 : 1*
BT 5	$Fe(ClO_4)_3.H_2O$	0.20	0.2039	4.81 : 1*

* In the case of 2,2'-bithiophene, the ratio is calculated on the basis that the precursor is, strictly speaking, a dimer. Therefore the number of true (heterocyclic ring) precursor units is double the number of 2,2'-bithiophene units.

It is clear that the addition of NDS had no beneficial effect at these concentrations. In every case the surface resistance of the specimens with NDS present was higher, and the more NDS present, the higher the resistance. The mass add-on data followed no obvious trend, with the values all approximately the same. This suggests that, although the presence of NDS in the solution had some effect on the polymerisation process (as evidenced by the higher resistance), it was probably not incorporated into the polymer.

It is possible to estimate the increase in mass add-on that would occur if NDS was replacing chloride as the dopant species. Taking the accepted dopant-to-heterocycle ratio as being 1:3, the molecular weight of a 'three heterocycles, one dopant anion' system can be calculated. For EDOT doped with chloride this is $[3 \times M_w(EDOT)] + [1 \times M_w(Cl^-)] \approx 461$. In comparison, for EDOT doped with NDS this is $[3 \times M_w(EDOT)] + [1 \times M_w(NDS)] \approx 715$. The latter is 55% greater than the former, so we can expect that fully doped EDOT/NDS will have a mass add-on approximately 55% greater than that of fully doped EDOT/chloride. Even taking into account the potentially large error in mass add-on (up to 10%) it would be obvious if a mass add-on change of this magnitude had occurred. Clearly it has not.

The dopant used here was the di-sodium salt of NDS. This means that not only were NDS anions added to the polymerisation solution, but also sodium cations. It is possible that these interfered in some way with the polymerisation process. It is also possible (and probably quite likely), that the di-sodium salt of NDS is poorly dissociated in methanol, and the effective availability of NDS was very low. However the maximum concentrations available in this trial were far in excess of the optimum ratio of dopant to heterocycle, so there should still have been sufficient NDS available to have some beneficial effect, if one was possible.

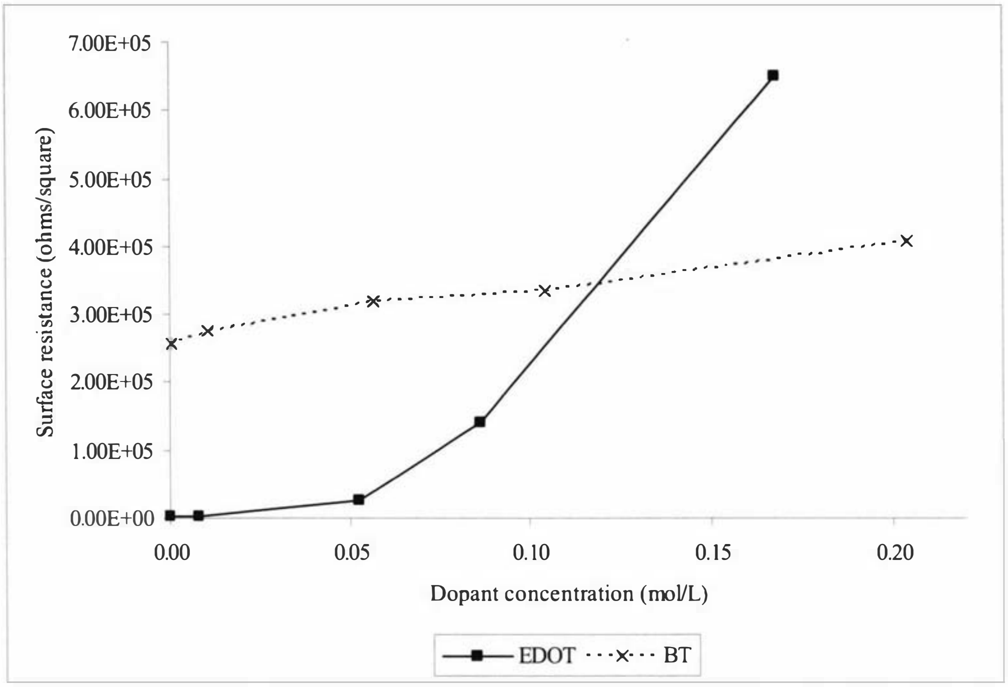


Figure 8.11. Surface resistance – additional dopant (di-sodium NDS, two precursors).

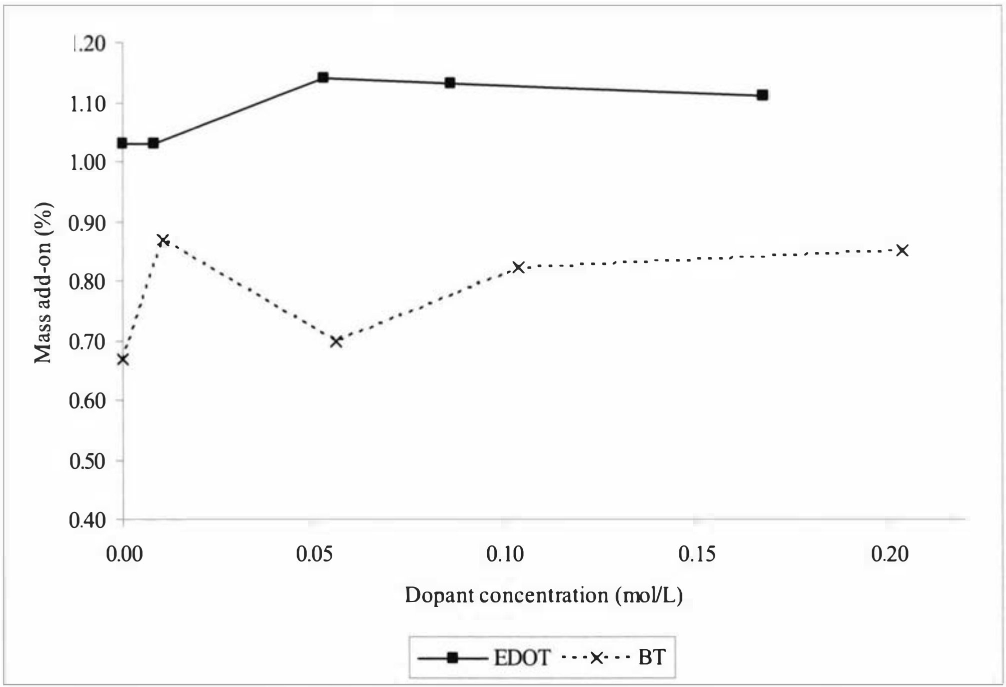


Figure 8.12. Mass add-on – additional dopant (di-sodium NDS, two precursors).

The intention was to examine ratios smaller than 1:3, but imprecision in the experimental design has meant that none of the poly(EDOT) specimens were prepared at less than 1:3, and only one of the poly(2,2'-bithiophene) specimens. Hence, this experiment failed to examine the behaviour at low dopant-to-precursor ratios.

8.6.3 Doping Poly(EDOT) with NDSA (Armstrong's Acid).

To address the concerns raised in the previous experiment, a second series of polymerisations were carried out using the acid form of NDS. The sodium cations were thereby eliminated from the polymerisation system. More care was taken to ensure that very low precursor-to-dopant ratios were studied. 2,2'-Bithiophene was excluded to reduce the number of specimens being treated, and because poly(EDOT) composites were of more interest. A total of 12 specimens of the polyester interlock fabric were prepared and treated in exactly the same way as those in the previous section. Reagent concentrations and ratios are provided in Table 8.18.

Table 8.18. Polymerisation solution details –1,5-naphthalenedisulphonic acid.

Specimen ID	Nominal NDS concentration (mol/L)	Actual NDS concentration (mol/L)	Mole ratio NDS : precursor
1	0	0	0
2	0.00140	0.00140	1 : 15.04
3	0.00281	0.00286	1 : 7.40
4	0.00351	0.00384	1 : 5.48
5	0.00422	0.00422	1 : 4.99
6	0.00562	0.00560	1 : 3.76
7	0.00703	0.00726	1 : 2.91
8	0.00703	0.00751	1 : 2.81
9	0.01406	0.01449	1 : 1.46
10	0.0211	0.0218	1 : 0.96
11	0.0422	0.0373	1.78 : 1
12	0.1055	0.1050	5.00 : 1

Polymerisation solutions were prepared using iron (III) chloride hexahydrate in methanol. Dopant concentrations and ratios are provided in Table 8.18. The difference (sometimes quite large) between the nominal and actual NDS concentrations is immaterial; what was important was to have a good range of values, particularly at low concentrations (ratios lower than 1:1).

Polymerisation was carried out as described in Section 4.4.4. All of the specimens were uniformly coated and dark grey-blue, and images of them can be found in Appendix 3 (8.6.3).

Figure 8.13 illustrates the effect of the dopant-to-precursor ratio on the polymer mass add-on and the composite surface resistance. Over the full range of dopant ratios, it appeared that the more NDS present, the higher the surface resistance. However, when the low ratios are examined more closely no pattern at all is present, with the surface resistance oscillating over a small range as the dopant ratio increases to ~1:3. These fluctuations were probably within the experimental error of the surface resistance of each specimen. An analysis of variance (ANOVA) across the eight lowest ratios (including no additional dopant) indicated no significant differences between these values. This ANOVA is summarised in Table 8.19. The F-statistic is less than the critical value (F_{CRIT}), so the null hypothesis (that the differences observed are the result of random error) cannot be rejected.

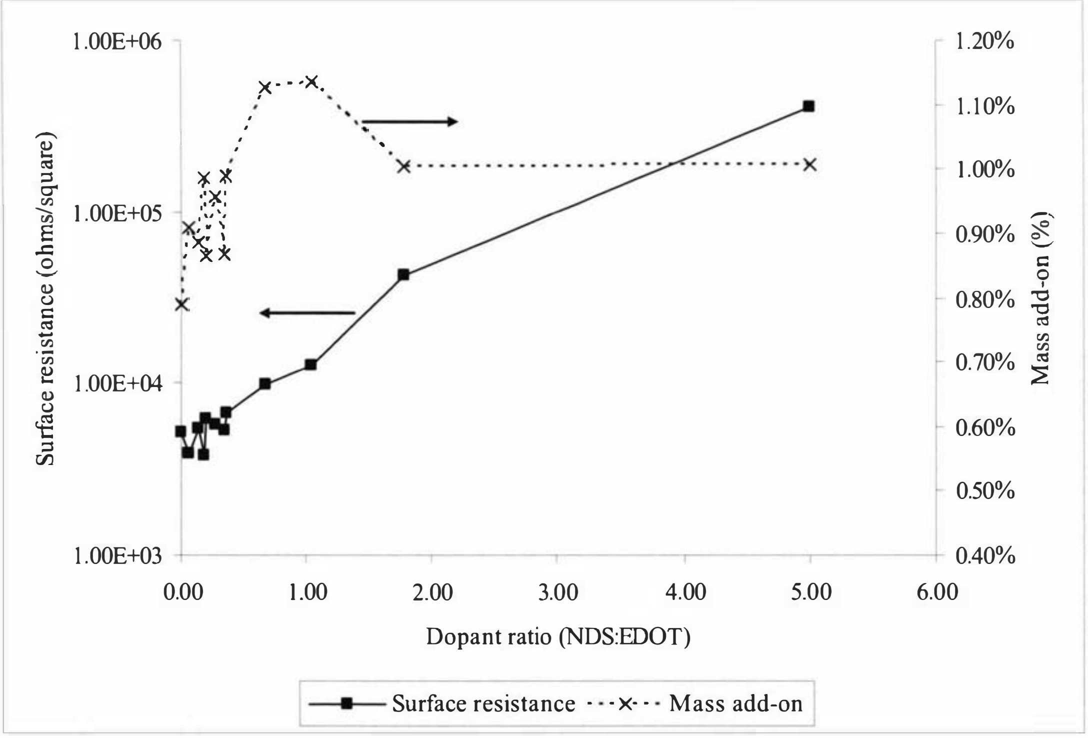


Figure 8.13. Surface resistance and mass add-on – additional dopant (NDSA).

Figure 8.13 indicates that the mass add-on also showed no clear relationship to dopant ratio at low ratios, although there was perhaps a higher mass add-on at some higher ratios. This may be due to a contribution from the dopant replacement phenomenon postulated in Section 8.6.2, whereby chloride anions are replaced in the polymer by heavier NDS anions. As previously, the increase in mass add-on was insufficient to confirm this.

Table 8.19. ANOVA for surface resistance of specimens prepared with dopant ratios < 1:3 (1% significance level).

Data Summary				
Ratio (NDS:EDOT)	Data count	Sum	Average (Ω/square)	Variance (Ω/square) ^{2}
0	16	82240	5140	4449187
1 : 15.04	8	31560	3945	537228
1 : 7.40	8	43840	5480	3194943
1 : 5.48	8	30390	3799	198869
1 : 4.99	8	49070	6134	3772427
1 : 3.76	8	46360	5795	5090829
1 : 2.91	8	42890	5361	630898
1 : 2.81	8	52930	6616	5311741

ANOVA						
Source of variation	Sum of squares	Degrees of freedom	Mean squares	F statistic	P-value	F_{CRIT}
Between ratios	5.47×10^7	7	7.82×10^6	2.528	0.02321	2.932
Within ratios	1.98×10^8	64	3.09×10^6			
Total	2.53×10^8	71				

8.6.4 Summary and Conclusions.

There was no advantage in providing additional aromatic sulphonate ions to the polymerisation solution. The substantial reduction in surface resistance reported for other techniques when NDSA or other aromatic sulphonic acids (or sulphonate ions) are used was not replicated here. There was in fact either no effect, or an increase in surface resistance, regardless of whether the di-sodium salt was used or the acid form.

Mass add-on values suggest that very little NDS was incorporated into the ICP in place of chloride. When NDS was present, the mass add-on tended to be only very slightly greater (if at all), and calculations indicate that, with complete replacement of chloride with NDS, the mass add-on should increase by 55%. Thus the conclusion is that little or no NDS is able to be incorporated into the polymer during polymerisation, and its presence may interfere with the polymerisation reaction to the detriment of the conductivity of the resultant composite.

8.7 Effect of Substrate Fibre Type.

8.7.1 Background.

The deposition of a conductive polymer onto a solid substrate is very likely to be influenced by the chemical and physical properties of the substrate surface. The interaction of the initial reagents (oxidant, precursor, solvent, and additional dopant if present) with the surface will be important, as will the interaction of intermediate polymerisation species (such as oligomers) and reaction by-products (such as the reduced form of the oxidant cation). Adsorption onto the surface and absorption into the fibres can occur, and will influence the reaction itself as well as the extent to which polymer is formed inside the fibre. Some aspects of the influence of fibre type are dealt with elsewhere, such as the ageing behaviour on different substrates (Section 8.11, although this is also described in this section) and the extent of polymerisation (assessed by light and transmission electron microscopy in Section 8.12). The work described in this section relates to the polymerisation behaviour and electronic properties of textile-ICP composites, prepared on various substrate fibre types using 3,4-ethylenedioxythiophene (EDOT), 2,2'-bithiophene and pyrrole precursors. The morphology of the fibres (before and after polymer deposition) was also examined using scanning electron microscopy (SEM).

In order to assess the effect of fibre type alone (essentially assessing the influence of the polymer that makes up the fibre), it is necessary to use substrates that are as similar in physical size and shape as possible. They must all have the same fibre diameter, yarn linear density and fabric structure. This is a very difficult set of criteria to meet (as discussed in Section 4.2), but the set of standard fabrics that has been sourced does overcome most of these issues, and allows a direct comparison of fibre type.

8.7.2 Preparation of Specimens and Experimental Design.

All seven standard fabrics were initially used for this work, and were treated as described in Section 4.4.4. Each solution was prepared immediately before use, to minimise the extent to which polymerisation might occur in the solution before impregnation onto the specimen. This is especially important for pyrrole, as its higher reactivity makes it liable to polymerise rapidly in solution. A preliminary experiment where the pyrrole solutions were all prepared at one time was unsatisfactory, as, even though they were used within 10 minutes of preparation, polymer deposition from the later treatments was clearly inferior, and polypyrrole particles could be seen in solution.

The glass fibre fabric was used for the EDOT and bithiophene treatments, but was excluded from the pyrrole treatment (the latter was carried out in a later experiment, by which time glass had been excluded from the experimental work because it was difficult to handle, and was too different in structure from the other standard fabrics to allow a valid comparison).

8.7.3 Results and Discussion.

Polymer deposition proceeded as expected for the EDOT set, with even and fairly rapid darkening of the specimens. The exception was the nylon fabric (specimen N), which (as can be seen from the images in Appendix 3, 8.7.3) was unevenly coated. This specimen was also much slower to darken (taking more than 60 minutes), whereas the other specimens were complete after 40 minutes. The polymer loading on the glass fabric (specimen G) appeared lower than that on the others (with the exception of N), with a paler grey-blue colour apparent.

The bithiophene set showed more variation between the different fibre types. Polypropylene (P), polyester (D) acrylic (O) and cotton (C) were all evenly coloured a dark reddish brown. The wool and glass fabrics were a brighter red-brown colour but still evenly coated, whereas nylon (N) was (as for EDOT) unevenly coated and pale. Darkening of the specimens was slower for the bithiophene specimens than for the EDOT specimens. Images of the rinsed and dried specimens are also provided in Appendix 3 (8.7.3).

The pyrrole set of specimens were all evenly coated, but with nylon (N) the darkest. It was a dark grey colour (as is expected for polypyrrole) while the others were mid-grey. It is likely that the deposition of polypyrrole onto nylon was heavier than onto the other substrates (which appears to be the opposite of the case for the thiophene-variants). The polymer formation appeared to proceed slightly faster than for EDOT (all complete within 30 minutes). The specimens are shown in Appendix 3 (8.7.3).

The polymer mass add-on and composite surface resistance are provided in Table 8.20 (standard deviation of surface resistance given in parentheses). These results are perhaps more easily interpreted in graphical form. The mass add-on data are presented in Figure 8.14. EDOT and pyrrole surface resistance results are shown in Figure 8.15, with the bithiophene results excluded (for obvious reasons) and the pyrrole/cotton specimen given a nominal value of 40 M Ω. The results for the glass specimen (G) were also not included, as this result was not available for pyrrole.

Table 8.20. Mass add-on and surface resistance – seven fibre types (three precursors).

Substrate	ICP precursor	Mass add-on (%)	Surface resistance (Ω/square)
Nylon	EDOT	1.24	138.2 (292.2) x 10^3
Polypropylene	EDOT	0.67	33.47 (38.02) x 10^3
Polyester	EDOT	0.70	2.512 (0.369) x 10^3
Acrylic	EDOT	0.70	5.788 (2.037) x 10^3
Wool	EDOT	0.13	11.18 (6.87) x 10^3
Cotton	EDOT	0.00	847.3 (559.9) x 10^3
Glass	EDOT	-0.28	127.0 (146.6) x 10^3
Nylon	Bithiophene	0.83	> 40 x 10^6
Polypropylene	Bithiophene	0.25	> 40 x 10^6
Polyester	Bithiophene	0.26	> 40 x 10^6
Acrylic	Bithiophene	0.28	> 40 x 10^6
Wool	Bithiophene	-0.08	> 40 x 10^6
Cotton	Bithiophene	-0.41	> 40 x 10^6
Glass	Bithiophene	-0.25	> 40 x 10^6
Nylon	Pyrrole	2.33	0.9461 (0.2457) x 10^3
Polypropylene	Pyrrole	0.35	31.14 (14.30) x 10^3
Polyester	Pyrrole	0.26	2.961 (0.561) x 10^3
Acrylic	Pyrrole	0.40	45.96 (9.34) x 10^3
Wool	Pyrrole	0.34	565.6 (254.7) x 10^3
Cotton	Pyrrole	-0.14	> 40 x 10^6

Note: Where the result '> 40 x 10^6' is given, it indicates that the resistance measured exceeded the maximum measurable with the ohmmeter used.

Despite the apparent unevenness of the ICP deposition on nylon, the highest mass add-on for all three precursors occurred on this substrate. However, this only corresponded to the lowest surface resistance with pyrrole. For EDOT, the surface resistance of the nylon specimen was the second highest. The mass add-on for the three other synthetic fibres showed similar behaviour for each of the precursors, with EDOT the highest (at ~0.70%), followed by pyrrole (at ~0.35%), and bithiophene having the lowest add-on (~0.25%). The lowest mass add-on was always on cotton, which for bithiophene and pyrrole was actually a mass loss. This suggests that the amount of ICP deposited is less than the mass lost by degradation of the substrate in the polymerisation solution. To investigate this further, 'blank' treatments were carried out. This work is described in Section 8.7.4.

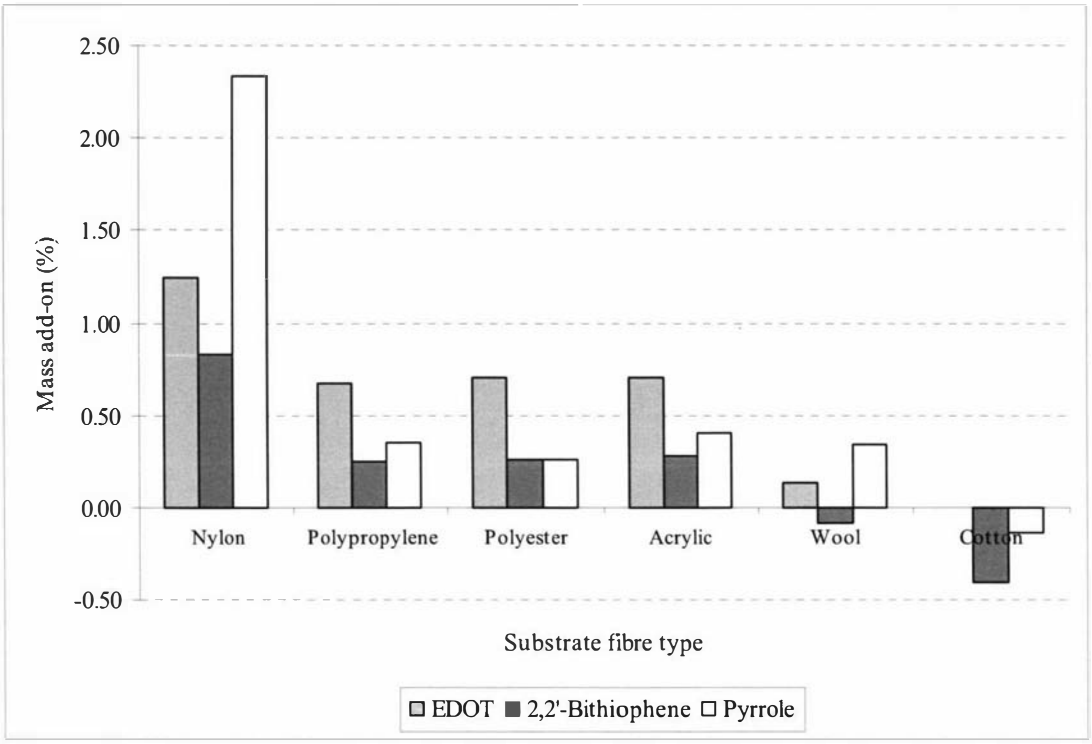


Figure 8.14. Mass add-on – six fibre types (three precursors).

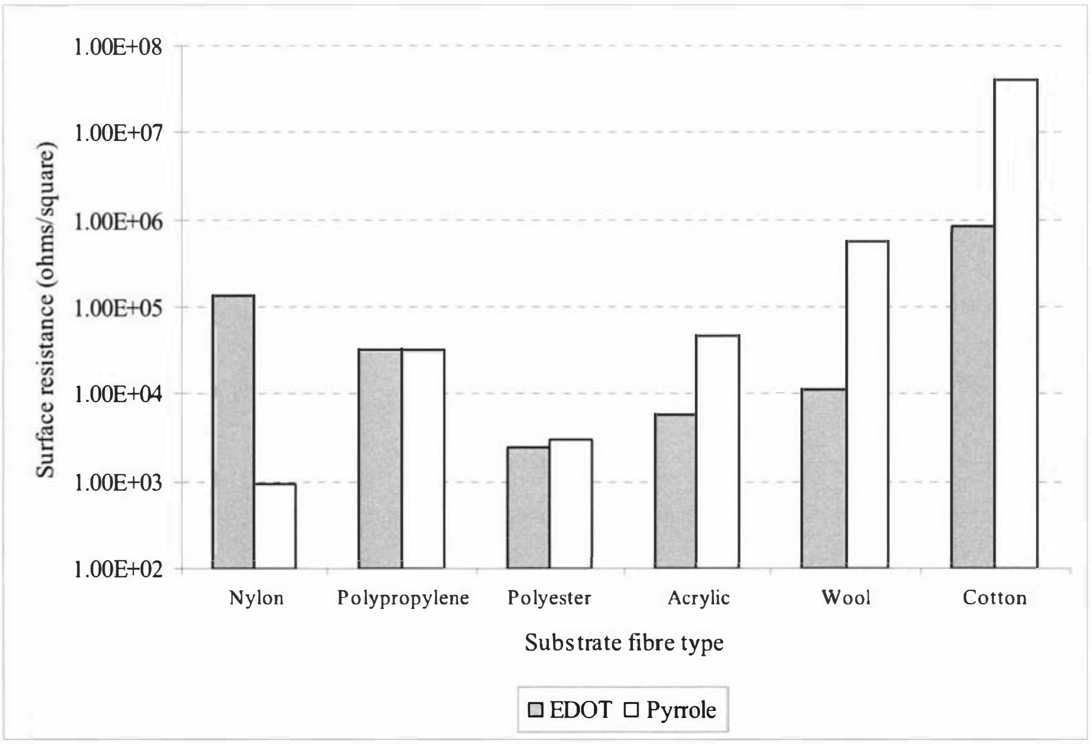


Figure 8.15. Surface resistance – six fibre types (two precursors).

It is also useful to assess these results by looking at the order of the substrates from lowest mass add-on to highest, and from highest resistance to lowest:

Mass add-on	Lowest	→				Highest
EDOT	C	W	P	D	O	N
Bithiophene	C	W	P	D	O	N
Pyrrole	C	D	W	P	O	N

Similarly, the same approach can be used for surface resistance (in this case ranked from highest to lowest):

Surface resistance	Highest	→				Lowest
EDOT	C	N	P	W	O	D
Pyrrole	C	W	O	P	D	N

Overall the mass add-on rankings are quite similar for all three precursors, with the EDOT and bithiophene rankings identical. This suggests that the interaction between polymerisation species and substrate is very similar for the two thiophenes. The pyrrole ranking is the same at the extremes (cotton, acrylic and nylon), but slightly different for wool, polyester and polypropylene.

Resistance may be considered an indicator of the 'quality' of the ICP that has been deposited, while mass add-on is obviously the 'quantity'. Surface resistance might be influenced by adsorption of polymerisation reagents onto the surface of the fibre, and by the chemical structure of the substrate fibre type acting as a template of sorts for ICP formation. The precursors are based on a heterocyclic ring, but pyrrole has a slightly hydrophilic group (-NH) while EDOT does not. There is also an obvious difference in size of the two molecules.

Considering each of the fibre types in turn:

Cotton: For both precursors the resistance was very high, which is likely to be due to the very low polymer mass add-on. While cotton is very absorbent, this has not resulted in a low surface resistance. Perhaps this is because the limited amount of polymer that is formed may be inside the fibre, and therefore, not contributing to surface conductivity

Wool: There were very different resistance values for the two precursors on wool; a high resistance for pyrrole, quite low for EDOT. The surface of the wool fibre is hydrophobic (as compared to its internal hydrophilic structure), so it is possible that the polar –NH group on pyrrole caused it to migrate into the fibre (resulting in high surface resistance), while the non-polar nature of EDOT kept it on the surface of the fibre (resulting in low surface resistance).

Polypropylene: The resistance values measured for pyrrole and EDOT on this relatively chemically-inert substrate were almost identical, and their ranking also very similar. Polymerisation was probably confined to the surface of the fibres (the fibre is very crystalline, due to its highly ordered nature).

Acrylic: This can probably be considered in the same way as polypropylene, in that the structure is highly crystalline. However some hydrogen bonding is present between the triple-bonded nitrogen and hydrogen atoms on adjacent chains, which implies that a limited absorption of pyrrole into the structure may occur, which in turn may explain the higher resistance for this precursor (that is, less ICP formation on surface).

Nylon: This moderately absorbent fibre had the highest mass add-on for both precursors, suggesting that the precursors were readily taken up by the substrate. However the surface resistance for EDOT was very high, suggesting that polymer formation was of poor quality, or occurred inside the fibre.

Polyester: This is the only substrate with aromatic groups (apart from a small proportion of the amino acid residues in wool). Thus we can expect that aromatic group interaction could be important, perhaps resulting in better orientation of the ICP (the existing aromatic chain structure acting as a template). For both substrates this hypothesis was supported by a low resistance at low mass add-on, implying that the quality of ICP formed on polyester was better than on the other substrates.

Overall, it was apparent that polyester was the best substrate for conductive polymer formation, with a low mass add-on and low surface resistance. Nylon provided a good substrate for polypyrrole, but with a higher mass add-on. Acrylic and wool were also good substrates for poly(EDOT). Cotton was a poor substrate for the formation of either of the conductive polymers assessed here.

SEM images were obtained for the poly(EDOT)-coated substrates. These (provided in Figures 8.16 to 8.20) indicate that the surface of the fibres was largely unchanged by deposition of the ICP, with the morphological features of the untreated specimens (shown in Section 4.2) clearly apparent here. The coating appeared to be mostly smooth and uniform on the fibre surfaces, except for a small number of loose particles, most apparent on wool. These could be scale fragments, rather than ICP.

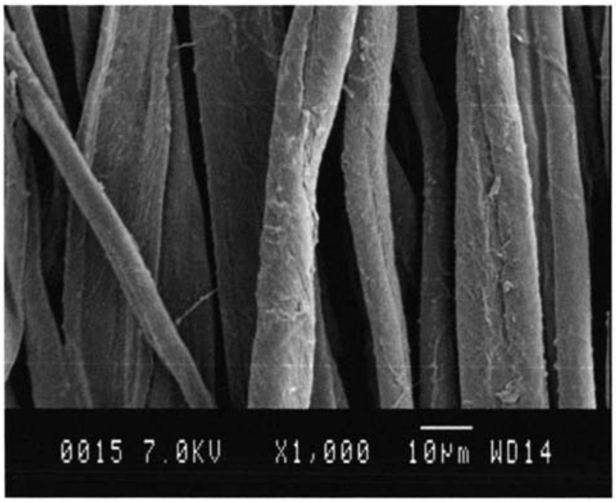


Figure 8.16. SEM: cotton-poly(EDOT) composite.

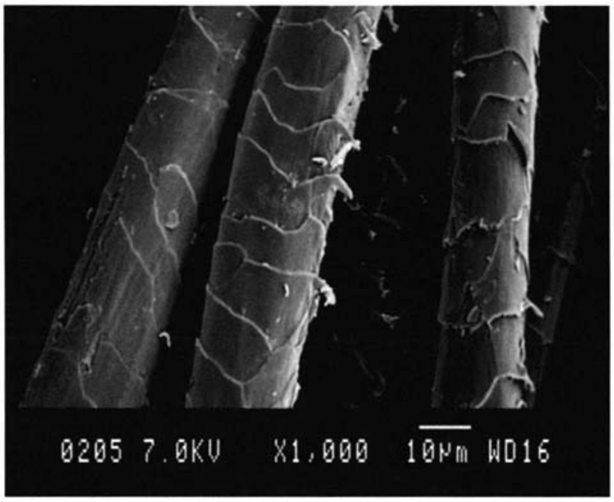


Figure 8.17. SEM: wool-poly(EDOT) composite.

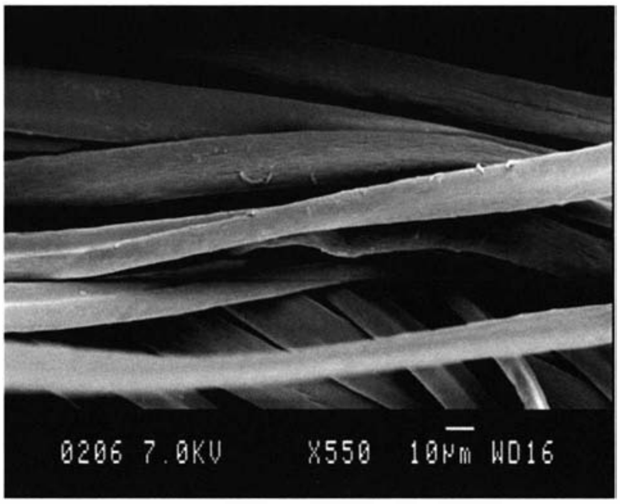


Figure 8.18. SEM: acrylic-poly(EDOT) composite.

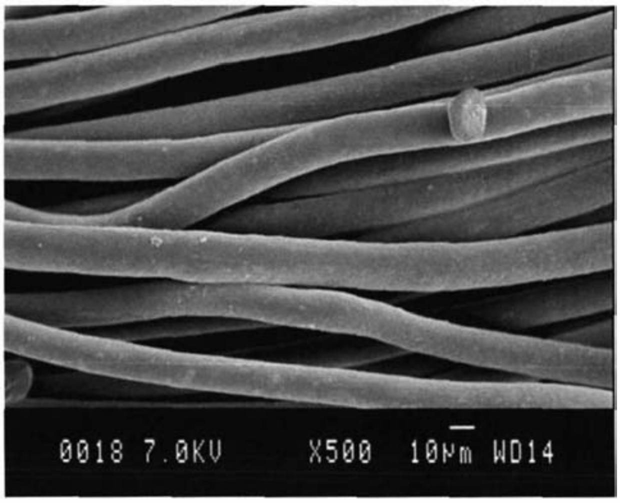


Figure 8.19. SEM: nylon-poly(EDOT) composite.

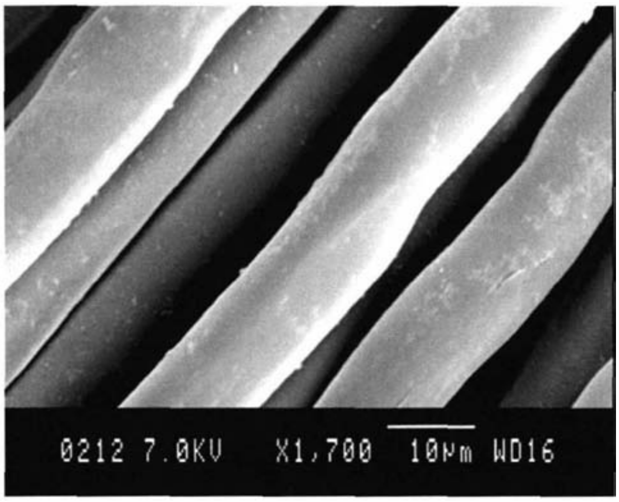


Figure 8.20. SEM: polyester-poly(EDOT) composite.

8.7.4 Ageing Behaviour.

The ageing behaviour of three of the poly(EDOT) composites prepared in this experiment was assessed by periodically re-measuring their surface resistance over a period of several months. During this time they were kept in a standard conditioned room (65% relative humidity and 20°C). The three with the lowest resistance were selected; they also represent a diversity of fibre types. They started at different resistance levels, so these measurements were converted into relative resistance (R′) values by dividing the resistance at each stage by that specimen's initial resistance. The progression of R′ over a six month period is illustrated in Figure 8.21.

The relatively poor ageing behaviour of acrylic is obvious (R′ increased by a factor of approximately nine after six months), as is the very good performance of wool (R′ largely unchanged after six months). It is surprising that fibre type should have such a great influence on the durability of the conductive poly(EDOT) deposited onto the fibre, and it must be concluded that either the type of poly(EDOT) formed on wool and polyester was more resistant to ageing than that formed on acrylic, or the fibre itself influenced the ageing behaviour. With regard to the former, it is possible that the aromatic groups on the polyester provide a template for poly(EDOT) formation, leading to a structure that was better ordered with better incorporation of dopant anions. With the regard to the latter, it may have been that the absorbent wool fibres acted as a 'reservoir' for excess dopant, which was taken up during polymerisation. It may then have migrated outwards into the poly(EDOT) coating as dopant was lost, thus maintaining conductivity. Neither of these explanations is wholly satisfactory, but investigations into the influence of fibre type are rare in the literature, and it is clearly an important parameter to take into account when developing this type of composite material.

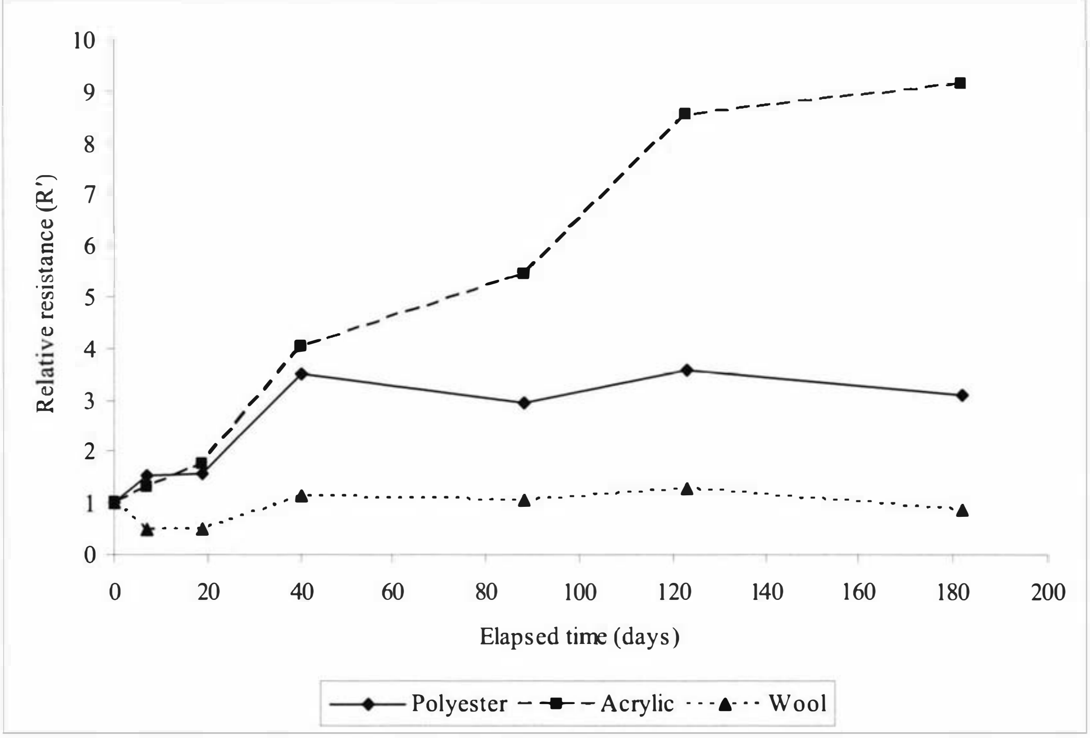


Figure 8.21. Progression of R′ with ageing of specimens with different fibre types.

8.7.5 Blank Treatments.

The possible reduction in specimen mass during treatment raises doubts about the exact polymer mass add-on that occurs (in addition to the measurement error inherent in the system, as discussed in Section 4.3.1). Mass reduction could be due to fibre loss from the cut ends of yarns (loss of entire yarns is prevented by the removal of edge yarns), and/or degradation by chemicals in the polymerisation solution. The oxidant is perhaps most likely to be responsible for the latter.

A series of three 'blank treatments' was carried out to investigate this:

a. Polymerisation solution prepared with oxidant only (no ICP precursor).
b. Polymerisation solution prepared with ICP precursor only (no oxidant).
c. Solvent only with no oxidant or ICP precursor.

Two specimens of six of the standard fabrics (N, P, D, O, W, C) were given blank treatments in 10 mL solutions, proceeding as normal. The solvent used was methanol, with iron (III) chloride hexahydrate as the oxidant (at a concentration of 1 mol/L) and EDOT as the precursor (at 0.03 g/10 mL). While the mass add-on is of most interest, the surface resistance was also measured to ensure that the conductivity observed elsewhere is provided by the deposited ICP and not by absorbed polymerisation chemicals. These results are provided in Table 8.21.

Table 8.21. Mass add-on and surface resistance – blank treatments.

Substrate	Solvent only		Oxidant only		Precursor only	
	Mass add-on (%)	Surface resistance*	Mass add-on (%)	Surface resistance	Mass add-on (%)	Surface resistance
Nylon	-0.04	N-M	1.30	N-M	-0.06	N-M
Polypropylene	-0.05	N-M	0.06	N-M	-0.06	N-M
Polyester	-0.08	N-M	-0.11	N-M	-0.13	N-M
Acrylic	-0.09	N-M	0.02	N-M	-0.07	N-M
Wool	-0.35	N-M	0.00	N-M	-0.46	N-M
Cotton	-0.24	N-M	0.00	763 M Ω	-0.31	N-M

* Note: 'N-M' indicates that there was no measurable electrical resistance (that is, it was in excess of 2.00×10^{10} Ω/square).

Solvent only: In all cases, the measured surface resistance was in excess of that measurable with the ohmmeter being used for this work. For the four synthetic fibres, the mass change was a very small reduction, while a slightly larger mass loss was apparent for the two natural fibres. This is most likely due to fibre loss from cut ends of yarn. The resilient ('springy') nature of wool fibres probably resulted in the cut yarn ends opening out, with fibres escaping more easily. The fineness and relatively short length of cotton may have contributed to it losing more fibre than the synthetic fibres. The appearance of the specimens was unchanged.

Oxidant only: One interesting feature of these results is the measurable resistance of cotton (although very high, being nearly 1 GΩ). It was observed that many of the specimens were permanently stained yellow after this blank treatment (images are provided in Appendix 3, 8.7.5). The high mass add-on of the nylon was manifested in its bright yellow colour, indicating a large amount of absorbed oxidant. The others had very low mass add-on, regardless of their colour. For the synthetics this was very pale, so oxidant absorption was very low, and the mass add-on was essentially the same as that for solvent only. For the two natural fibres the colour was somewhat darker, but with zero mass change. As the 'solvent only' results indicated mass loss, it is likely that oxidant was absorbed to reasonably high levels (perhaps ~0.3 – 0.4%).

The wool specimen's resistance exceeded measurable levels, but in cotton the absorbed iron (III) chloride provided a level of conductivity; perhaps with absorbed moisture assisting in this phenomenon. Both cotton and wool are hygroscopic fibres, with approximately 8 and 13% water present in their molecular structure at 65% relative humidity. The water may interact with an absorbed ionic salt (such as iron (III) chloride) in such a way as to provide ionic conduction in the fibre, although at a very low level. This was only observed for cotton, so there are probably other fibre-specific factors that are also influencing the electrical resistance.

Precursor only: These results are very similar to those for 'solvent only', suggesting that mass change phenomena that applied in that case were the only factors applying here. None of the precursors, if absorbed, are likely to provide a mechanism for electrical conductivity, and this is reflected in the fact that all resistances exceed measurable levels.

Overall, it appeared that the action of the solvent alone was to remove a small percentage of the mass of the specimen; less than 0.1% for synthetic fibres, and less 0.5% for natural fibres. The action of the oxidant in changing mass was negligible, except for nylon, where a substantial mass increase occurred. These amounts suggest that, for the synthetic fibres other than nylon, the mass add-on results obtained in the various experiments reported in this work are a good indication of reality, whereas the true polymer mass add-on for cotton and wool is probably slightly higher than that measured.

8.8 Effect of Process Variables.

8.8.1 Background.

The so-called 'process variables', are a series of miscellaneous parameters related to the polymerisation process, not to the chemical reagents used. They are parameters that would be of particular interest if the process were scaled up, but also potentially reveal information about the polymerisation process and the chemical reactions that occur.

8.8.2 Solution Impregnation Time.

This refers to the length of time that the specimens spend in the polymerisation solution before removal and solvent evaporation. It was investigated for three substrates, as different fibre types will have different absorption properties, and the effect of the time spent in the polymerisation solution may vary. The substrates were three of the standard woven fabrics; polypropylene (P), polyester (D) and wool (W), providing a full range of likely behaviour. Polypropylene is a non-absorbent fibre, polyester slightly absorbent and wool very absorbent.

Three specimens were prepared in the usual way from each fabric. Polymerisation was carried out as described in Section 4.4.4, with each specimen placed in the solution for 10 seconds, four minutes or 60 minutes. Each 10 second solution was agitated for the full length of the impregnation time, each four minute solution was agitated for 10 seconds every minute, and the 60 minute solutions were agitated for 10 seconds every 15 minutes. The treated specimens are shown in Appendix 3 (8.8.2), and although the images don't show a marked colour difference between the specimens, the wool specimen that had been impregnated for 60 minutes was noticeably darker than the other two wool specimens. It also had a slightly yellowish tint. The polymer mass add-on and composite surface resistance are provided in Table 8.22 (standard deviation of surface resistance given in parentheses).

These data are more clearly interpreted when graphed, as shown in Figures 8.22 and 8.23. Mass add-on was virtually unchanged across the three impregnation times for the two synthetic fabrics. However, for wool there was a small mass loss with only ten seconds impregnation, a moderate increase with four minutes, and large increase with 60 minutes. The implication is that with longer impregnation there was more absorption of reagents into wool, and hence more polymer deposited. There was no additional absorption at longer times with the two synthetics.

Table 8.22. Mass add-on and surface resistance – impregnation time.

Substrate	Impregnation time	Mass add-on (%)	Surface resistance (Ω/square)
Polypropylene	10 seconds	0.73	$5.833\ (2.758) \times 10^3$
Polypropylene	4 minutes	0.95	$7.714\ (4.035) \times 10^3$
Polypropylene	60 minutes	0.74	$5.495\ (2.093) \times 10^3$
Polyester	10 seconds	0.82	$1.390\ (0.387) \times 10^3$
Polyester	4 minutes	1.02	$1.230\ (0.205) \times 10^3$
Polyester	60 minutes	0.98	$1.222\ (0.229) \times 10^3$
Wool	10 seconds	-0.08	$3.934\ (2.262) \times 10^3$
Wool	4 minutes	0.37	$3.978\ (2.298) \times 10^3$
Wool	60 minutes	4.10	$2.519\ (1.040) \times 10^3$

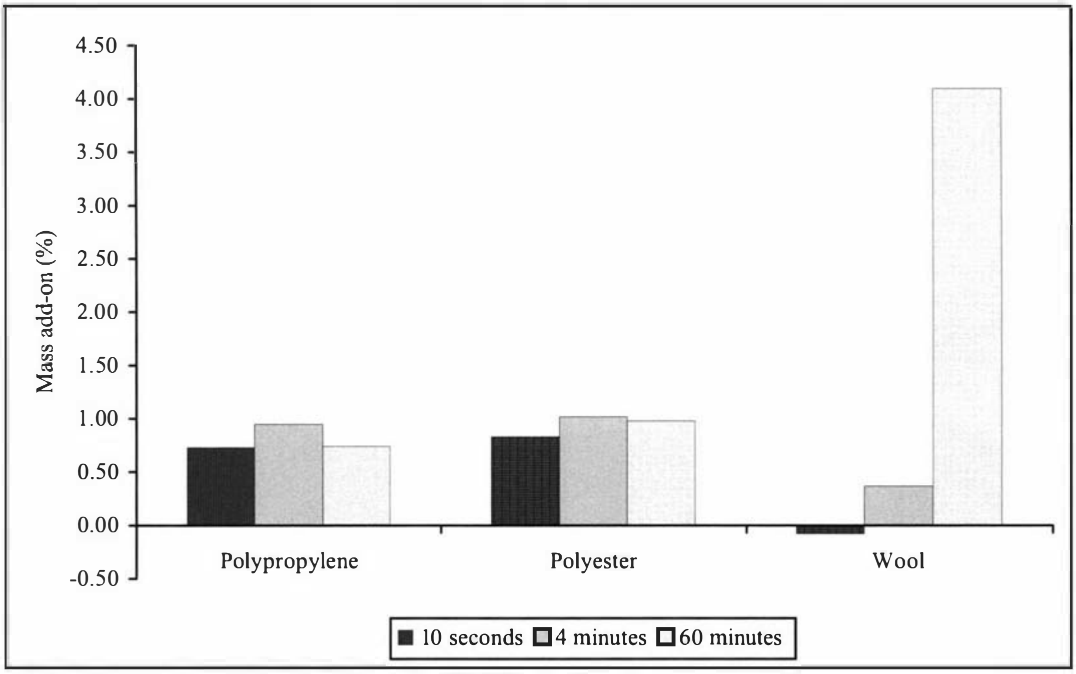


Figure 8.22. Mass add-on – impregnation time (three substrates).

The surface resistance of the polypropylene-poly(EDOT) composite appeared to be higher for four minutes than either ten seconds or 60 minutes. However the large variability (standard deviations in Table 8.22) of these results needs to be taken into account before any conclusion can be drawn. Statistical analysis, in the form of a Student's t-test for the difference of means, was carried out to compare the resistance at each impregnation time for each substrate, and the results summarised in Table 8.25. In each case, a two-tailed test was used at the 95% significance level. The null hypothesis (H_0, that the difference between the means is the result of random error) is rejected if the calculated t-statistic (t_{STAT}) is greater then t_{CRIT} (or if the t_{STAT} is negative, then H_0 is rejected if t_{STAT} is less than t_{CRIT}).

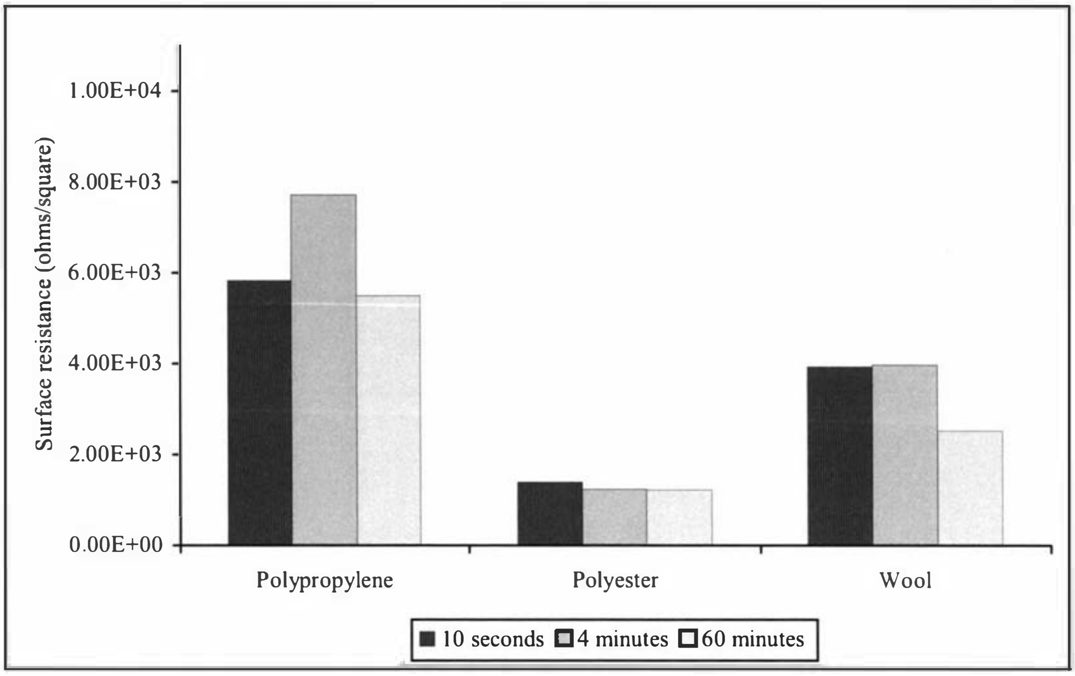


Figure 8.23. Surface resistance – impregnation time (three substrates).

Table 8.23. Statistical analysis of difference of mean surface resistance for different impregnation times.

			95% level		90% level	
Substrate	Comparison	t_{STAT}	t_{CRIT}	Significant difference?	t_{CRIT}	Significant difference?
Polypropylene	10 sec / 4 min	-1.089	2.179	No	1.782	No
Polypropylene	10 sec / 60 min	0.276	2.160	No	1.771	No
Polypropylene	4 min / 60 min	1.381	2.201	No	1.796	No
Polyester	10 sec / 4 min	1.031	2.201	No	1.796	No
Polyester	10 sec / 60 min	1.059	2.201	No	1.796	No
Polyester	4 min / 60 min	0.081	2.145	No	1.761	No
Wool	10 sec / 4 min	-0.038	2.145	No	1.761	No
Wool	10 sec / 60 min	1.608	2.228	No	1.812	No
Wool	4 min / 60 min	1.635	2.228	No	1.812	No

Note: Statistical analysis carried out using Data Analysis tool in Microsoft Excel.

Although there were large differences between some of the mean values (such as polypropylene at 4 minutes and 60 minutes), the variability of the measurements prevents the differences from being statistically significant. Regardless, the closeness of the t_{STAT} values to t_{CRIT} for the mean values for wool/10 seconds or wool/4 minutes, and wool/60 minutes, suggests that there may have been something happening which was not random error. The mass add-on certainly suggests that these specimens were very different to the each other. For absorbent fibre types it may be beneficial to increase the impregnation time, in order to decrease surface resistance and increase polymer loading (further analysis of the effect of the increased impregnation time on wool fibres is reported in Section 8.12.2). There was no benefit in increasing the impregnation time for non-absorbent synthetic fibres beyond four minutes.

8.8.3 Solvent Evaporation Time.

In previous work, the polymerisation solution solvent was allowed to evaporate for one or two hours, which was known to be sufficient to allow the polymerisation reaction to run to completion. This time was allocated arbitrarily, and may exceed that which is actually required. This may be detrimental to the composite properties, in that the excess of oxidant that is present may have a deleterious effect on the conductive polymer that has already formed if allowed to remain in contact with it for a prolonged period. The underlying substrate may also be degraded.

The solvent evaporation time required to reach completion of polymerisation will vary from substrate to substrate, as different structures and fibres will allow the solvent to escape at different rates. Because there are a large number of combinations of solvents and substrates available, it was decided to assess the effect of evaporation time on one typical substrate, the polyester interlock fabric (the most commonly used), using only the preferred solvent, methanol. The standard woven fabrics are about the same weight as this fabric, so the minimum evaporation time established for this fabric was likely to be suitable for use on the others. The evaporation time for different fabrics should be optimised on a substrate-by-substrate basis, if it is necessary to minimise processing times for commercial or other reasons.

Polymerisation was carried out as described in Section 4.4.4, with the evaporation times given in Table 8.24. The specimens are shown in Appendix 3 (8.8.3). As expected, there was no apparent polymerisation apparent on the specimen that had no solvent evaporation time. The five minute evaporation time also appeared to have no polymer deposited. The 15 minute specimen had polymer formation at the edges only, as this is where the solvent evaporates most rapidly. Specimens with evaporation times of 30, 60 and 120 minutes appeared to have undergone complete polymerisation, as they were uniformly dark across their surface.

Mass add-on and surface resistance are provided in Table 8.24 (standard deviation of surface resistance provided in parentheses), and illustrated graphically in Figure 8.24 (note that a log scale has been used for resistance). There was a clear improvement in both mass add-on and surface resistance up to 30 minutes, but no advantage to evaporation times longer than this. The latter is confirmed in Table 8.25, which provides a summary of an ANOVA carried out on surface resistance data for evaporation times of 30 minutes and above (95% confidence level, i.e. alpha = 0.05).

Table 8.24. Mass add-on and surface resistance – solvent evaporation time.

Evaporation time (minutes)	Mass add-on (%)	Surface resistance (Ω/square)
0	-0.08	$> 40 \times 10^6$
5	-0.04	$> 40 \times 10^6$
15	0.17	$0.455 (0.620) \times 10^6$
30	0.93	$10.35 (2.32) \times 10^3$
60	0.92	$11.80 (2.43) \times 10^3$
120	0.85	$9.73 (2.69) \times 10^3$

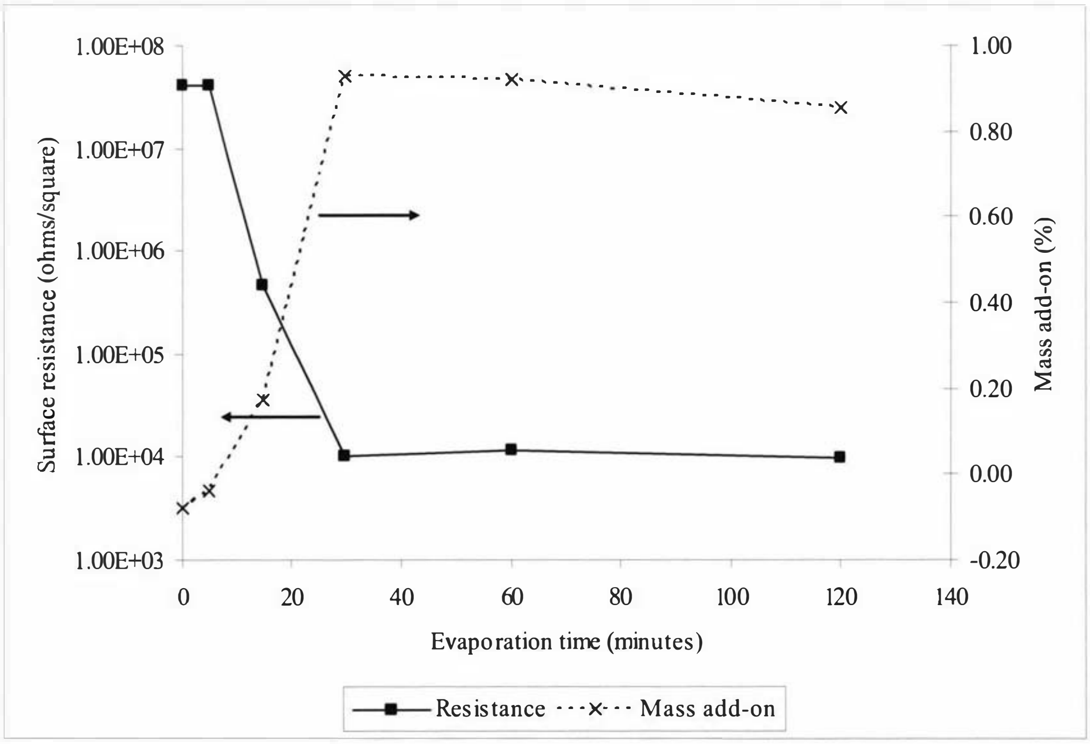


Figure 8.24. Mass add-on and surface resistance – solvent evaporation time.

As F_{CRIT} is greater than the F value for this confidence level, it was not possible to reject the null hypothesis (i.e. that the observed differences are due to random error). In other words, the differences between the mean values for evaporation times of 30 minutes or greater are not significant. Longer evaporation times were neither beneficial nor detrimental to surface resistance.

Table 8.25. ANOVA for evaporation times of 30 minutes and above (surface resistance).

Source of variation	Sum of squares	Degrees of freedom	Mean squares	F	P-value	F_{CRIT}
Between groups	17941008.3	2	8970504.17	1.452	0.257	3.467
Within groups	129760325	21	6179063.1			
Total	147701333	23				

Note: Statistical analysis carried out using Data Analysis tool in Microsoft Excel.

8.8.4 Solution Depletion with Multiple Dips.

Throughout this work (with only occasional exceptions), one polymerisation solution has been prepared for each specimen to be treated in. The solution volume is approximately 10 mL and the specimen mass ranges between about 0.15 and 0.4 grams. Very little of the solution volume is used up in the treatment, so it may be possible to treat multiple specimens in one polymerisation solution. This would allow more efficient use of the reagents. In this experiment, multiple specimens of the polyester interlock fabric were treated successively in the same polymerisation solution.

Ten specimens of the polyester interlock fabric were treated one after the other in a single polymerisation solution, as described in Section 4.4.4. The specimens from ten successive treatments behaved identically during polymerisation, and had the same appearance at completion (as shown in Appendix 3 (8.8.4)). There was only about a quarter of the polymerisation solution remaining after the tenth specimen was treated, and it was not possible to fully immerse the last few specimens. The solution did wick into these specimens, and agitation ensured that they were thoroughly impregnated with the reagents. The amount of solution consumed per specimen can be estimated; based on approximately 7.5 mL of solution being used for ten specimens, it is about 0.75 mL per specimen.

Mass add-on and surface resistance results are presented in Table 8.2, with standard deviation of surface resistance provided in parentheses. Also provided is the results of a series of Student's t-tests for the significance of the difference between the mean resistance values for each treatment and the first treatment.

Table 8.26. Mass add-on and surface resistance – successive treatments from one polymerisation solution.

Specimen number	Mass add-on (%)	Surface resistance (Ω/square)	Significantly different to first?
1	1.00	12.60 (3.86) x 10^3	---
2	0.92	11.63 (3.73) x 10^3	No
3	1.01	11.41 (3.50) x 10^3	No
4	0.71	10.15 (1.63) x 10^3	No
5	0.97	12.28 (0.86) x 10^3	No
6	0.94	14.74 (3.27) x 10^3	No
7	0.85	16.14 (1.99) x 10^3	Yes
8	0.88	19.73 (4.83) x 10^3	Yes
9	0.93	22.56 (4.20) x 10^3	Yes
10	0.89	37.10 (5.85) x 10^3	Yes

Note: Statistical analysis was carried out using the Data Analysis tool in Microsoft Excel, two-tailed with a 95% confidence level.

These data are also plotted in Figures 8.25 and 8.26, where the eventual increase in surface resistance can be clearly seen. There didn't appear to be any progression in the mass add-on values, with the lowest (0.71%) occurring for the fourth specimen, and the highest (1.01%) occurring for the third. It is worth noting that the lowest resistance occurred at the lowest mass add-on (fourth treatment). It is possible that solution depletion occurred in such a way that the precursor concentration had, by this stage, reached its optimum value. The value of 0.03 g/10 mL is known to be close to (but not precisely) the optimum value.

The reason why mass add-on should remain basically consistent, but surface resistance increase is not immediately apparent. It would be expected that as the reagents were depleted, the mass add-on would reduce. One explanation may be that while there were sufficient reagents present to allow polymerisation to proceed as normal, depletion of the oxidant meant that full doping was prevented. However even this could have been indicated in mass add-on values (less-doped polymer would weigh less, even if the same molar quantity has formed). Also, there are three times as many dopant ions (Cl^-) as there are oxidant ions (Fe^{3+}), so this explanation seems unlikely unless a huge excess of dopant anions is required to achieve full doping. If this were an absorbent natural fibre such as wool, it would be possible that the 'polymer' mass add-on for later specimens could be absorbed iron, with the precursor having been thoroughly depleted. However this seems unlikely in a non-absorbent synthetic.

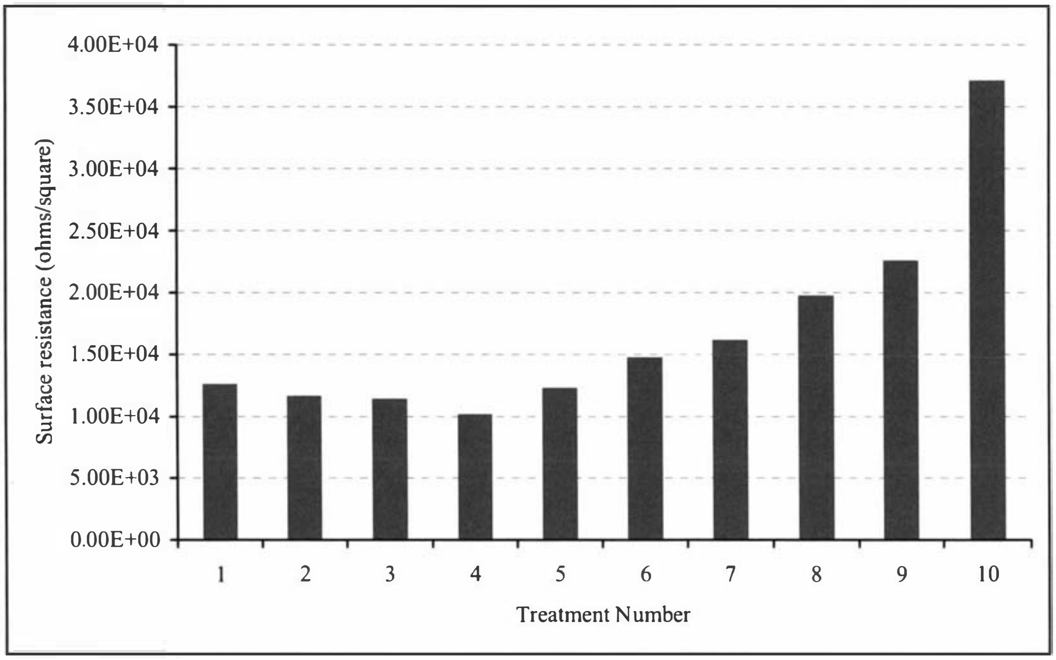


Figure 8.25. Surface resistance – polymerisation solution depletion.

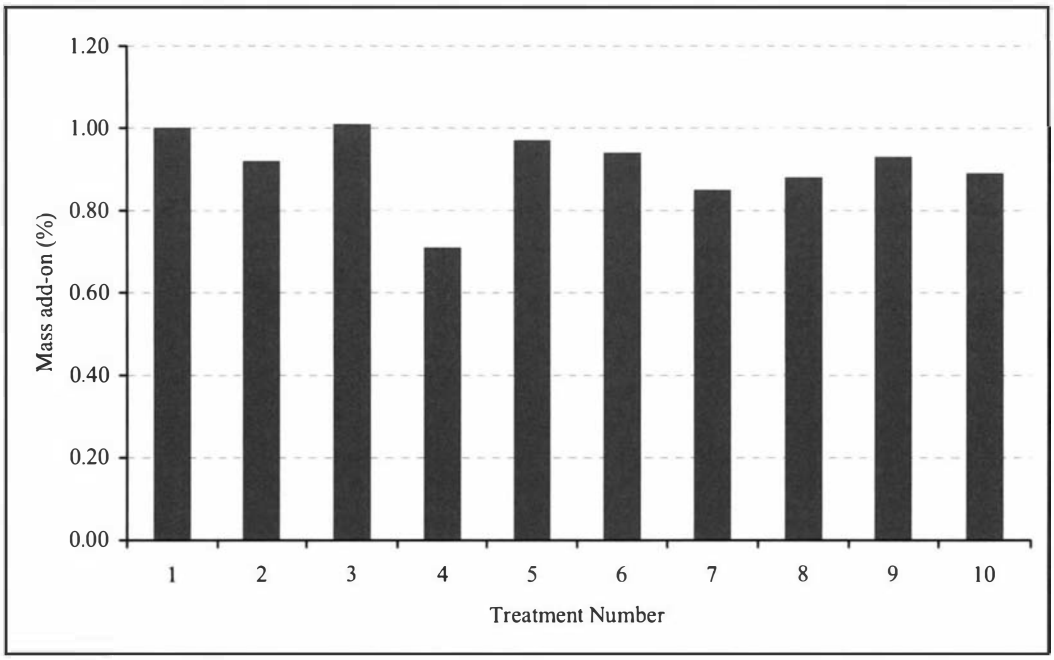


Figure 8.26. Mass add-on – polymerisation solution depletion.

8.8.5 Viability of Oxidant Solution Over Time.

Throughout this work, the oxidant solution has been prepared directly before use because of concerns over the long term viability of iron (III) chloride solutions (the same concerns could be equally valid for solutions prepared with other oxidants). These concerns came about because of occasional experiences where old oxidant solutions (up to a few days since preparation) gave poor results, and a repeat of the experiment with fresh oxidant worked as expected. A formal experiment was carried out to confirm this behaviour. Because this experiment takes the form of repeated identical polymerisation treatments in separate solutions, it also gives an indication of the between-treatment consistency of the system.

Two sets of five specimens were prepared from the polyester interlock fabric, and two sets of five polymerisation solutions were prepared using either freshly prepared iron (III) chloride hexahydrate in methanol, or an equivalent solution that had been prepared 16 days previously. These sets are referred to 'new' and 'old', respectively. The treated specimens are shown in Appendix 3 (8.8.5), and it is clear that the specimens prepared using 'old' oxidant solution were not as dark as those prepared using 'new'. This is indicative of lower polymer mass add-on, as confirmed by results provided in Table 8.29.

Table 8.27. Mass add-on and surface resistance – 'new' and 'old' oxidant solutions.

Specimen	Mass add-on (%)	Surface resistance (Ω/square)
New 1	1.00	4.63 (2.00) x 10^3
New 2	0.58	4.72 (1.10) x 10^3
New 3	0.74	4.16 (1.45) x 10^3
New 4	1.01	3.93 (1.30) x 10^3
New 5	0.92	3.83 (0.98) x 10^3
Overall mean (SD)	0.85 (0.19)	4.26 (1.38) x 10^3
Old 1	0.40	41.1 (19.4) x 10^6
Old 2	0.50	59.3 (37.0) x 10^6
Old 3	0.48	28.1 (12.0) x 10^6
Old 4	0.70	29.9 (13.8) x 10^6
Old 5	0.64	57.2 (38.5) x 10^6
Overall mean (SD)	0.54 (0.12)	43.1 (28.6) x 10^6

A Student's t-test for the difference between the mean mass add-on for new and old oxidants confirms that the difference is statistically significant at the 95% confidence level (details provided in Appendix 4, 8.8.5). Statistical analysis is unnecessary for the difference in surface resistance between new and old oxidant as it is four orders of magnitude. It is clear that only freshly-prepared oxidant should be used.

The between-treatment consistency of surface resistance results was analysed for both 'old' and 'new' results using ANOVA (summarised results are provided in Table 8.28, 95%

confidence level, i.e. alpha = 0.05). For both sets, the null hypothesis (that the difference between means is due to random error) cannot be rejected, so we can conclude that the differences in surface resistance between the different treatments are not significant. For the 'new' set the range of values is from 3.71 to 4.72 kΩ, being only approximately ±12% around the overall mean of 4.26 kΩ. For the 'old' set the range of values is from 28.1 to 59.3 MΩ, being approximately ±36% around the overall mean of 43.1 MΩ.

Table 8.28. ANOVA for 'new' and 'old' oxidant solutions (surface resistance).

Source of variation	Sum of squares	Degrees of freedom	Mean squares	F	P-value	F_{CRIT}
NEW						
Between groups	5164035	4	1291008.75	0.650	0.631	2.641
Within groups	69555762.5	35	1987307.5			
Total	74719797.5	39				
OLD						
Between groups	6.914×10^{15}	4	1.728×10^{15}	2.428	0.066	2.641
Within groups	2.492×10^{16}	35	7.119×10^{14}			
Total	3.183×10^{16}	39				

Note: Statistical analysis carried out using Data Analysis tool in Microsoft Excel.

Consistent and good results were achieved with a freshly prepared oxidant solution, while an old oxidant solution yielded poor and more variable results. The latter was evidenced by the wider range of values achieved for equivalent treatments, and the closeness of the ANOVA-calculated F statistic to the critical value of F (2.428 and 2.641 respectively) for the 'old' series.

8.8.6 Summary and Conclusions.

The effects of various process variables have been established. Impregnation time has little influence on composite properties for non-absorbent fibres (such as the synthetic fibres), but does have a major effect on mass add-on, coupled with a possible influence on surface resistance for the absorbent wool substrate. Mass add-on was increased, and resistance possibly decreased, with longer impregnation. Solvent evaporation time should be about 30 minutes for the polyester interlock / methanol combination, but exceeding this is not detrimental (up to the maximum evaporation time tested of 120 minutes). It should probably be optimised for each combination of solvent and substrate.

A single 10 mL polymerisation solution can be used for treating up to five or even six specimens of about 0.2 g mass. This also suggests that a single specimen of about one gram could be treated successfully in this amount of polymerisation solution. The oxidant solution used must be fresh; preferably prepared immediately before use.

All of the above results were taken into account in subsequent experiments; both to optimise the properties of the textile-poly(EDOT) composites prepared, and to minimise wastage of reagents and time.

8.9 Effect of Multiple Coatings.

8.9.1 Background.

As previously seen, a high polymer mass add-on does not necessarily lead to a lower composite surface resistance. In Section 8.2, optimum electrical properties were achieved at around one percent polymer mass add-on when add-on was increased via a higher precursor concentration. This section describes an alternative approach to building up polymer mass add-on; using multiple layers applied successively at the optimum precursor concentration. This approach could result in textile-ICP composites with lower resistance, as more ICP will be available to carry the electric charge, and with each layer having the lowest possible resistance.

This multi-layer approach should be a means for creating a high loading of relatively high-quality polymer, but an important issue is the effect that subsequent polymer deposition treatments have on the existing layers of ICP. Polymerisation is carried out from a strongly oxidising solution, which is kept in contact with the substrate for up 60 minutes. Under these conditions, it is likely that damage is done to surface layers of ICP. If the deterioration in electrical properties of the underlying layers is sufficiently high, then the additional layer may be the only conductive layer. In this situation the mass add-on will increase, but surface resistance will not decrease with successive polymer depositions. If the detrimental effect on pre-existing polymer layer is only slight, then there is scope to significantly decrease the resistance. One possible way to predict the extent of reduction is to treat each ICP layer as an equal resistor in parallel with the other layers; but this is not a good simulation of the situation, as the layers are not insulated from each other, and the surface resistance measurement does not necessarily supply current directly to all layers. In reality, the situation is probably too complex to model easily.

The objective of the series of experiments reported in this section was to determine the extent of any improvement in electrical properties resulting from applying successive layers of poly(EDOT) to various substrates under optimum conditions. The build up of mass add-on was also monitored, and SEM images of composites with multiple layers were collected.

8.9.2 Treatment-by-Treatment Analysis.

For this investigation four specimens of polyester interlock fabric were used, cut to exactly the dimensions required for the surface resistance measurement (15 mm wide by 30 mm long); two specimens cut along the wales and two cut along the courses. This resulted in the same number of measurements made as used elsewhere; but cutting the specimens before treatment allowed them to be measured after each treatment, and then re-treated. The knit fabric was chosen because it is more stable at the edges than a woven fabric, which can lose threads and thus confound any attempt to measure mass add-on. Also loss of threads along the length of the specimen would result in a reduction of specimen width, which would result in a narrower specimen than is required for surface resistance measurement. As this knit fabric does not fray, it is a better candidate for an analysis of multiple treatments.

The specimens were prepared as described in Section 4.4.4. Post-treatment conditioning time was shortened slightly to 22 hours before measuring their surface resistance and mass. By doing this, each treatment could be completed in a 24 hour period, and successive polymerisations could be carried out at more efficient daily intervals. The specimens were treated 12 times, and darkened progressively to a very dark blue (the four specimens are shown after each of the first four polymer depositions in Appendix 3, 8.9.2; after this point they were too dark for further changes to be easily discernible). Test results are provided in Table 8.29 (the standard deviation of surface resistance is given in parentheses), and the progression of surface resistance and mass add-on is illustrated in Figure 8.27.

Table 8.29. Mass add-on and surface resistance – multiple-coated specimens.

	Mass add-on (%)		Surface resistance (Ω/square)
Coating number	Relative to initial mass	Relative to previous mass	
1	1.01	1.01	5028 (1730)
2	2.16	1.14	1686 (241)
3	3.21	1.02	602.3 (79.7)
4	4.70	1.45	537.6 (98.1)
5	6.30	1.53	501.8 (85.2)
6	7.94	1.54	363.4 (45.0)
7	9.47	1.42	270.5 (30.5)
8	11.38	1.74	241.1 (27.0)
9	12.57	1.07	184.4 (30.5)
10	14.40	1.62	176.8 (27.0)
11	16.41	1.76	190.0 (45.9)
12	18.35	1.67	160.5 (13.1)

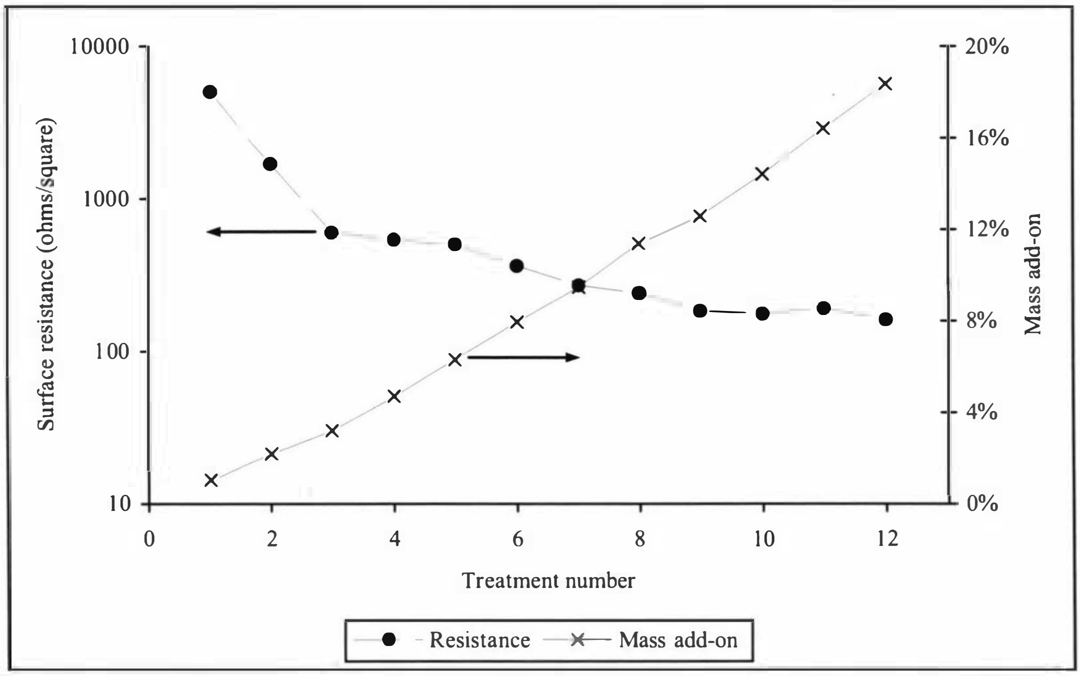


Figure 8.27. Change in surface resistance and mass add-on with multiple poly(EDOT) layers.

Clearly the additional coatings decreased the resistance and increased the mass add-on with each treatment. This decreasing resistance suggests that the treatment process did not cause excessive damage to the existing substrate, and there was conductive contact between the layers. While the mass add-on had a roughly linear relationship with the number of treatments, the resistance reduced rapidly at first, then levelled out. Over the first six treatments the resistance reduced by 92.8%; the further reduction from treatments seven to twelve was only 55.8%. After twelve coatings had been applied, the surface resistance was remarkably low at only 160.5 Ω/square, but the mass add-on was in excess of 18% and the fabric felt stiff and inextensible. Given the magnitude of resistance improvement that occurred after five or six treatments (with a mass add-on of six or seven percent), this number seems to be a good compromise between electrical and mechanical properties, with an order of magnitude reduction in surface resistance. The levelling-out behaviour seems logical, as in the early stages, the electrically insulating substrate has more influence on the overall composite resistance than later, when a larger amount of poly(EDOT) has been deposited.

The variability in the surface resistance measurement appeared to be less for treatments after the initial one. The coefficient of variation (CV; standard deviation as a percentage of mean) of surface resistance after one treatment was 34.4%. For the remaining treatments the CV was generally in the range 11-18, except for the 11th (24.2%) and 12th treatments (8.2%). This was probably due to a levelling effect; second and subsequent treatments had the effect of filling the gaps that existed after the first treatment. The result was more consistency in the surface resistance measurement, and a lower CV. The more-even coating that resulted is an additional advantage to the multi-layer technique.

There is some indication that mass add-on per treatment is higher for the later treatments than the earlier ones. The average mass add-on for the first six treatments is 1.28%, while for the last six it is 1.55%. The difference is even more marked when only the first and last three treatments are considered. The average of the first three is 1.06%, while the last three average 1.68% add-on. This may be because the poly(EDOT) coated surface is chemically more receptive to further depositions of poly(EDOT), or it may simply be that the surface develops an irregular morphology with increasing treatments, and a greater surface area is available for deposition relative to the substrate mass.

8.9.3 Behaviour on Standard Fabrics.

Specimens were prepared with multiple poly(EDOT) treatments for an assessment of their bending behaviour, the results of which are reported in Section 8.10.1. Five of the standard fabrics were treated for this work, with one set having one layer of poly(EDOT) deposited, and another having five layers. They were 250 x 25 mm strips, given either one or five successive treatments, with full rinsing and drying between each treatment. The fabrics were the standard woven fabrics: polypropylene, polyester, acrylic, wool and cotton.

The specimens are shown in Appendix 3 (8.9.3, duplicated in 8.10.1). Polymer mass add-on and surface resistance measurements were made as usual, except that the resistance measurements were made without cutting specimens to the appropriate width, so that the fabric strips could be used undamaged for the bending assessment. While this means that the results cannot be compared with other surface resistance measurements in this work, the five-layer and one-layer can be compared with each other for each of the fabrics. Mass add-on and surface resistance values are provided in Table 8.30, along with the factor by which each has changed between one and five layers.

These data confirm the expected decrease in surface resistance and the increase in mass add-on across the full range of fibre types. The spread of resistance values is three orders of magnitude with only one layer, but all fibre types have resistance of the same order of magnitude after five. This is because the substrate properties become progressively less important as the poly(EDOT) builds up; deposition of the ICP being made onto a layer of poly(EDOT), rather than the fibre surface. Similarly, the highest mass add-on after one treatment is more than double the lowest; after five the highest is only about 30% greater than the lowest.

Table 8.30. Mass add-on and surface resistance – one and five layers (five standard fabrics).

Substrate[1]	Mass add-on (%)			Surface resistance (Ω/square)		
	One layer	Five layers	Factor increase[2]	One layer	Five layers	Factor decrease[3]
P	0.57	3.13	5.5	2195	657.4	3.3
D	0.63	3.85	6.1	754.6	139.1	5.4
O	0.73	4.00	5.5	1624	149.1	10.9
W	0.36	4.06	11.3	2680	131.1	20.4
C	0.35	3.85	11.0	250600	789.8	317.3

Notes:

1. P – polypropylene, D – polyester (Dacron®), O – acrylic (Orlon®), W – wool, C – cotton.
2. Five-layer mass add-on ÷ one-layer mass add-on.
3. One-layer surface resistance ÷ five-layer surface resistance.

The change factors in Table 8.30 illustrate this further, with the lowest mass add-on after one treatment (W and C) increasing by the greatest factor after five, and the highest surface resistance after one treatment decreasing by the greatest factor after five (C). Multiple treatments minimise the effect of the substrate, meaning that quite conductive composites can be prepared on any substrate by this 'multi-layer technique'.

8.9.4 Behaviour with Alternative Oxidants.

All of the previous experiments reported in this chapter used iron (III) chloride hexahydrate as the oxidant. This section describes work where two other iron (III) salts used were used to prepare multi-layer specimens. As these specimens were also used for the elemental analysis work reported in Section 8.12.3, the standard polyester woven fabric was used rather than the polyester interlock (the woven fabric has a more reliably known specification than the interlock, and is therefore more reliable as a control substrate for elemental analysis).

Specimens were prepared using the oxidants given in Table 8.31 at a concentration of 0.8 mol/L oxidant in methanol. Images of the three specimens, with five layers of poly(EDOT) deposited, are provided in Appendix 3 (8.9.4). In Section 8.5, single-layer mass add-on and surface resistance data were reported for this substrate, prepared in the same way as here. Those data are included for comparison in Table 8.31 (referred to as 'one layer').

Table 8.31. Mass add-on and surface resistance – one and five layers (three oxidants).

Oxidant[1]	Mass add-on (%)			Surface resistance (Ω/square)		
	One layer	Five layers	Factor increase[2]	One layer	Five layers	Factor decrease[3]
Cl	0.77	3.85	5.0	2600	150.0	17.3
ClO_4	0.89	6.39	7.2	304	64.6	4.7
NO_3	0.81	3.62	4.5	553	98.9	5.6

Notes:

1. Hydrated iron (III) salt of the anion given.
2. Five-layer mass add-on ÷ one-layer mass add-on.
3. One-layer surface resistance ÷ five-layer surface resistance.

The multi-layer technique had the same effect with the alternative oxidants as with iron (III) chloride, although the factor by which resistance decreased after five treatments was proportional to the resistance after one layer. After one treatment, the resistance of the perchlorate-doped specimen was almost one ninth of that of the chloride-doped specimen, whereas after five it was about two fifths. Regardless, the resistance of the five-layer perchlorate-doped specimen was remarkably low; the lowest resistance of any specimen prepared in this work.

With chloride and nitrate, the mass add-on after five treatments was roughly five times that of one treatment, suggesting that roughly the same amount of polymer was deposited at each treatment. For perchlorate there appeared to be an increase in amount of polymer deposited per treatment, as the mass add-on after five treatments was more than five times that after one treatment.

8.9.5 Surface Morphology of Multiple-Coated Specimens.

Mass add-on increased roughly linearly with multiple treatments, and a stiffening of the fabric was observed. However the effect of this additional polymer on the morphology of the polymer layers is not known. Scanning electron microscope (SEM) images of the fibre surfaces from previous experiments have indicated that a single poly(EDOT) coating is fairly uniform and smooth. The extent to which this is preserved through multiple coatings is of interest, as is the extent to which polymer accumulates in the fibre interstices, rather than on the surface of the fibres. To investigate this, a series of specimens were prepared with a different number of chloride-doped poly(EDOT) layers and examined with SEM.

The polyester interlock fabric was used, as its structure is more stable and better able to cope with the multiple treatments and rinses. Smaller specimens were prepared, as sufficient data had already been collected on the surface resistance and mass add-on behaviour with multiple treatments. They were 30 x 15 mm strips, cut along the wales of the fabric, exactly the correct width for the surface resistance measurement. Thus one surface resistance measurement could be quickly made on each fabric face, to confirm the expected resistance behaviour. Specimens were prepared with one, two, five and ten layers of poly(EDOT), according to the technique described in Section 4.4.4.

Images of the four specimens prepared are provided in Appendix 3 (8.9.5). The heavier polymer load of those having more layers is illustrated by the darker colouration. Only two surface resistance measurements were made on each specimen (rather than the usual eight), and the mass add-on will be less accurate due to the small specimen size. Nevertheless, these data are provided in Table 8.32, and confirm the expected behaviour in both surface resistance and mass add-on.

Table 8.32. Mass add-on and surface resistance – SEM specimens (one, two, five and ten layers).

Number of layers	Mass add-on (%)	Surface resistance (Ω/square)
1	1.00	3150
2	2.65	1480
5	7.20	467
10	14.98	186

Scanning electron microscope images of these four specimens are shown in Figure 8.28. Each image is a representative example of the several taken of each specimen, and all are at the same magnification. The slightly polygonal shape of the fibres is not uncommon for synthetic fibres, and is unrelated to the polymer deposition (it is apparent in Figure 4.10 for the untreated fabric). The specimens were sufficiently conductive to not require gold-coating before SEM examination.

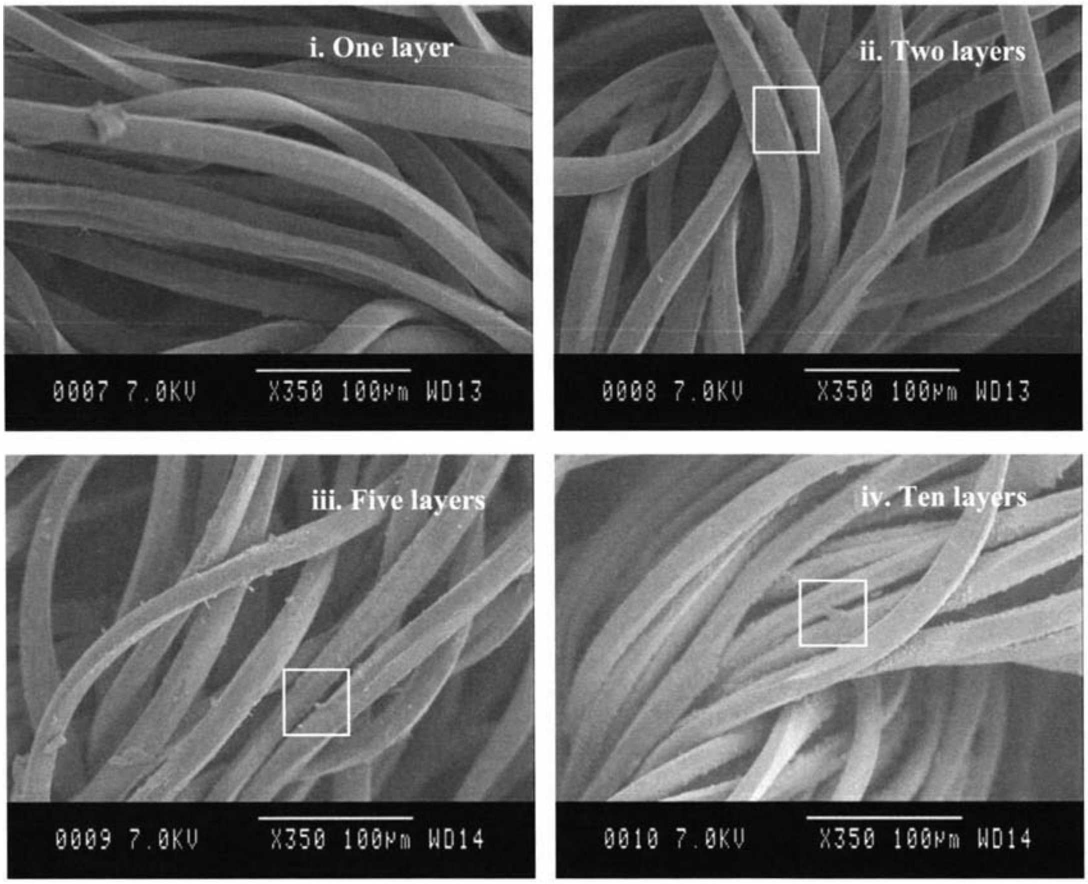


Figure 8.28. SEM images – multiple layers of poly(EDOT).

The image of the single-layer specimen (i) shows a generally uniform and smooth coating of poly(EDOT). One item of particulate is present – probably foreign material, given the lack of other similar particles elsewhere.

With two layers present (ii), the basic fibre shape is still clearly visible and the coating mostly smooth and uniform. Several areas of poly(EDOT) coating are visible as lines running along the fibres (these are the edges of areas of deposited polymer). They appear to be lifted slightly from the fibre surface in some areas; almost flaking off. One such area is highlighted.

Image (iii) shows five layers. There are numerous loose particles of poly(EDOT) present on the surface of the fibres, as well as edges of polymer flakes visible. There are also areas (such as that highlighted) where it appears that poly(EDOT) may be bridging between fibres. These structures, if sufficiently numerous, could cause the fabric to become stiffer and less extensible, as they would prevent fibres from behaving independently of each other when the fabric is deformed.

Once ten layers of poly(EDOT) have been deposited on the substrate (iv), it becomes clearly visible on the surface of the fibres, and somewhat irregular in morphology. There are still smooth areas, but also rough areas, flakes, and one very clear (and thick) 'bridge' between adjacent fibres (highlighted). However even at this loading (approximately 15% polymer mass add-on), the poly(EDOT) seems to be predominantly fibre surface located, and not loosely distributed through the substrate.

8.9.6 Summary and Conclusions.

The multi-layer technique is obviously a good method for substantially reducing the surface resistance of textile-poly(EDOT) composites. While the mass add-on tended to increase linearly with multiple treatments, the resistance decreased rapidly at first before levelling off after approximately six treatments. This suggests that a maximum of six layers is optimal, unless particularly low resistance is required. The approach was effective on all substrates, with the fibre type having progressively less influence on the composite surface resistance as layers of conductive polymer are added.

The application of additional poly(EDOT) layers also reduced resistance and increased mass add-on when other oxidant types were used. In fact, with iron (III) perchlorate as the oxidant, five successive depositions of poly(EDOT) resulted in a composite with surface resistance of only 65 Ω/square – the lowest achieved anywhere in this research. Coupled with the stability of perchlorate-doped poly(EDOT) established in Section 8.4, this is a very interesting and potentially useful material. Iron (III) nitrate was also successfully used to prepare multi-layer composites with very much reduced surface resistance.

Examination of the composite morphology under SEM indicated that although one or two layers of poly(EDOT) on the substrate had a smooth and uniform appearance, as more were added a small amount of loose polymer particulate formed. Also the surface of the polymer-coated fibres became less smooth, with some 'bridging' of poly(EDOT) between fibres. These structures are likely to have a detrimental effect on the mechanical properties of the composite, reducing extensibility and increasing stiffness. Linkages of this type between fibres were only apparent with five or more layers applied, and a mass add-on in excess of 7%. However, even at very high loadings (for example after ten layers were applied), the majority of poly(EDOT) formed appeared to be associated with the surfaces of the fibres and not loose within the textile structure.

By using the multi-layer technique and restricting the total mass add-on to approximately 5%, it is possible to reduce the surface resistance of a textile-poly(EDOT) composite by an order of magnitude without causing substantial change to the mechanical properties of the substrate. The single-dip polymerisation process appears to encourage epitaxial polymerisation, rather than the formation of polymer in solution (which then accumulates in the substrate). This means that fibre interstices remain relatively free of polymer deposition, and therefore the fibre and yarn movement at these points is not substantially hindered, and the mechanical properties of the substrate are not adversely affected.

8.10 Effect on Fabric Properties.

8.10.1 Fabric Bending Properties.

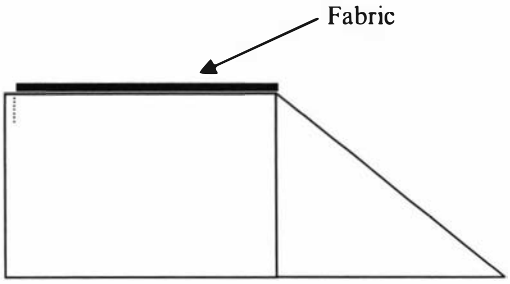
8.10.1.1 Background.

An important property of textiles that sets them apart from other planar materials (such as paper or plastic sheeting) is the ability to drape smoothly around a three-dimensional form. This is due to textiles being assembled from two somewhat mechanically-independent levels of sub-components. The lowest level is the fibre, which is assembled to form a yarn, then the yarns assembled to form the fabric. The fabric is made up of resilient polymer fibres that behave (to some degree) independently of each other, and yarns that can also behave separately. As a result, textiles have mechanical properties (such as bending and tensile/compressive properties) that are superior to non-textile planar materials of equivalent area density (mass per unit area). Textiles span a wide range of mechanical properties; knitted fabrics being the easiest to deform mechanically, through woven fabrics, to non-woven fabrics that tend to be rigid and inextensible. Apparel textiles demand high levels of drape, extensibility and shear, to allow them to be tailored to the three dimensional body shape, and permit comfortable movement during use. Therefore in the development of wearable systems (including wearable electronics), it is important that these properties are not compromised.

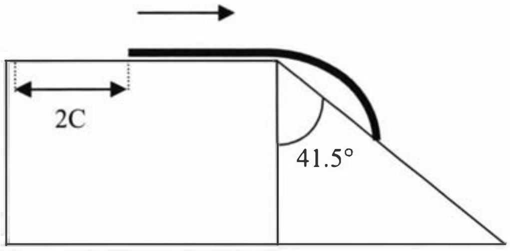
Applying a conductive polymer coating may stiffen and reduce the extensibility of a textile. If the polymer coating forms a thin, uniform layer around the fibres, then it will increase fibre bending stiffness, which will in turn increase fabric stiffness. The effect will be more substantial if the polymer accumulates in fibre interstices, or if the polymer coating is thick enough to cause fibres to make contact with each other over a longer length (or even become 'glued' together). The fibres are less able to behave independently of each other during bending and other deformation, and the fabric will become stiffer and less extensible.

8.10.1.1 Test Method.

One way of assessing this effect is to measure the fabric's flexural rigidity. Flexural rigidity is defined as "the ratio of a small change in bending movement per unit width of the material to the corresponding small change in curvature" [156]. There are a number of ways of measuring this, but a simple and convenient method is described by the British Standard test method BS3356:1990 ("Determination of bending length and flexural rigidity of fabrics"). In this method, a 2.5 cm wide strip of fabric is placed on a smooth horizontal surface, and slid gradually forwards over an edge, bending under its own weight, until the tip of the fabric strip reaches an angle of 41.5° below the horizontal. This is illustrated in Figure 8.29. The length at which this occurs is recorded and used to calculate flexural rigidity.



Starting position.



End point.

Figure 8.29. Principle of BS3356:1990 – Determination of bending length and flexural rigidity of fabrics.

The fabric flexural rigidity (G, in units of mg·cm – 'milligram centimetres') is calculated as:

$$G = 0.1\ M\ C^3$$

where: M = fabric mass per unit area (g/m^2), and

C = average fabric bending length (cm), which is 0.5 x the overhanging length measured from the test.

The test is carried out in the standard conditions for textile testing [144]; i.e. 20°C (± 2°C) and 65% relative humidity (± 5%).

Because the fabric mass per unit area is used in the calculation for flexural rigidity, it is necessary to measure this property for the fabrics after each of the polymer deposition treatments. While the 'as received' mass per unit area is already known (provided in Table 4.2) it will obviously change when the fabric is treated (ICP coating added and/or chemical finishes removed). The fabric may also 'relax' during these treatments and change its dimensions, usually shrinking (in length and/or width). The change in mass per unit area with each treatment was briefly investigated, and the results are given in Table 8.33. Full results are provided in Appendix 4 (8.10.1).

Table 8.33. Specimen mass per unit area (g/m^2, bending specimens).

	As received	Prepared	Oxidant only	1 x poly(EDOT)	5 x poly(EDOT)
Polypropylene	196	203	207	208	213
Polyester	126	141	140	140	144
Acrylic	161	173	173	173	179
Wool	135	148	150	151	157
Cotton	153	172	178	177	183

8.10.1.3 Experimental Design and Preparation of Specimens.

The flexural rigidity of five of the standard woven fabrics (described in Section 4.2) was tested. The nylon standard fabric was excluded because of the difficulties in achieving a uniform coating on it, and the apparent degradation caused to it by the coating system. The five fabrics used were polypropylene (P), polyester (D), acrylic (O), wool (W) and cotton (C). Specimens were prepared to be tested 'as received'; after the routine solvent followed by water rinse; after a blank treatment with oxidant only; after a single poly(EDOT) coating procedure; and after five successive poly(EDOT) coating procedures. To do this, five specimens (thin strips) were cut from the bulk sample of each fabric in the warp and weft directions. The specimens were cut 25.5 cm long and 3 cm wide, then threads were removed from the edges to reduce the fabric dimensions to just over 25 cm long and 2.5 cm wide. After treatment, the final few threads were removed from the edges to bring the specimen dimensions to exactly 25 x 2.5 cm, this being the appropriate size for the standard test. Note that this leaves a 'fringe' of threads along each edge of the fabric extending beyond the specified dimensions, but this fringe does not interfere with the fabric bending behaviour as the threads are separate from each other and perpendicular to the direction of bending. Just before testing, the yarn fringe at each end of the specimen was carefully trimmed off to provide a clean, well-defined end to observe during bending. As discussed previously, preparation of specimens of woven fabrics in this way is necessary to prevent loss of threads during the ICP coating procedure and subsequent rinses.

Fabrics were given a light steam press to remove any creases that might interfere with the specimen's natural bending behaviour. The fabric specimens were prepared as follows:

As received: No further treatment given.
Prepared: 'As received' specimen rinsed in acetone, allowed to dry, rinsed in de-ionised water, allowed to dry.
Oxidant only: 'Prepared' specimen rolled loosely along its length, then placed in a blank polymerisation solution (that is, as described in Section 4.4.4 but without the precursor). Specimen was unrolled for solvent evaporation.
1 x poly(EDOT): As for oxidant only specimen, except oxidant solution also contained 0.03 g/10 mL EDOT.
5 x poly(EDOT): As for 1 x poly(EDOT) except that 5 successive treatments were carried out, with the specimen rinsed and dried between each treatment.

Images of five specimens prepared in this way for each standard fabric are provided in Appendix 3 (8.10.1).

At the completion of specimen preparation, there were two specimens (warp and weft) of each fabric type for each level of treatment. Each of these was tested four times for bending length: at each end of the fabric strip, and face-up/face-down. In this way, four measurements were recorded for each specimen, and warp and weft combined to give eight measurements for each fabric. It should be noted that this sampling procedure deviates slightly from that set out in the standard, which uses more replicates from each fabric, and does not rely on testing both ends of the fabric strips. However, as the overhanging lengths were expected to be much less than half the length of the specimen, both ends could be used, thus providing useful additional data when preparing larger numbers of specimens is impractical.

The untreated specimens weighed from 0.8 to 1.4 g. This represented a scaling-up of the procedure, where previously specimens weighing only ~ 0.25 g were treated. Polymer mass add-on and composite surface resistance were measured for each of the ICP-coated fabric specimens to check the treatment efficacy. It should be noted that the resistance measurements made here are not directly comparable with those obtained elsewhere, as a non-standard procedure was followed (fabric specimens were not cut to the exact width of the testing apparatus as the strips were required to be undamaged for the bending test), although they would be expected to be reasonably similar, and certainly of the same order of magnitude. The relative resistance of the different fibre types should also be similar to those measured previously. These results are given in Tables 8.34 and 8.35 (average of warp and weft). Note that results for the 'as received' and 'prepared' specimens are not given, for obvious reasons.

Table 8.34. Mass add-on – bending specimens.

	Oxidant only	1 x poly(EDOT)	5 x poly(EDOT)
Polypropylene	-0.05 %	0.57 %	3.13 %
Polyester	-0.02 %	0.63 %	3.85 %
Acrylic	-0.02 %	0.73 %	4.00 %
Wool	-0.05 %	0.36 %	4.06 %
Cotton	-0.42 %	0.35 %	3.85 %

Table 8.35. Surface resistance – bending specimens.

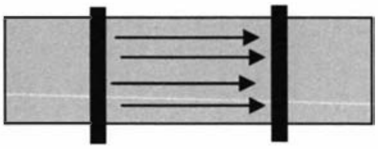
	Oxidant only	1 x poly(EDOT)	5 x poly(EDOT)
Polypropylene	> 20 GΩ[1]	2.195 kΩ	657.4 Ω
Polyester	> 20 GΩ	754.6 Ω	139.1 Ω
Acrylic	> 20 GΩ	1.624 kΩ	149.1 Ω
Wool	> 20 GΩ	2.681 kΩ	131.1 Ω
Cotton	1.168 GΩ	250.6 kΩ	789.9 Ω

Notes:

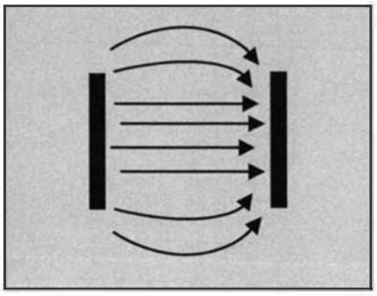
1. The highest resistance measurable on the ohmmeter used.

Despite the slight difference in testing procedure, the resistance and mass add-on data for 1 x poly(EDOT) can be compared with the data in Section 8.7. Mass add-on was similar to the values observed previously; very close in the case of the synthetic fibres, and slightly higher for the natural fibres. The mass add-on for the natural fibres was at a lower level, and is therefore more sensitive to mass loss caused by one-off factors such as a single yarn being lost from a specimen edge. The mass add-on results obtained on this occasion are probably more reliable, because they were based on larger specimens. Resistance data differed substantially from that reported in Section 8.7; in all cases it was lower on the larger specimens treated here. This was likely to be because the resistance measurement method used here was not restricted to a measurement of current passing directly between the electrodes, but also allowed current to pass between the electrodes by a multitude of other routes, as shown in Figure 8.30.

The fibre types were ranked in a similar way to that found earlier; the only difference being a swapping in position of polypropylene and wool. This probably occurred because the ratio of polymerisation solution to specimen was much lower in this case, the specimens being approximately four times larger. This had a more significant effect on an absorbent fibre such as wool than non-absorbent polypropylene. When the ratio of wool to solution was increased, depletion of the solution could become sufficient to reduce efficacy of the polymerisation solution. Nevertheless, these specimens were generally comparable to those prepared previously, and were therefore suitable for further analysis. These results also confirmed that the multi-layer technique had the same effect for all fibre types (as discussed in Section 8.9).



Situation 1: Electrical pathways when fabric width is ≤ length of terminals.



Situation 2: Electrical pathways when fabric width is > length of terminals.

Figure 8.30. Possible current pathways in conductive textiles.

8.10.1.4 Bending Length and Flexural Rigidity.

The results of flexural rigidity testing (average of warp and weft) are illustrated in Figure 8.31. Full data, including bending length for warp and weft separately, and corrected fabric mass per unit area, are provided in Appendix 4 (8.10.1). As mentioned earlier, the formula for calculating flexural rigidity uses the fabric mass per unit area. The values in Table 8.33 were used for this.

In general, the treatments had surprisingly little effect on the fabric flexural rigidity. For the synthetic fabrics (polypropylene, polyester and acrylic), there was a general increase in flexural rigidity as the specimen progresses from prepared through to 5 x poly(EDOT). For the remaining fabrics there was no substantial increase in rigidity; in fact for cotton, the 5 x poly(EDOT) treated fabric had a lower rigidity than the prepared fabric.

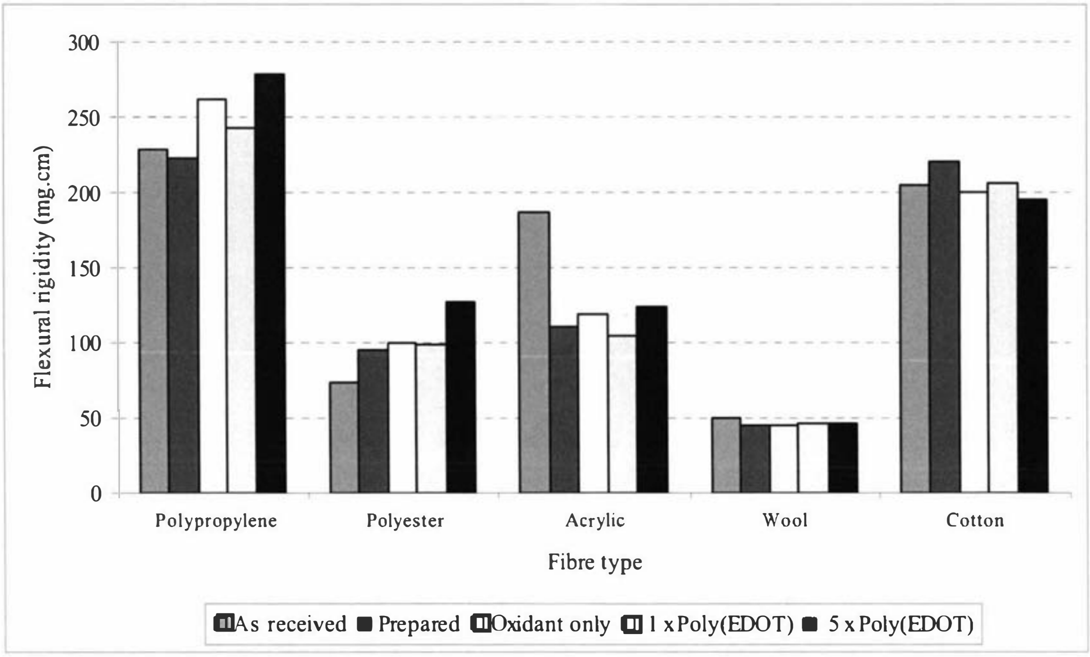


Figure 8.31. Flexural rigidity of standard fabrics.

For polypropylene, the preparatory treatments marginally reduced the rigidity (perhaps removing a fabric finish which causes some inter-fibre or inter-yarn adhesion), while 'oxidant only' caused a slight increase. With five layers of polymer added, the expected stiffening of the fabric had occurred. However, even in this case, the flexural rigidity of the fabric with five layers of polymer was only 24.9% higher than it was when prepared for treatment.

The polyester fabric showed a progressive increase of flexural rigidity, although there was no difference between 'oxidant only' and 1 x poly(EDOT). Five layers of the polymer increased the flexural rigidity by 33.2% as compared to the value for the prepared fabric.

The preparatory rinse had a major effect on the rigidity of the acrylic fabric. It was observed that after being lightly steam pressed (before carrying out the treatments) this fabric seemed to have become stiffer. Possibly a finish had been applied to this fabric that caused the fabric to stiffen when heated and/or exposed to steam, which was then removed by the preparatory rinses. This removal of finishing agents was not reflected in the fabric mass per unit area data; any loss of specimen mass was more than compensated for by specimen shrinkage (that is, while the specimen mass decreased, the specimen area also decreased). The rigidity after a single polymer treatment was actually slightly lower than it was after specimen preparation, confirming that a single treatment (giving a mass add-on of approximately 0.5 – 1.0 %) had little or no effect on the fabric's mechanical properties. Five layers increased the flexural rigidity by 12.6% compared to 'prepared'.

The wool fabric showed virtually no change in flexural rigidity with any of the treatments. As seen previously, the preparatory rinses slightly reduced the rigidity. An alternative mechanism by which this could occur (for all fabrics, but particularly for wool), is the mechanical action of the rinse processes causing fabric relaxation. Fabric relaxation can be considered a means whereby the internal energy put into the fabric during manufacture and finishing (for example weaving, or flat setting such as decatising or stentering) is released, so that the fabric takes on a low energy, fully relaxed state. It is quite possible that this state may have a lower rigidity than the fabric possesses after finishing. Five layers of polymer increased the wool fabric's flexural rigidity by only 2.85%, as compared to before treatment.

The behaviour of the cotton fabric is difficult to explain. The preparatory rinse caused an increase in rigidity, but subsequent treatments all showed a reduction in rigidity. Even more surprising is the reduction in rigidity in moving from one to five layers of poly(EDOT). Table 8.36 shows the progression of the fabric mass per unit area (M) and the bending length (C), in an attempt to locate where the unexpected behaviour is occurring

Table 8.36. Change in properties for cotton fabric.

State of fabric	Change from previous state (%)	
	M	C
As received	NA	NA
Prepared	+12.4	-0.45
Oxidant only	+3.5	-3.36
1 x poly(EDOT)	-0.5	+1.62
5 x poly(EDOT)	+3.4	-2.05

The flexural rigidity of the specimen is directly proportional to the fabric mass per unit area, but proportional to the bending length cubed; which means that small changes in bending length have a greater effect on flexural rigidity than a similar magnitude change in mass per unit area. The large increase in flexural rigidity in the transition from 'as received' to 'prepared' was due to a large increase in M and only a very small change in C (the fabric becomes stiffer if the mass increases but the bending length stays the same). In the transition from 'prepared' to 'oxidant only', the reduction in bending length dominated, even though there was an equal increase in mass, hence the large reduction in the flexural rigidity. In the transition from 'oxidant only' to '1 x poly(EDOT)' there was virtually no mass change, so the small increase in bending length was the only influence on flexural rigidity. The fabric was no heavier, but had a slightly longer bending length, and so must have been slightly stiffer. Finally, in the transition from '1 x poly(EDOT)' to '5 x poly(EDOT)' the fabric mass increased, but not by enough to compensate for the reduction in bending length (and therefore the fabric became less stiff).

If the same comparison is made to the whole transition from 'as received' to '5 x poly(EDOT)', there was an increase in fabric mass of 19.6% and a decrease in bending length of 4.23%. The result was a small decrease in flexural rigidity (due to the cubed term); in other words, a decrease in the fabric's stiffness. It became heavier but also bent more easily; therefore there could not have been substantial 'gluing together' of the fibres and yarns. It is possible that poly(EDOT) formed inside the fibre on the cotton substrate. This would also help to explain the high surface resistance of cotton-poly(EDOT) composites with only one or two treatments. Initially the fibre surfaces were not being covered in a uniform layer of poly(EDOT), but as the number of treatments increased, more poly(EDOT) was formed on the surface, and the resistance approached that of non-absorbent substrates such as polyester. This pattern can be seen by comparing the surface resistance data in Table 8.35. After one treatment, the resistance of the cotton substrate was 330 times that of polyester, but after five, the factor was only 5.7. Wool may behave similarly as it is also absorbent; after one treatment its surface resistance was 3.5 times that of polyester, but after five it was a factor of 0.94.

8.10.1.5 Conclusions.

With one poly(EDOT) coating applied, both acrylic and cotton had flexural rigidity that was no higher than it was before treatment ('prepared'), and polypropylene, polyester and wool were higher by only 3 to 9%. After five treatments, all substrates except for cotton increased in flexural rigidity, sometimes by a substantial amount (from 3 to 33%). These results, coupled with the surface resistance data for the specimens, may reveal something about how the polymer forms on different fibre substrates. On absorbent substrates (particularly cotton), there is evidence to suggest that, although polymer is being deposited and the mass increasing, it may initially be formed inside the fibre, and only after repeated applications does polymer build up on the fibre surface.

8.10.2 Fabric Burst Strength.

8.10.2.1 Background.

Another property important to the performance of textiles over time is their mechanical strength. There are a number of ways of assessing this, from simple tensile strength to more complex tests that determine the resistance of a fabric to tearing. Perhaps the most versatile fabric strength test is burst strength. Although it does not replicate a specific circumstance of wear (except perhaps in some specialised situations for protective apparel), it gives a direct indication of the fabric strength that does not require a large number of tests with the fabric held in various orientations. The basic principle of the test is to inflate a diaphragm against the fabric while it is clamped in place at its edges. The pressure at which rupture occurs indicates the fabric's burst strength.

The chemical process to which the fabric specimens are exposed during the single-dip ICP coating treatment is relatively aggressive: a strong oxidiser is impregnated into the fabric and allowed to remain there for between 30 and 60 minutes (depending on the evaporation rate of the solvent from the substrate). This may degrade the textile fibre polymer, which would result in a loss of fabric strength. This degradation might also be expected to cause a loss of mass of the substrate, but the mass change data from various blank treatments (provided in Section 8.7.4) indicates that this does not occur to any substantial extent. This serves to indicate the robust nature of textile fibre polymers, in that those that have come to be in common usage (represented by the fibres in the standard set used in this work) are very resistant to chemical attack. It should be noted that the nylon fabric has been omitted from this trial, as it was substantially degraded by the ICP coating treatment and uniformly conductive composites could not be prepared from it. Nylon is also a very robust polymer, but is known to be degraded by mineral acids [157]. Aqueous solutions of iron (III) chloride are strongly acidic, and it is possible that this is also the case (to some degree) for methanol-based solutions. This may limit nylon's usefulness in textile-ICP composites prepared by the single dip technique.

While the aggressive chemical conditions used during ICP coating treatments are expected to cause a loss of strength, the addition of a layer of polymeric material to the surface of the fibres could increase the strength of the material. The fibre diameter (as reported in Section 8.12.2) is increased by up to ~0.25 μm, which could give an increase in fibre, yarn and fabric strength. This increase could, to some extent, compensate for any degradation caused by the aggressive chemical treatment that brings about polymerisation. Therefore it may be that, while 'oxidant only' treatments cause a reduction in strength, this may be compensated for by the addition of a polymer coating.

8.10.2.2 Test Method.

Fabric burst strength was tested according to IWS TM 29 (May 2000), a method based closely on ISO 2960-1974(E) [158]. In this test the fabric is clamped over an elastic diaphragm, which is then inflated steadily until the fabric ruptures. The fluid pressure in the diaphragm at which rupture occurs (after correction for the pressure required to inflate the diaphragm in the absence of a specimen) gives the fabric bursting strength. The distance above the plane of the fabric at which rupture occurs gives the bursting distension. These are analogous with breaking stress and strain respectively in a simple tensile breaking test. These tests were carried out at WRONZ using a Mullen tester, which uses air as the diaphragm inflating fluid.

The standard requires that ten tests be made on each fabric. This would have required preparation of a larger treated piece of fabric than was practical, so a 20 x 20 cm square fabric specimen was prepared, which allowed four or five tests. This is sufficient to determine whether the treatment processes are having any substantial effect on fabric strength. A large drop in strength (probably greater than 25%) would be necessary for the fabric's durability in use to be compromised. This is because, in most situations, the forces applied to fibres, yarns and fabrics during manufacture are much greater than those applied during use, unless the fabric is designed for a specific high-performance technical application, such as protective apparel. A reduction of 25% or more is large enough to make it likely that it will be statistically significant, even with the reduced number of tests carried out. The fabrics are also very uniform in structure, so there should be little variation between individual tests on the same specimen.

8.10.2.3 Preparation of Specimens and Experimental Design.

There were five fibre types represented in the test: polypropylene (P), polyester (D), acrylic (O), wool (W) and cotton (C). Four specimens of each fabric were prepared; to allow testing of the fabric 'as received', after preparatory rinsings, with blank oxidant treatment, and with one polymer coating treatment. It would have been interesting to include a fifth specimen with multiple coatings of polymer applied to it, but the larger size of specimens required for this test and the consumption of raw materials (fabric and reagents) that this would have entailed made this impractical. The specimens prepared were sufficient to determine the effect on fabric strength of the polymer treatment and the preparatory routine.

Square fabric specimens (20 cm x 20 cm) were cut from the bulk sample, with their sides parallel to the warp and weft. The burst strength test is non-directional, so there was no need to prepare specimens representative of warp and weft separately. The edges of these specimens were overlocked using a domestic four-thread overlocker, without trimming. In previous tests it was not possible to use overlocking as a means of securing the fabric edges, as the overlocking stitches would have interfered with mass add-on measurements and other fabric properties such as bending. Since the edges of the fabric are not involved in the burst strength test, and mass add-on data had already been collected in many previous trials, overlocking was used as a simpler alternative to the careful fraying of the fabric edges that was employed on other occasions. After overlocking, fabric specimens were prepared as described for the bending assessment (Section 8.10.1), except that '5 x poly(EDOT)' was excluded.

These treatments represented a further scaling up of the process used previously. Polymer mass add-on and composite resistance were measured to confirm that the blank treatment and polymerisation had proceeded as expected. Neither of these measurements was carried out in way that allows direct comparison with the results described in other sections. This is due, in the case of mass add-on, to the use of overlocking (which introduces a proportion of fibre that is not representative of the bulk of the sample). In the case of surface resistance, this is due the non-destructive nature of the test used, with the specimen not cut to the exact width of the testing apparatus (as described in more detail in Section 8.10.1). These data are still useful to confirm that the treatments have resulted in specimens consistent with those created previously. Mass add-on data are provided in Table 8.37, and surface resistance data are provided in Table 8.38.

Table 8.37. Mass add-on – burst strength specimens.

	Oxidant only	1 x poly(EDOT)
Polypropylene	0.26 %	0.51 %
Polyester	-0.03 %	0.59 %
Acrylic	0.00 %	0.64 %
Wool	-0.05 %	0.39 %
Cotton	-0.20 %	0.40 %

Table 8.38. Surface resistance – burst strength specimens.

	Oxidant only	1 x poly(EDOT)
Polypropylene	> 20 GΩ[1]	26.04 kΩ
Polyester	> 20 GΩ	1.366 kΩ
Acrylic	> 20 GΩ	2.258 kΩ
Wool	> 20 GΩ	3.176 kΩ
Cotton	3.147 GΩ	694.8 kΩ

Notes:

1. The highest resistance measurable on the apparatus used.

The mass add-on values were consistent with those in Section 8.10.1; particularly those for 1 x poly(EDOT), which are all very close to the values given in Table 8.34. The sole oxidant-only result that stands out was that for polypropylene. This specimen had yellow staining at the edges, where the overlocking threads were. It was very difficult to rinse this yellow substance (presumably iron (III) chloride) out of the fabric after the impregnation and evaporation procedures. The 0.26% mass add-on probably represents this residual material. However, as it was confined to the very edges of the specimen it did not interfere with the fabric burst strength test.

In every case the resistance values obtained here were slightly larger than those obtained in Section 8.10.1. The fibre types were ordered the same as previously, except for wool and polypropylene which had swapped positions. Polyester, acrylic and wool increased (compared to Section 8.10.1) by less than a factor of two, while cotton increased by a factor of three and polypropylene by a factor of 12. Polypropylene may have been disadvantaged in the scaling up of the process by its higher mass per unit area, meaning that there was substantially more of it in the polymerisation solution than of the other fabrics (approximately 8.1 g compared with 5.3-6.7 g for the other fabrics). This may have meant that insufficient reagents were present relative to the amount of substrate to provide as thorough a treatment as the earlier experiments. Bearing this in mind, the results (including mass add-on) were sufficiently close to those found previously to justify the use of these specimens for burst strength testing.

8.10.2.4 Burst Strength Results.

The progression of fabric burst strength at each stage in the treatment process is illustrated in Figure 8.32. The data are the average of four tests made on each fabric specimen. Full data, including standard deviation and the time taken to burst, are given in Appendix 4 (8.10.2). The fabrics did vary substantially in strength, and, with the exception of the polypropylene fabric, did so in the expected order: polyester, acrylic, cotton and wool (from strongest to weakest). Polypropylene is not particularly strong, but this polypropylene fabric was slightly heavier than the other fabrics, and its higher strength may be due to this.

It is apparent from these results that neither the polymer coating treatment nor a blank oxidant only treatment had any substantial effect on the fabric burst strength. The polyester and acrylic fabrics are the only ones for which the burst strength of the polymer-coated version was weaker than the fabric as it was received, and this by only 1.8% and 4.6% respectively. The cotton fabric appeared be stronger just from the pre-polymerisation preparation process –

probably a result of the small amount of shrinkage that this fabric was observed to undergo during this process, which had the effect of making the prepared fabric slightly more densely constructed than it was originally, with more threads (warp and weft) to resist fabric rupture per unit area of the fabric.

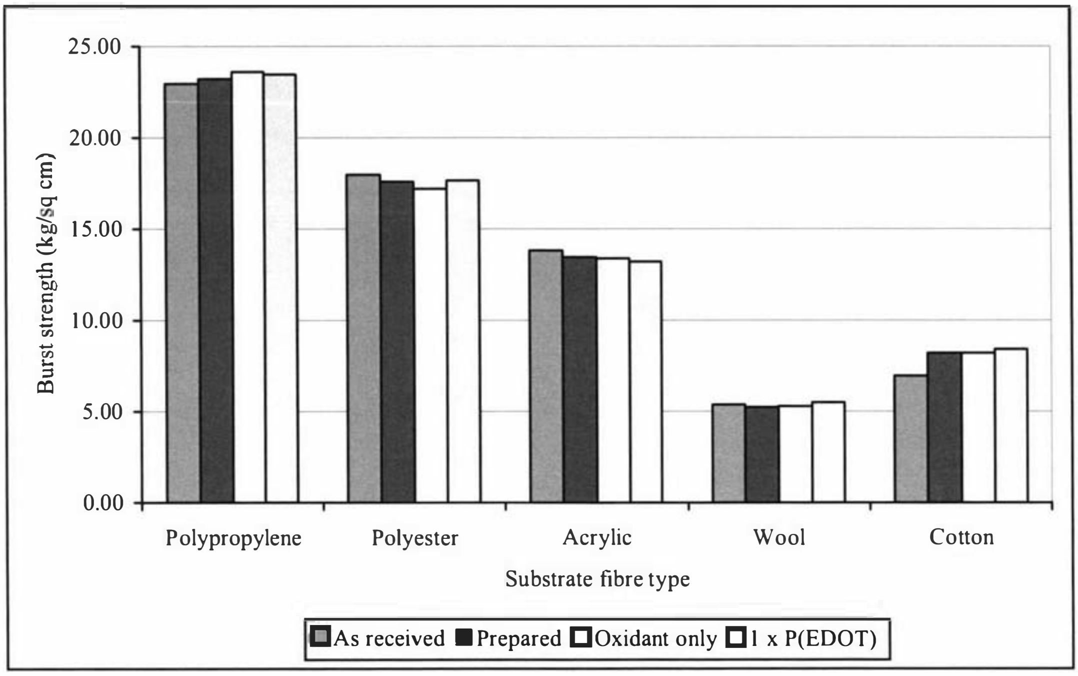


Figure 8.32. Burst strength of standard fabrics.

8.10.3 Summary and Conclusions.

The most important conclusion to be drawn from these data is that the single-dip polymer coating process had little effect on the mechanical properties of the fabric. Both fabric burst strength and bending behaviour (two straightforward tests of the fabric's mechanical properties) were unaffected, or only slightly affected, by the addition of poly(EDOT) coatings.

There are many more laboratory tests that could be used to determine the influence of ICP coatings on the fabric's mechanical properties, including the more subtle KES and FAST systems [159], which assess the fabric bending, shear, compression and tensile properties at low loads. These are particularly useful for objectively measuring fabric handle (how it feels) and for predicting how a fabric will behave in tailoring. They would be useful to carry out in future research if the textile-ICP composites were to be used in applications such as garment-based wearable devices.

8.11 Durability of Textile-ICP Composites.

8.11.1 Background.

In Sections 8.4.2.3 and 8.7.4, the long-term ageing behaviour of composites in ambient conditions was examined, and the effect of oxidant counter-ion and fibre type respectively assessed. It was necessary to carry out a broader examination of durability under different conditions, to answer some key questions about the polymers, methods of preparation and substrates. In particular, the following issues were addressed:

- Does a textile-poly(EDOT) composite have better durability of electrical properties than a textile-polypyrrole composite? The expectation is that it will, as thiophene-based ICPs are reportedly more stable over time than polypyrrole [5,6].
- What ageing process causes the greatest deterioration, and do washing and similar textile care procedures cause a greater deterioration than ageing in ambient conditions? For any use in a 'smart' textile device, the durability issue must be addressed, and care processes that cause unacceptable deterioration identified and alternatives found.
- What influence does the textile substrate (particularly the fibre type) have on composite durability? It is likely that some influence will be found, as the fibre type of the substrate is influential on many other textile-IPC composite properties.
- What influence does the dopant anion have on composite durability? The dopant anions that have been used (as counter-ions to Fe^{3+} in the oxidant) vary in size and composition. It is likely that larger anions, once incorporated into the ICP, will be less likely to be lost over time or with subsequent ageing processes, but other factors may also have an influence.
- Can the durability (as well as the initial electrical properties) be improved by applying multiple layers of ICP? Perhaps the outermost layers provide a degree of protection for the inner ones, or perhaps the coating can be made more uniform by this technique, and thus better avoid localised failures.

It should be noted that, in the context of this section, the term 'composite durability' refers specifically to the deterioration of electrical properties; i.e. the change in surface resistance.

An extensive trial was carried out to answer the above questions, with 48 specimens undergoing various ageing or durability-testing processes over several months, having regular measurements made of their electrical properties.

8.11.2 Methodology.

An experimental design was devised to minimise the influence of factors other than those being investigated. Three fabric substrates were used: the standard woven fabrics from polypropylene, polyester and wool. These give a good range of fibre properties, from the chemically-inert polypropylene through to the more complex wool fibre. Previous experiments determined that these fabrics also covered a wide range of surface resistance values, with polyester generally having the lowest, and polypropylene the highest.

16 rectangular specimens (35 x 20 mm) were cut from each of the fabrics, with the long dimension oriented along the warp direction of the fabric. Threads were removed from their edges until they measured 30 x 15 mm plus fringe, the correct width for testing the surface resistance by the usual method (as described in Section 4.3). They then underwent the usual preparation process of rinsing, drying, and conditioning (as described in Section 4.1).

Each of the three substrates was coated with poly(EDOT) by the method described in Section 4.4.4, with each of the polymerisation set-ups described in Table 8.39, making a total set of 12 specimens. This set of 12 specimens was duplicated four times, with each set undergoing a different ageing process.

Table 8.39. Polymerisation conditions for durability specimens.

Code	Precursor	Precursor concentration	Oxidant*	Oxidant concentration	Solvent	Number of ICP layers
A	EDOT	0.03	$FeCl_3$	1.0 mol/L	CH_3OH	1
B	EDOT	0.03	$FeCl_3$	1.0 mol/L	CH_3OH	5
C	Pyrrole	0.03	$FeCl_3$	1.0 mol/L	CH_3OH	1
D	EDOT	0.03	$Fe(ClO_4)_3$	1.0 mol/L	CH_3OH	1

* The hydrated versions of the oxidants given were used.

These specimens allowed an investigation (for each ageing process) into the effect of precursor (and hence conductive polymer, comparing EDOT with pyrrole), the effect of oxidant counter-ion (and hence dopant anion, comparing chloride with perchlorate) and the effect of the number of ICP layers applied (one compared with five). The three different substrates were also compared.

Control: This set of 12 specimens was kept in standard conditions (20°C, 65% relative humidity) for the duration of the durability assessment.

Elevated temperature: This set of 12 specimens was taken from standard conditions and placed in a conventional laboratory oven at 100°C for one hour, allowed to cool in the laboratory for one hour, then returned to standard conditions.

Rinsed: This set of 12 specimens was taken from standard conditions and rinsed in groups of three different substrates that had undergone the same polymerisation conditions. They were rinsed for two minutes in 500 mL of distilled water, with gentle agitation provide by a magnetic stirrer. They were then pressed against absorbent paper to remove excess water and air-dried in the laboratory before being returned to standard conditions.

Washed: This set of 12 specimens was taken from standard conditions and washed in groups of three substrates that had the same polymerisation conditions. They were washed for 2 minutes in 300 mL of tap water at between 40 and 50°C, with a standard detergent at a concentration of 1 g/l. The standard detergent was of the type described in ISO Test Method 6330, Annex B [160], having anionic surfactants, sodium silicate, carbonate and tripolyphosphate. Gentle agitation was provided with a magnetic stirrer, then the specimens were transferred to a beaker with 300 mL of cold tap water and rinsed for a further two minutes. They were finally removed and pressed against absorbent paper before being air-dried and returned to standard conditions.

The testing routine was structured so that all sets were assessed at the same time, in the standard conditioned room. The procedure ran for several weeks thus:

1. Specimens placed into the standard conditioned room for at least 24 hours before measurement of surface resistance carried out.
2. All specimens (except control set) removed from conditioned room, and ageing/durability treatment carried out approximately simultaneously.
3. After drying or cooling in laboratory conditions (1 – 2 hours), specimens were returned to the condition room.
4. After a minimum of 24 hours, the specimens again had their surface resistance measured.

The process was repeated for ten cycles. The routine can be thought of as four sets of specimens ageing in the same conditions, with three of the sets periodically receiving different treatments to accelerate the ageing process. Note that each surface resistance measurement was the average of the surface resistance measured on each face of the specimen.

Each of the ageing/durability processes was expected to affect the textile-ICP composite in a different way. The elevated temperature treatment accelerates ageing that occurs by a chemical mechanism (such as oxidation), and would also tend to drive off any volatile components in the ICP. The rinse treatment removes any remaining water-soluble components that are not well bound (chemically or physically) into the composite (distilled water was used, so any chemical degradation from this process should be minimal). The wash treatment was potentially the most destructive, as it involved an elevated temperature, tap water (providing numerous impurities such as chlorine and salts) and a (relatively) chemically aggressive detergent.

8.11.3 Results and Discussion.

A very large quantity of data was collected from this series of tests: 480 data points in total; each being an average of two readings. Hence the analysis of this data presented some challenges. Each specimen started at a different surface resistance, with perchlorate-doped poly(EDOT) lower resistance than chloride-doped, five layers lower than one layer, and so on. A direct comparison of resistance was of limited value, as the focus of this investigation was the change in resistance over time and with durability/ageing cycles. To follow this progression, the relative resistance (R') was calculated from each data point. This was the specimen's resistance at any time divided by its initial resistance (as measured before any of the ageing/durability cycles were carried out). These initial resistance values are provided in Table 8.40, and followed much the same pattern observed previously; perchlorate-doped poly(EDOT) having lower surface resistance than chloride-doped poly(EDOT), five layers having lower resistance than one layer, and poly(EDOT) having a lower resistance than polypyrrole. The effect of the substrate fibre type is as expected, with polyester always the lowest, followed by wool, then polypropylene (with the exception of the situation for polypyrrole, where the positions of wool and polypropylene are reversed).

The progression of R' over repeated ageing/durability cycles was plotted for each specimen, and is the easiest way of observing significant trends in the results. These plots have been prepared for each substrate and condition of ageing. Each of the four conditions of polymerisation is a separate series on each chart. The set of charts for polyester are shown here as Figures 8.33 to 8.39, while those for the other substrates are provided in Appendix 4 (8.11.2). They followed essentially the same pattern as those for polyester, so can be excluded from the analysis at this stage. Table 8.41 provides the final relative resistance values for all substrates, as a means of making comparisons across the full range.

Table 8.40. Initial surface resistance values.

Substrate	Initial surface resistance (Ω/square)			
	A EDOT/Cl x 1	B EDOT/Cl x 5	C Pyrrole/Cl x 1	D EDOT/ClO$_4$ x 1
Polypropylene	5.73 (4.93) x 10^3	5.66 (3.18) x 10^2	2.57 (0.60) x 10^4	6.94 (4.87) x 10^2
Polyester	1.46 (0.49) x 10^3	2.64 (1.02) x 10^2	3.37 (0.52) x 10^3	2.66 (0.58) x 10^2
Wool	2.85 (1.59) x 10^3	3.16 (1.51) x 10^2	5.65 (7.58) x 10^6	6.04 (1.02) x 10^2

Note: At this initial stage there were 12 sets of four identical specimens with the same substrate and polymerisation conditions. Therefore, the results in Table 8.40 are the average of these four specimens, with the standard deviation provided in parentheses.

8.11.3.1 Control.

All of the specimens showed R' values that fluctuated somewhat, with a trend of gradual increase in resistance after an initial decrease (Figure 8.33). The fluctuation was more marked later in the assessment (cycles six to ten); presumably as a result of localised deterioration of the ICP coating causing the placement of the terminals on the specimen to have a greater influence on the measured resistance.

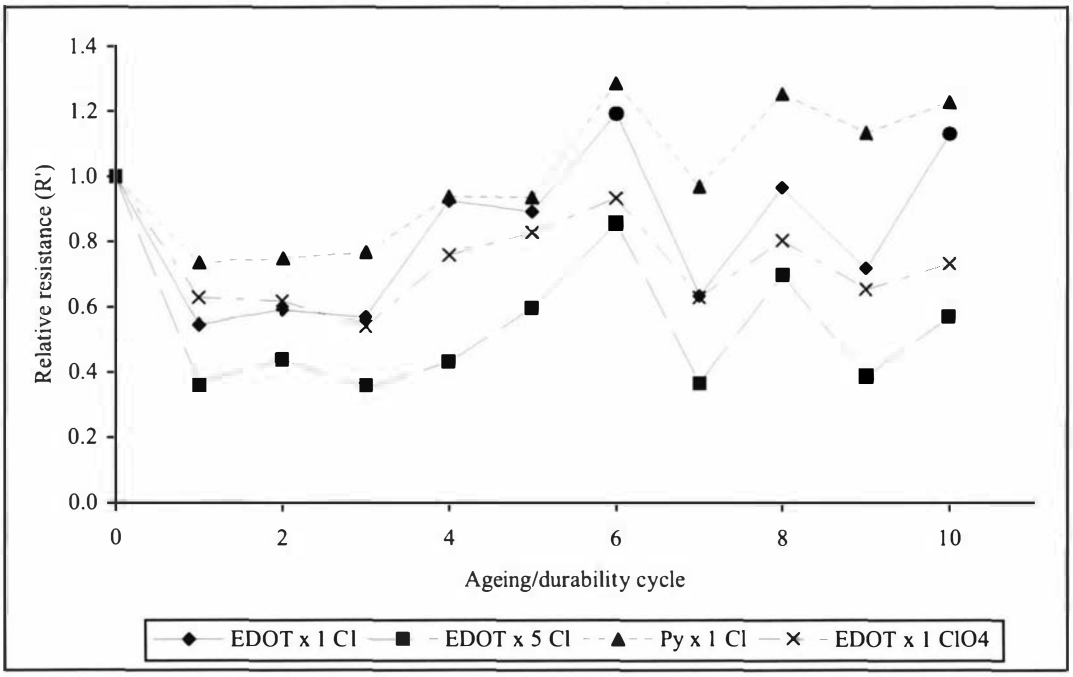


Figure 8.33. Progression of R' – polyester, control.

Of some concern was the way that for each specimen, the fluctuations up and down seem to be synchronised. In other words, on any particular occasion the resistance values for all specimens were relatively low or high. This suggests a systematic error in resistance measurement, or possibly inconsistencies in the environmental conditions. Resistance measurements throughout this work were made with the resistance meter (ohmmeter) functions of either a Fluke 19 or a Center 122S multimeter (always the same meter for every measurement of a particular experiment; in this case the Fluke), both of which had new batteries, and were recalibrated annually. Hence a systematic error in the measurement system seems unlikely, but cannot be completely ruled out. The relative humidity and temperature levels in the conditioned room did fluctuate somewhat – the standard [144] allows for ±2°C and ±5% relative humidity. If the ICPs were particularly sensitive to temperature and/or relative humidity, this would be an explanation for the fluctuations. Sensitivity to moisture is well known for polypyrrole [128] but less likely for poly(EDOT). Sensitivity to temperature has been observed for ICPs [127] but no data are available for chemically polymerised poly(EDOT).

The initial decrease in resistance was quite marked, and is a feature of particular interest. This 'conditioning' of the composites may relate to the absorption of substances from the environment into the composite. The progressive absorption of CO_2 into polypyrrole has been observed over a short period of time after its preparation [3], and the absorption of moisture from the atmosphere could also be responsible for changes in resistance during the first few days (although less likely for poly(EDOT)). The time-scale involved here was three days between preparation and initial measurement, and another three days between that measurement and the measurement made after the first durability/ageing cycle.

8.11.3.2 Elevated Temperature.

Figure 8.34 indicates the progression of R' as successive elevated temperature cycles were carried out. In contrast with Figure 8.39, there was a clear trend of increasing resistance (which confirms that this process does accelerate the deterioration process) except for the ClO_4-doped poly(EDOT), which remained remarkably stable over time. The worst performance was that of Cl-doped polypyrrole, reaching more than ten times its original resistance after ten cycles. This result indicates better stability of poly(EDOT) by comparison with polypyrrole when exposed to accelerated conditions of ageing by elevated temperature.

In Figure 8.35 the same data are plotted, except that the polypyrrole series has been removed to allow the relationship between the three poly(EDOT) specimens to be more easily observed. The stability of the ClO_4-doped specimen is clear, while both Cl-doped specimens appeared to age at approximately the same rate, regardless of the number of layers of EDOT.

It is possible that the five-layer version was marginally better. Some of the same synchronised fluctuations observed for the control set were also apparent here, with the same explanations applicable.

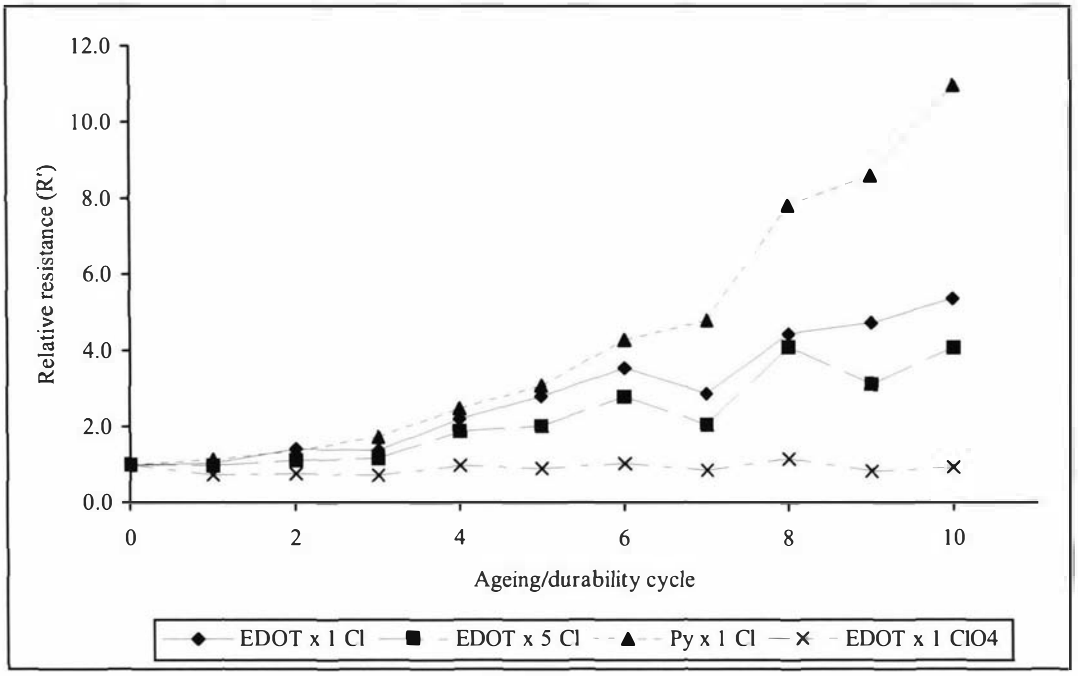


Figure 8.34. Progression of R' – polyester, elevated temperature.

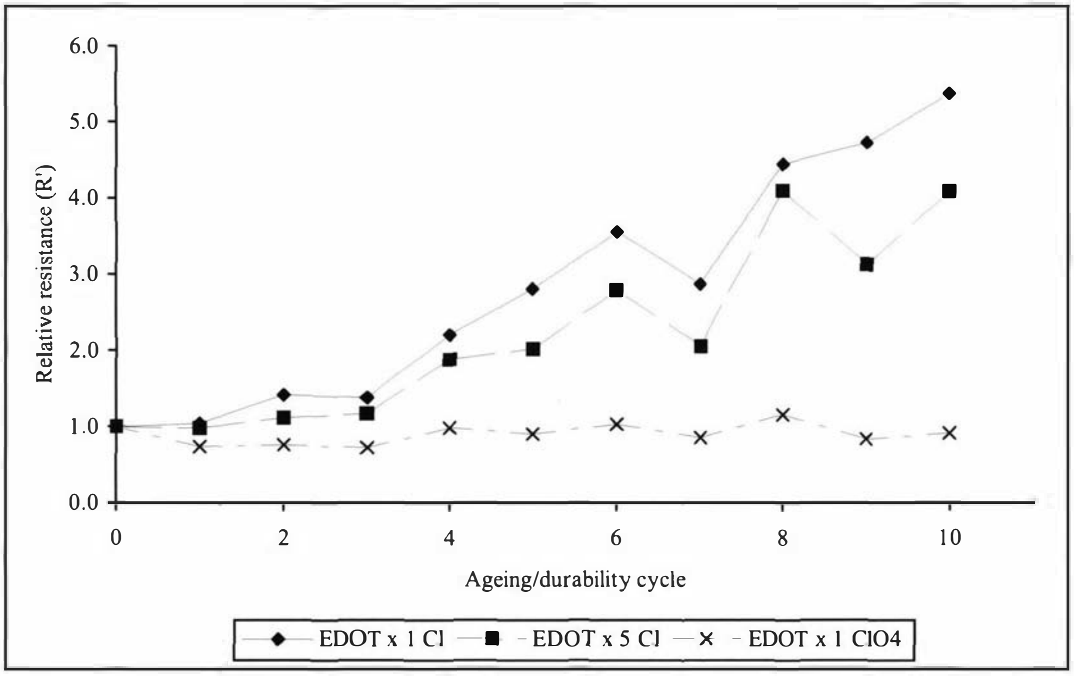


Figure 8.35. Progression of R' – polyester, elevated temperature, polypyrrole excluded.

It seems that, as predicted, the larger perchlorate anion was better trapped in the ICP than chloride, and was less prone to loss under conditions of elevated temperature. Polypyrrole was also clearly much less stable than poly(EDOT) under these conditions, with degradation of the polymer backbone possibly accelerated.

8.11.3.3 Rinsed.

It is immediately apparent from Figure 8.36 that the polypyrrole composite performed far worse than all of the poly(EDOT) specimens; to the extent that it is impossible to draw any conclusions about the poly(EDOT) specimens from this chart. Therefore the same data has been plotted in Figure 8.37 without polypyrrole present. From this figure it appears that there was very little difference in performance between the poly(EDOT) specimens, although the ClO_4-doped specimen finished at the lowest value by a small amount.

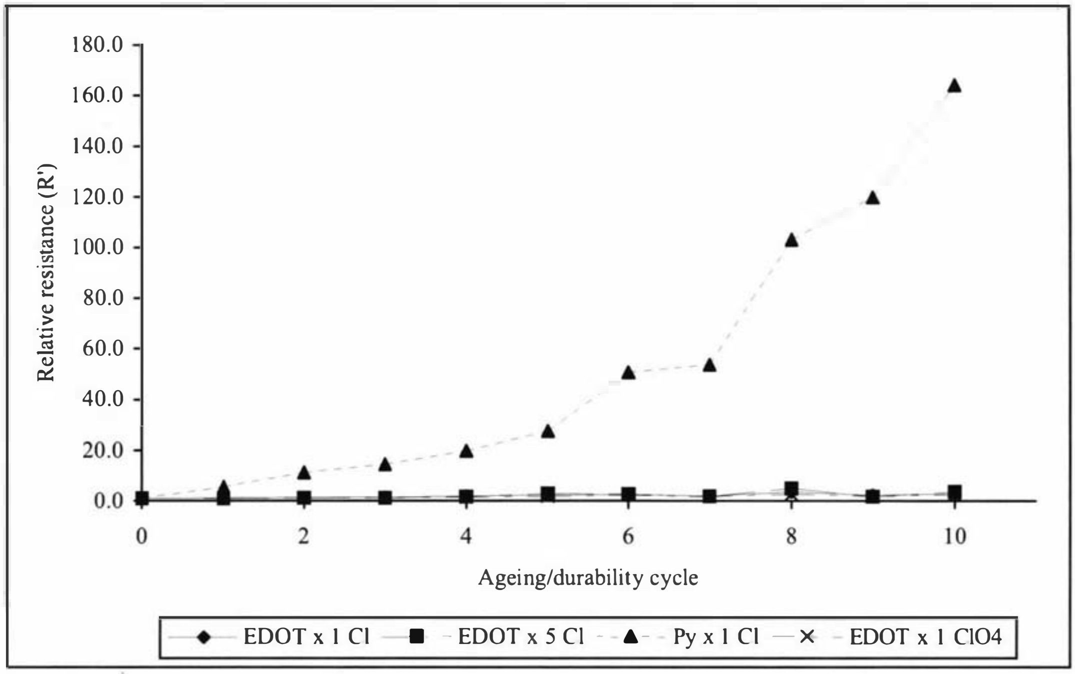


Figure 8.36. Progression of R' – polyester, rinsed.

Rinsing in distilled water caused an accelerated degradation in the composite's electrical properties, compared with the control. Presumably water provided a degree of mobility for species that can be lost from the polymer (such as the dopant anions). The gentle agitation employed could also have caused some physical breakdown of the polymer coating. Both of these phenomena would contribute to the increased resistance that was observed. The polypyrrole specimen performed worse in the 'rinsed' assessment than in the 'elevated temperature' assessment, finishing at a value more than 100 times its original, as compared to only ten times for the elevated temperature. This suggests that the mechanisms that cause degradation in polypyrrole were more apparent in the water rinse than in hot air. The Cl-doped poly(EDOT) specimens were at roughly the same level after the rinsing series as they were after the elevated temperature series. Of note however, was the performance of the ClO_4-doped poly(EDOT) in water (final R' ~2.5) compared to hot air (final R' ~0.9). One explanation could be that the water provided an opportunity for the perchlorate anion to migrate out of the ICP, while heat did not.

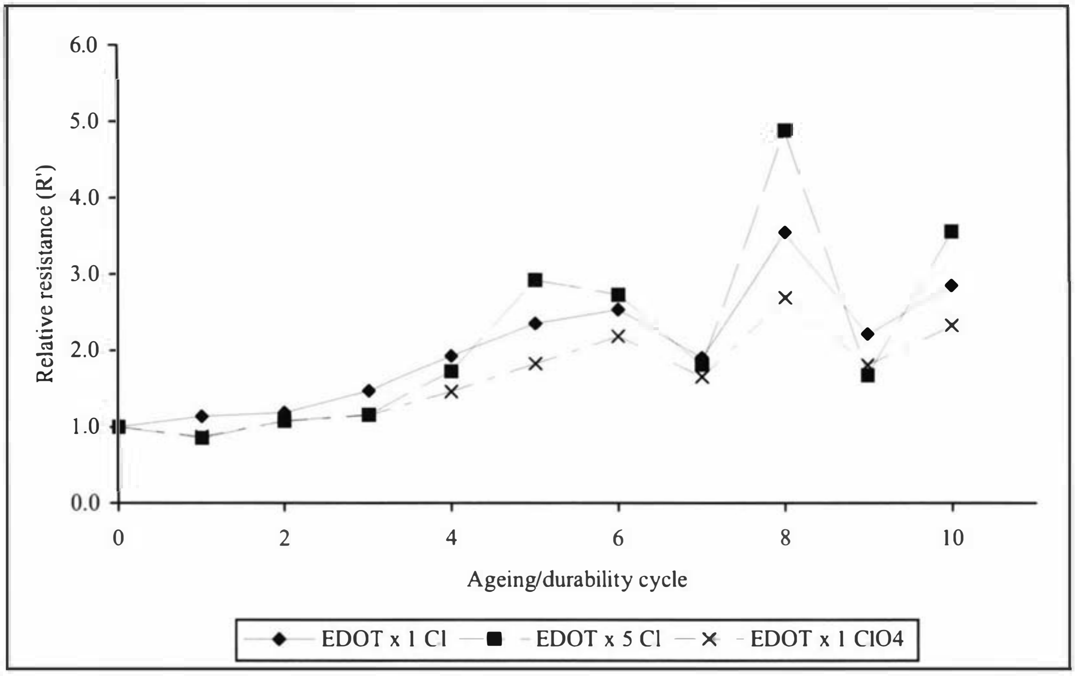


Figure 8.37. Progression of R' – polyester, rinsed, polypyrrole excluded.

8.11.3.4 Washed.

From Figure 8.38 it is clear that the washing the polypyrrole specimen in hot tap water with detergent had a substantial effect on its R'. It was necessary to remove the polypyrrole series and re-plot the data to observe the progression for the poly(EDOT) specimens, and this is shown in Figure 8.39. The polypyrrole specimen showed the greatest deterioration in comparison with the rinsed specimens. Its deterioration was substantial, reaching over 700 times its initial resistance by the end of the assessment. Clearly it was very much more susceptible to degradation in these conditions than in distilled water rinsing, probably as a result of the high temperature and the chemically aggressive detergent. The detergent also acts as a wetting agent, which means that any water-related deterioration (such as the removal of dopant ions) would be increased when detergent is present.

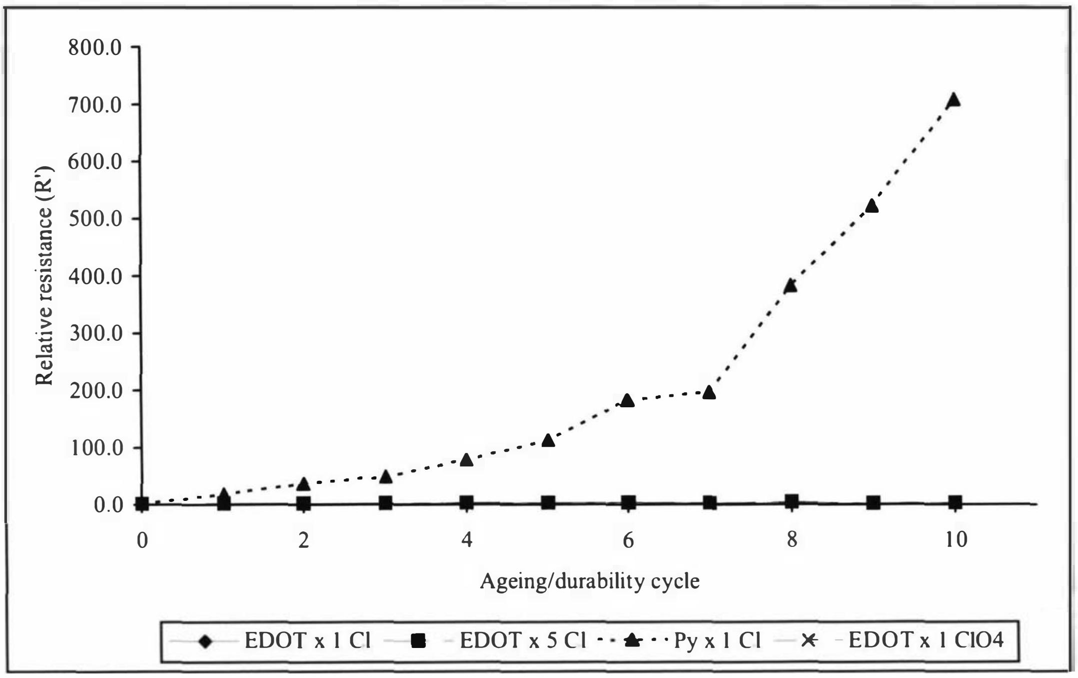


Figure 8.38. Progression of R' – polyester, washed.

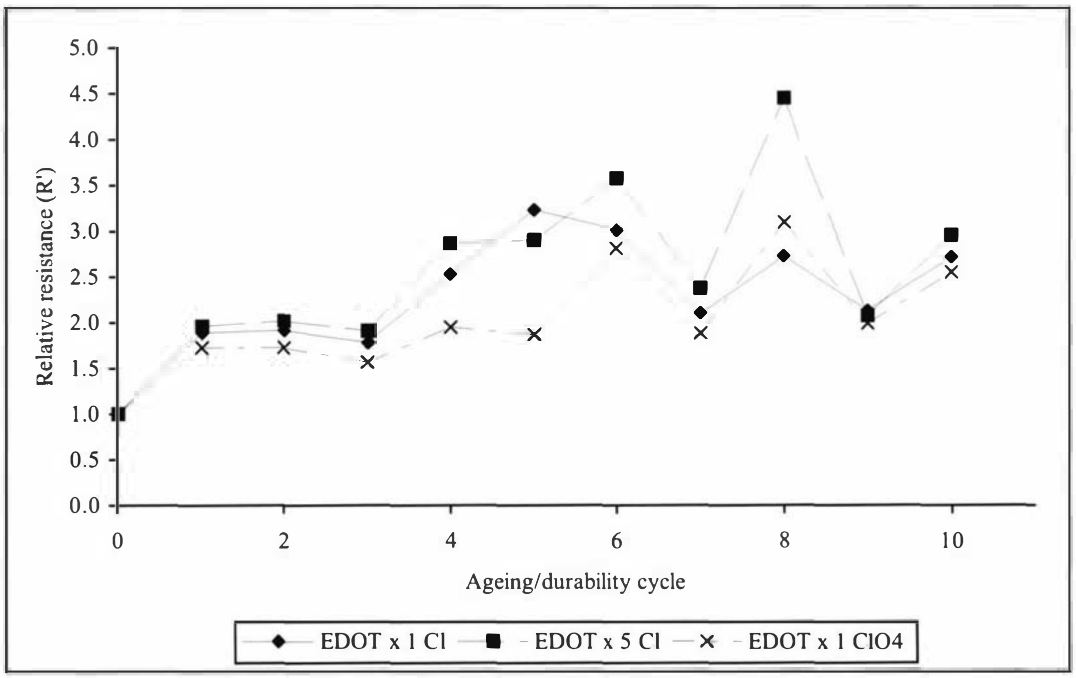


Figure 8.39. Progression of R' – polyester, washed, polypyrrole excluded.

In spite of the harsher conditions associated with this situation, the poly(EDOT) specimens deteriorated in a way roughly similar to that when distilled water was used, with final R' values of between two and three.

8.11.3.5 Other Results.

The final results (i.e. after all ten durability/ageing cycles) for all four substrates are provided in Table 8.41. This allows the other substrates to be assessed and compared with polyester.

Table 8.41. Final R' values, all substrates.

		Final R'			
Ageing Conditions	Substrate	A EDOT/Cl x 1	B EDOT/Cl x 5	C Pyrrole/Cl x 1	D EDOT/ClO_4 x 1
Control	Polypropylene	0.829	0.586	3.289	0.543
	Polyester	1.132	0.570	1.230	0.733
	Wool	0.836	0.548	14.3	0.792
Elevated temperature	Polypropylene	2.23	1.79	30.9	0.590
	Polyester	5.36	4.08	11.0	0.910
	Wool	2.61	2.65	138	1.65
Rinsed	Polypropylene	1.49	3.60	975	3.04
	Polyester	2.85	3.57	164	2.33
	Wool	3.10	2.47	105	2.03
Washed	Polypropylene	6.56	3.73	2670	2.60
	Polyester	2.71	2.95	708	2.55
	Wool	2.30	2.52	1990	3.29

Considering first the control set, the same basic trend is evident for polypropylene and wool as for polyester. The poly(EDOT) specimens changed very little from their initial resistance values, in fact all of the poly(EDOT) specimens (with the exception of the single layer of Cl-doped poly(EDOT)), had slightly lower resistance at the end of the assessment than at the beginning. In comparison, the polypyrrole resistance increased somewhat, more so for polypropylene and wool than for polyester. Polypyrrole on wool aged particularly badly, reaching a final resistance 14 times greater than its original.

At the elevated temperature, the same general conclusion can be drawn for wool and polypropylene as for polyester. The polypyrrole specimen was clearly the worst (again particularly poor on wool), and the ClO_4-doped poly(EDOT) the best. There was very little to separate the two Cl-doped poly(EDOT) specimens (one-layer compared with five-layer).

After undergoing the distilled water rinse ageing/durability assessment, the same outcome was observed for wool and polypropylene as for polyester. Very little difference between the performances of the three poly(EDOT) specimens was observed, with the performance of the Cl-doped one-layer similar to that of the five-layer, and the ClO_4-doped version changing by about the same factor. Polypyrrole composites performed poorly with all substrates; polypropylene in particular deteriorating by a factor of nearly 1000.

The washing process had a substantial effect on all of the polypyrrole composites. Polypropylene and wool performed worse than polyester, with final resistance values about 2000 times worse than the original values. This represents a change from the kΩ range to the MΩ and even the GΩ range. Again, it is hard to separate the performances of the poly(EDOT) composites; with the exception of the Cl-doped polypropylene composite, they all deteriorated by a factor of about three.

8.11.4 Summary and Conclusions.

As expected, all of the ageing/durability treatments accelerated the deterioration of the electronic properties of the composites. The resistance of the control sets of specimens showed only a gradual increase, after an initial decrease. All of the other processes showed an increase in resistance through progressive treatments. The initial decrease in resistance seen with the control specimens is an interesting phenomenon; perhaps being some kind of conditioning process as the ICP absorbs something from the atmosphere (such as water or CO_2) that improves conductivity.

By far the most striking result from this work is the particularly poor durability of the polypyrrole composites. This was apparent for all ageing/durability conditions used. It was especially apparent for specimens that had been washed, with the polypyrrole composites having final R' values between 700 and 2700, compared with 2.5 to 6.5 for the poly(EDOT) composites. The three poly(EDOT) specimens were roughly equal in performance in most conditions, other than the set aged by periodic exposure to an elevated temperature in the laboratory oven. For this set, the ClO_4-doped poly(EDOT) clearly performed better than the Cl-doped versions. There was no apparent difference between the Cl-doped poly(EDOT) composites prepared with either a single layer or with five layers of the ICP. The initial resistance of the ClO_4-doped poly(EDOT) and five-layer Cl-doped poly(EDOT) specimens was very much lower than the single layer Cl-doped poly(EDOT), so the fact that their durability performance is no worse makes these a preferred means of preparing textile-poly(EDOT) composites.

There were no clear durability relationships associated with the substrate fabric fibre type, although the polypyrrole composites prepared on a wool substrate were particularly poor in dry conditions (control and elevated temperature), and polypyrrole prepared on a polypropylene substrate particularly poor in wet conditions (rinsed and washed). There was no clear pattern with poly(EDOT), nor were there particularly large differences in performance for the different substrates under the various conditions.

Synchronised fluctuations that were observed in the resistance readings for all the specimens around ageing durability cycles six to ten are of some concern, as they point to a possible systematic error in measurement. While they do not cast doubt upon the main conclusion of this work (notably the superiority of poly(EDOT) over polypyrrole in all conditions, and of ClO_4-doped poly(EDOT) over Cl-doped poly(EDOT) at high temperature), they are nevertheless alarming. To ensure that they weren't the result of an instrument error in the ohmmeter, a brief trial was carried out to assess the consistency of performance of the meter, and to determine the between-measurement variability that is inherent in these specimens and their measurement. This was done by making measurements on a single specimen at ten-minute intervals, with the meter and other testing apparatus switched off and packed away between each measurement, just as it was during the original experiment. This test was carried out several months after the durability assessment, and the specimens used were the control set, polypropylene, EDOT/Cl x 1 and EDOT/ClO_4 x 1. The results of twelve consecutive measurements are provided in Table 8.42, and graphed in Figure 8.40.

The results indicate that a reasonable variation in successive measurements on the same specimen is possible, most likely because of variation in the exact placement of the measurement apparatus on the specimen, from measurement to measurement. As there is likely to be slight variation in the ICP coating along the length of the specimen, this will bring about variability in the resistance reading. The nature of the electrical contact between the measurement apparatus and the specimen could also affect the resistance reading; influenced by the precise position of the apparatus in relation to the yarns in the substrate. If the terminal on the apparatus slips into a channel between two adjacent yarns, the electrical contact is likely to be better than if it sits exactly on top of a yarn. This sort of variability is inherent in non-homogeneous materials such as textiles, and unavoidable in their measurement.

Figure 8.40 indicates the fluctuation in R' for these two specimens (relative resistance calculated from the above data, taking the first reading as the value by which the others are normalised). The variability from reading to reading (discussed above) is apparent, but there is no obvious synchronous fluctuation between the specimens. Between measurement five and nine, for example, the two specimen's readings are moving in opposite directions. Any instrument error can therefore be ruled out, which means that the fluctuation behaviour observed for the specimens during the durability assessment must be from some other (unknown) source.

Table 8.42. Variability of resistance measurements.

Measurement	Surface resistance (Ω/square)	
	EDOT/Cl x 1	EDOT/ClO_4 x 1
1	4490	364
2	4340	352
3	4820	371
4	4210	369
5	5050	434
6	4710	490
7	4700	512
8	5360	426
9	5230	476
10	4980	445
11	5510	416
12	5400	418
Mean	4900	423
Standard deviation	428	52.3
Coefficient of variation	8.73%	12.36%
Minimum value (% below mean)	5510 (+12.5%)	512 (+21.1%)
Maximum value (% above mean)	4210 (-14.1%)	352 (-16.7%)

The data here also serve to indicate the long-term stability of electrical performance for these two specimens. These measurements were made seven months after the last measurements made during the ageing durability assessment, when the surface resistance of these two specimens was 4.75 kΩ/square (Cl-doped) and 376 Ω/square (ClO_4-doped). They were stored in plastic bags and sealed, with no special attempt made to exclude air. The durability of electrical performance continues to be impressive, with average values on this occasion of 4.90 kΩ/square (Cl-doped) and 423 Ω/square (ClO_4-doped). This performance is very encouraging, and shows that textile-poly(EDOT) composites offer a superior alternative to textile-polypyrrole composites.

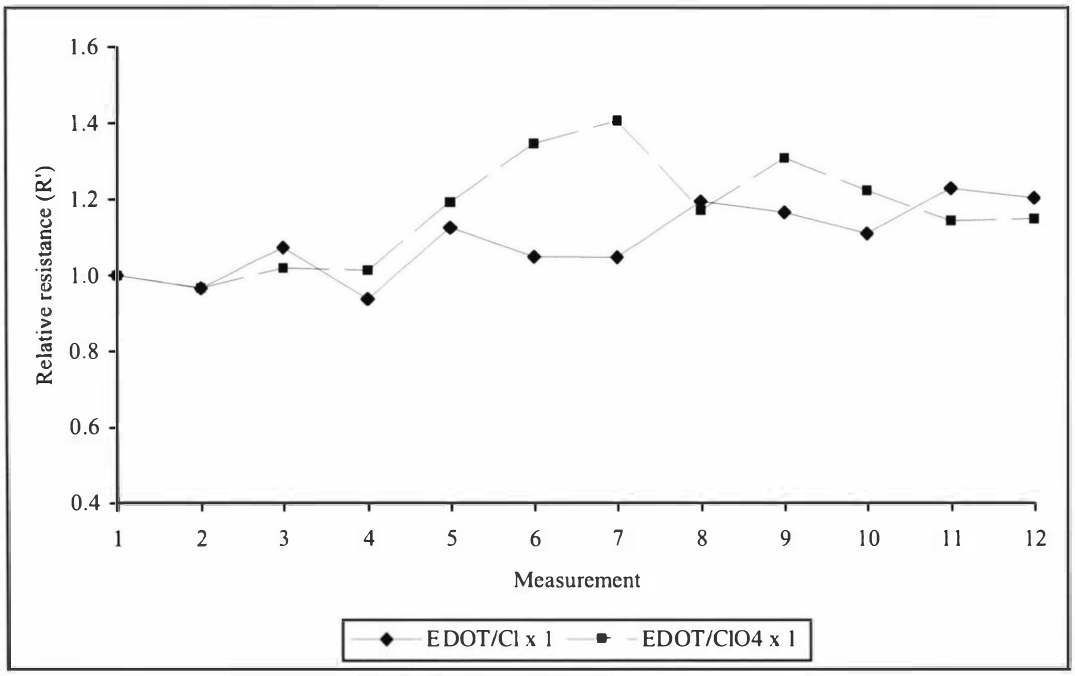


Figure 8.40. Variability of R' over successive readings.

8.12 Characterisation of Textile-ICP Composites.

This section describes a variety of techniques that were used to characterise the textile-ICP composites prepared by the single dip method. Microscopy techniques were employed, alongside theoretical analysis and elemental analysis. Scanning electron microscopy (SEM) is omitted from this section, as it has been documented elsewhere (Sections 8.7 and 8.9).

8.12.1 Thickness of Coating and Extent of Polymerisation.

8.12.1.1 Background.

It is useful to know the thickness of the polymer coating that is deposited onto the fibres by the single dip (or any other) deposition technique. The obvious way of doing this is to examine fibre cross-sections under conventional light or transmission electron microscopy (TEM). With this approach, it is also possible to determine if polymer formation is confined to the surface of the fibres, or also occurs inside the fibre. The major disadvantage is that it is very labour intensive to measure a statistically useful number of fibres, as it is likely that the polymer coating is not uniform along the length of a single fibre. Because fibres are treated in an assembled form (usually in the fabric), there are some areas of the substrate that the polymerisation solution will penetrate more easily, and be more likely to accumulate in, thus producing thicker polymer coatings than other areas.

It is possible to use the mass add-on to calculate the average thickness of the poly(EDOT) coating deposited onto the fibres, by determining the volume of the poly(EDOT) from the mass add-on and the ICP's density, and calculating the thickness of an annular ring of poly(EDOT) around the fibres. As stated, this requires the density of the poly(EDOT) to be known, which depends on the exact method of synthesis and any dopant anions that are present. As the density of Cl-doped, chemically polymerised poly(EDOT) was not known, this approach was not used.

An alternative is to use a fibre diameter analysis system to measure the diameter of fibres that have been coated with poly(EDOT), and derive the coating thickness from this. Comparison with untreated fibre is necessary in this case, and it is also necessary to make the (reasonable) assumption that the coating forms an annular ring around the cylindrical substrate fibres. Automated fibre diameter testing systems (using image analysis techniques) exist, which measure the diameter of large numbers of fibres from a single sample, and potentially several diameters along the length of some fibres. One system in use (and available at WRONZ) is

OFDA (Optical Fibre Diameter Analyser) [146]. The only drawback is that these systems are designed to measure fibre dimensions to an accuracy of about 0.1 μm. Given the inherent variability of the diameter of the substrate fibre and potential variability in the coating thickness, it would be prudent to have a difference in diameter between treated and untreated fibres of at least 0.5 μm. This may not be the case with a standard polymer deposition treatment. One way to overcome this problem is to measure the diameter of treated fibres that have had multiple coatings, and then to calculate the average thickness of one coating. Previous results (see Section 8.9, Table 8.29) indicated that when multiple coatings were used, the amount of polymer added (mass add-on) per treatment remained constant. Therefore it is reasonable to assume that the thickness of each layer was approximately the same.

Having taken the above-mentioned issues into account, fibre diameter measurement, light microscopy and TEM were used to analyse the coating thickness and the extent to which polymer formed inside the fibres. The results of this work are discussed in this section.

8.12.1.2 Methodology.

Loose fibre was preferred to yarn or fabric for this work, as it is a more porous form of the textile and allows the polymerisation solution to be more evenly absorbed through the substrate. As this may result in a thicker coating on the fibres than would occur in a fabric or yarn, the results obtained here can be considered maximum coating thickness. Wool and polyester fibres were used; being an absorbent natural fibre with substantial chemical functionality, and a relatively chemically inert synthetic fibre, respectively. Fibre details are given below:

Wool:	24.5 μm diameter (nominal), untreated, processed to top.
Polyester:	1.5 dtex (11.8 μm diameter), 40 mm length, loose staple.

Five ~0.25 g samples of each fibre type were prepared for treatment by the usual method. Two samples of each fibre type were set aside to be untreated controls for microscopy and fibre diameter measurement. The remaining three samples were labelled and treated as follows (W and P refer to wool and polyester, respectively):

W4 x 1, P4 x 1: The fibre specimen had Cl-doped poly(EDOT) deposited onto it by the technique given in Section 4.4.4. A four-hour drying time was used, as the solvent evaporated relatively slowly from the thick 'mat' of loose fibre.

W60 x 1, P60 x 1: As for W4 x 1 and P4 x 1, except that an impregnation time of 60 minutes was used to determine if polymerisation would take place inside the fibre if a longer time was allowed for the reagents to be absorbed into the fibre.

W4 x 5, P4 x 5: The process described for W4 x 1 and P4 x 1 repeated on the same specimens five times to build up a thicker coating, giving measurable change in fibre diameter.

The fibre samples that had been treated only once (W4 x 1, P4 x 1, W60 x 1 and P60 x 1) were a little uneven (some areas darker in colour than others), suggesting that the polymer had formed an uneven layer on the fibres. W60 x 1 had a noticeable yellowish hue, presumably from the additional absorption of iron that occurred with the longer impregnation time. These specimens were submitted for microscopic analysis (light and TEM), with a requirement that only dark, uniform fibres be chosen for examination.

The fibre specimens that had five coatings applied were uniformly dark in colour. The polyester fibres had clumped together somewhat, but could be teased apart without any apparent damage to fibres or poly(EDOT) coating. These specimens were submitted to the WRONZ Testing Laboratory for OFDA fibre diameter measurement.

8.12.1.3 Results.

A. Fibre Diameter Measurement.

The fibre diameter analysis provided the mean and standard deviation of fibre diameter, the number of measurements made and other data relevant to the objective measurement of fibres. Coating thickness was calculated on the basis that the coating formed an annular ring around the fibres, as shown in Figure 8.41.

The treated fibre diameter (D) is equal to the sum of the untreated fibre diameter (d), plus the total coating thickness (T) multiplied by two:

$$D = d + 2T$$

Therefore:

$$T = (D - d) \div 2 \qquad (1)$$

With five coatings applied, the average individual coating thickness (t) is one-fifth of the total coating thickness:

$$t = T \div 5 \qquad (2)$$

Substituting (2) into (1), and rearranging yields:

$$t = (D - d) \div 10 \qquad (3)$$

Using equation 3, the average coating thickness was calculated from the untreated and treated fibre diameters. These data are provided in Table 8.43.

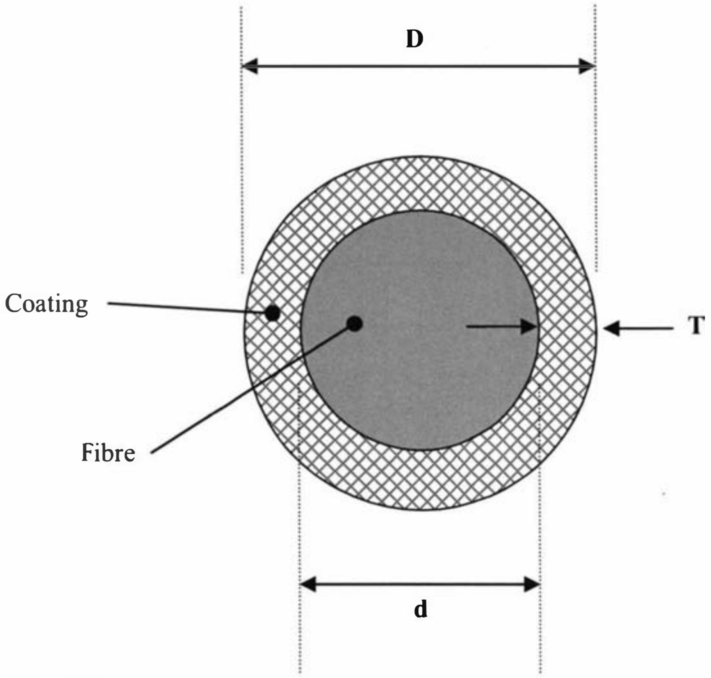


Figure 8.41. Annular polymer coating around cylindrical fibre.

Table 8.43. Fibre diameter and coating thickness.

Specimen	Mean fibre diameter (μm)	Standard deviation of diameter (μm)	Number of measurements	Calculated average coating thickness (nm)
W control	24.7	6.1	7657	---
W4 x 5	27.1	6.5	7805	240
P control	12.3	2.7	7393	---
P4 x 5	14.2	2.3	5022	190

The untreated fibre was close to its specified diameter in both cases. The standard deviation for the polyester was much lower than that for wool, indicating the expected lower variability for this man-made extruded fibre compared to a natural fibre. After treatment, the fibre diameter had increased by 9.7% for wool and 15.4% for polyester, allowing the coating thickness to be calculated with some confidence.

B. Light Microscopy.

Visibly well-coated fibres were mounted on acetate tabs, and examined under stereo and transmitted light microscopy at between 4x and 400x magnification, before dehydration and subsequent TEM processing. The untreated wool fibres were (as expected) white in colour, variable in diameter, and with undamaged exocuticle scales visible.

W4 x 1 fibres at two magnifications are shown in Figure 8.42. The polymer coating appeared (for the most part) as a pale blue shading to the fibres, with occasional specks of darker material. This suggests that the polymer formed a thin, reasonably uniform layer on the fibres, with smaller areas where polymer deposition was heavier, or where loose polymer formed away from the fibre surface subsequently accumulated. An image of a W60 x 1 fibre is shown in Figure 8.43, and it can be seen that this loose granular polymer is again present. There was also an underlying yellowish coloration to the wool for the W60 x 1 specimens, (not visible in Figure 8.43). This was presumably staining from iron (III) chloride.

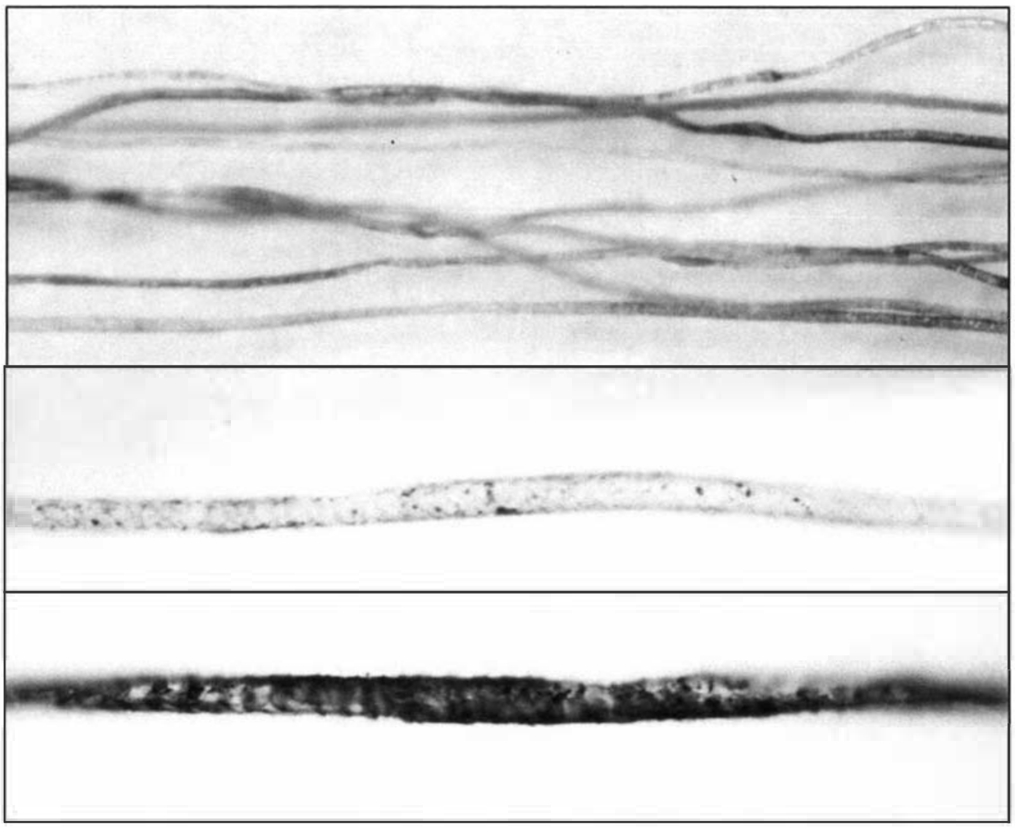


Figure 8.42. Light microscopy: W4 x 1, poly(EDOT) on wool (top image 42x magnification, middle and bottom images 185x magnification).

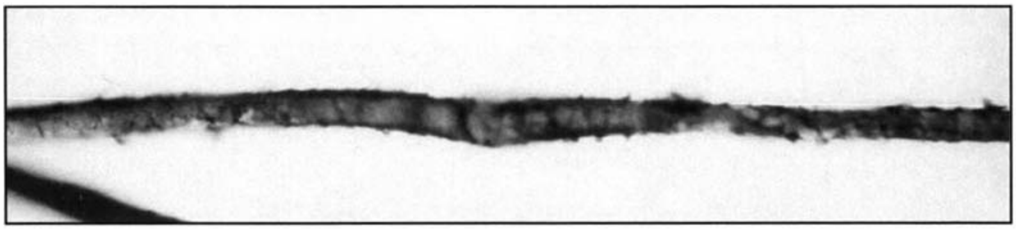


Figure 8.43. Light microscopy: W60 x 1, poly(EDOT) on wool (185x magnification).

The untreated polyester fibres were smooth and featureless under magnification, but also showed a degree of variability of blue coloration after polymer coating. This was to a lesser degree than on the wool fibres (i.e. they were more evenly coated), but with the same basic morphology of a thin, uniform coating, upon which were found irregular, heavier deposits (Figure 8.44). There was no apparent difference between the P4 fibres and the P60 fibres, and no underlying yellow discoloration.

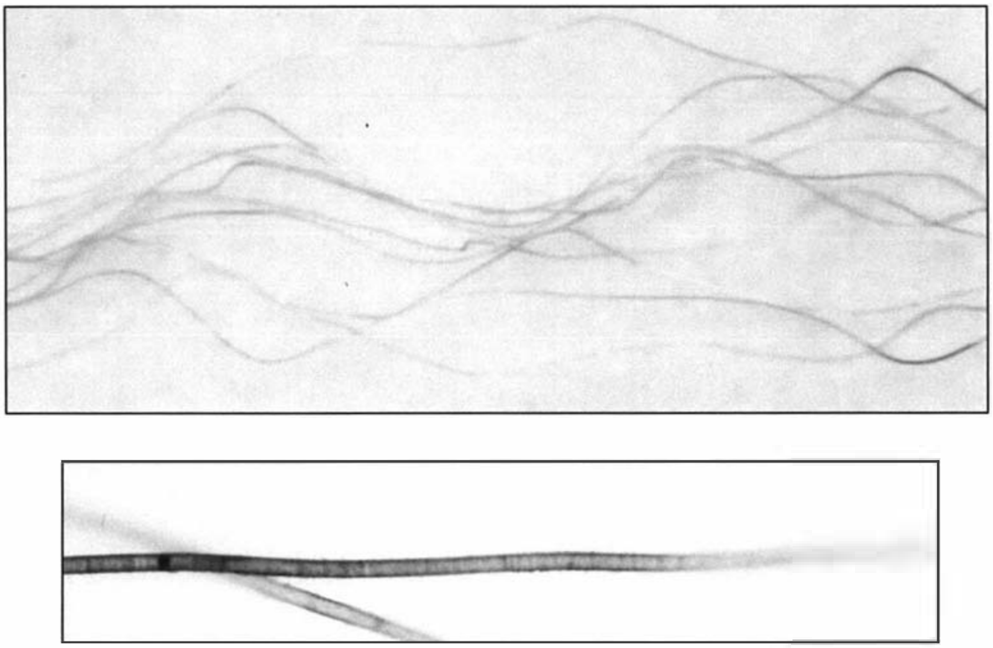


Figure 8.44. Light microscopy: P4 x 1, poly(EDOT) on polyester (top image 42x magnification, bottom image 185x magnification).

C. Transmission Electron Microscopy (TEM).

Ten visibly well-coated fibres were selected for TEM examination from each of the six samples (W control, W4 x 1, W60 x 1, P control, P4 x 1 and P60 x 1). These were prepared according to the method of Nelson and Woods [161]. They were mounted across acetate tabs, dehydrated in absolute ethanol for 30 minutes, followed by one hour in 50% acrylic resin in ethanol. The samples were then given four changes of resin, and polymerised for 19 hours at

58°C. Ultra-thin (60-90 nm) transverse sections were cut using a Reichert-Jung Ultracut E ultramicrotome fitted with a Delaware diamond knife, and these sections were captured on 200 mesh copper and 200 mesh gold grids; both coated with formvar/carbon.

Initial examination using a Philips EM 300 transmission electron microscope (80 kV) revealed that the poly(EDOT) coating was clearly visible on the treated fibres, so no further staining was used (typically uranyl acetate or lead citrate would be employed to stain the fibres and allow the fibre ultrastructure to be visible). This means that, in the control specimens, very little could be seen; just faint outlines of the cell membrane complex surrounding the cuticle cells for wool. The polymer coating however could be clearly observed for the treated specimens. In the following figures the structural elements of the wool fibres are indicated by abbreviations as follows:

Co – cortex, the cells in the interior of the fibre.
Cu – cuticle, the cells on the exterior of the fibre.
En – endocuticle, innermost cuticle cells.
Ex – exocuticle, outermost cuticle cells.

Figure 8.45 shows WC, the untreated wool fibre. This image illustrates the lack of fibre structure visible without staining. The cuticle and cortex are indicated, with some contamination on the surface of the fibre indicated with an arrow.

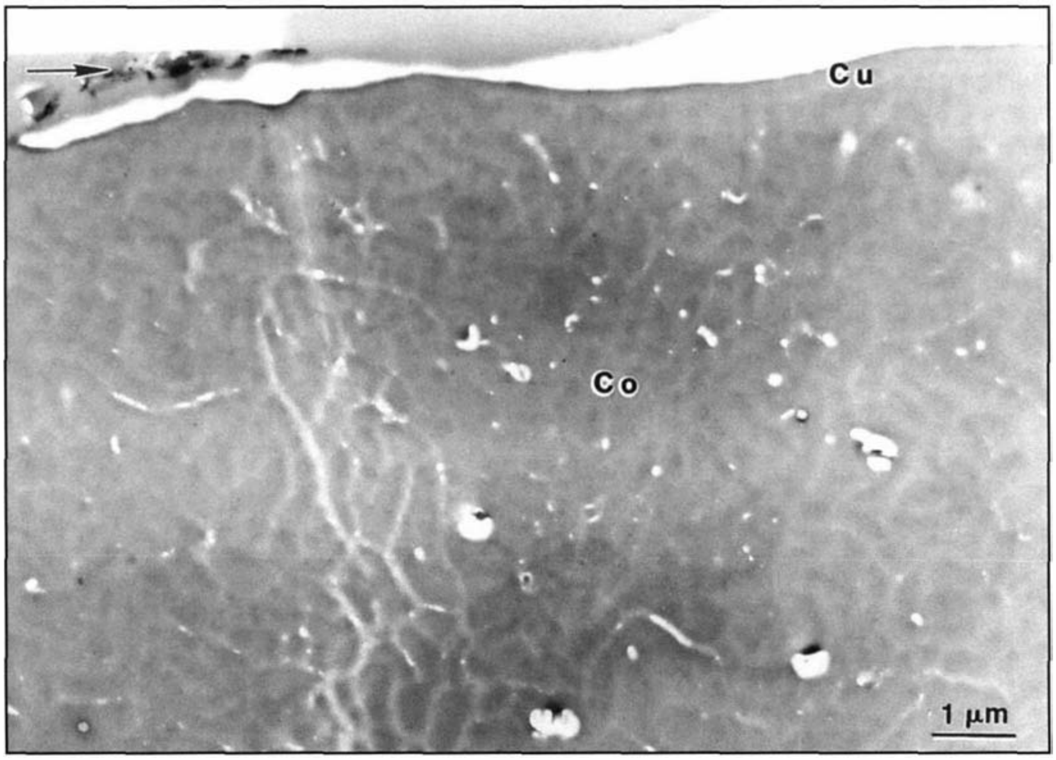


Figure 8.45. TEM: WC, untreated wool (magnification 13,500x).

By comparison, Figure 8.46 shows two images of W4 fibres, with the poly(EDOT) coating clearly visible on the outside of the fibre following the contours of the surface fibre scales (indicated by the arrows in the upper image). In the lower image, the coating has become detached from the fibre surface during the sectioning process.

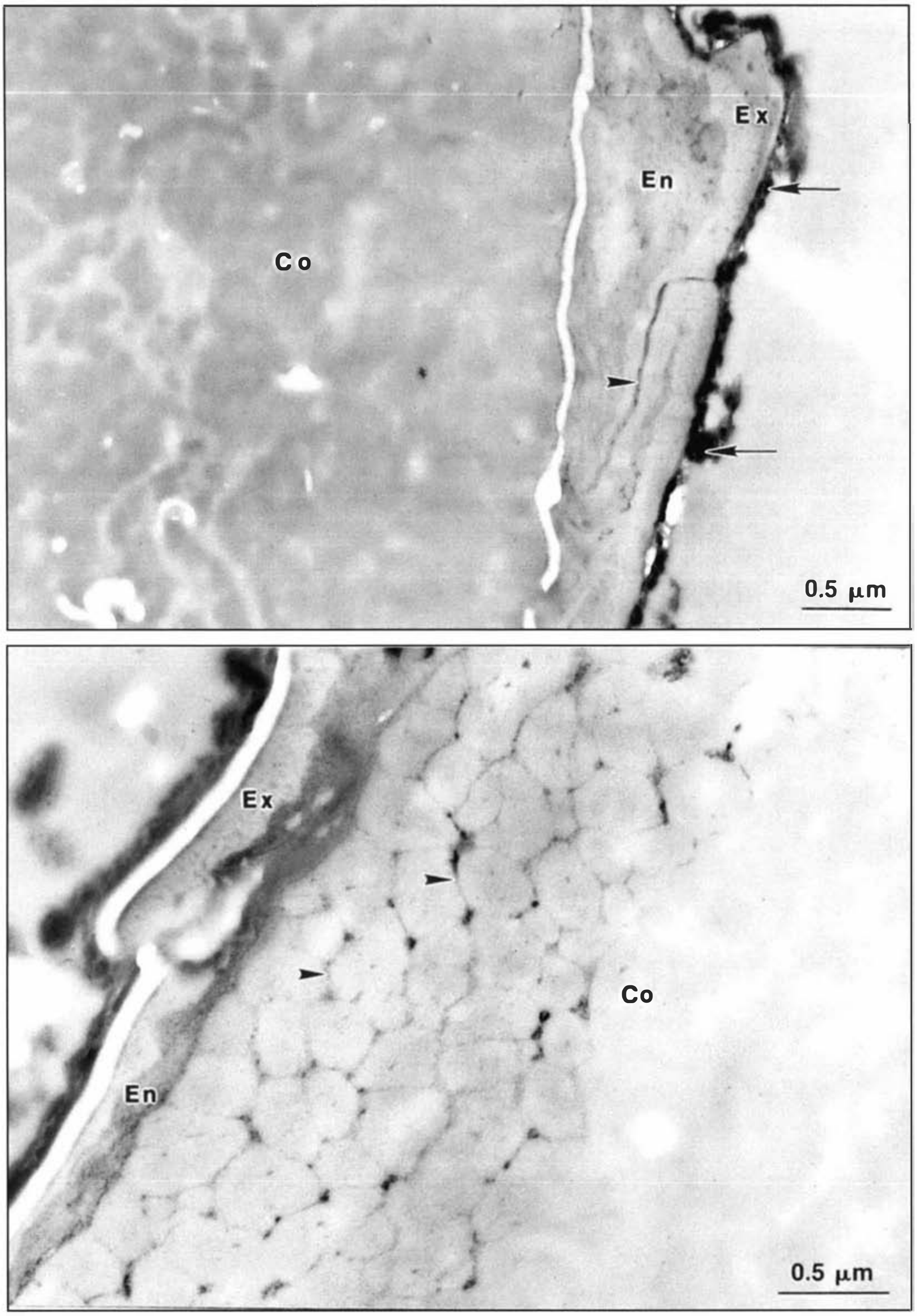


Figure 8.46. TEM: W4 x 1, poly(EDOT) on wool (top image magnification 30,950x, bottom image 39,250x).

All the fibres of this type that were examined had electron-dense deposits in the cuticle, which enhanced its ultrastructure as compared to Figure 8.45. These deposits can be seen as darkening of the cuticle cell membrane complex (indicated by an arrowhead in the upper image). The outermost cells of the cortex were also more clearly defined by the presence of electron-dense material in the intermacrofibrillar material of these cells (arrowheads in lower image). There did not appear to be any deposition of polymer further inside the cortex.

For specimen W60, the deposits in the outer cortex were typically larger and darker between the macrofibrils (arrowheads on Figure 8.47) than for W4, and also present in the cortical cell membrane complex (arrows in Figure 8.47). The electron-dense material was taken to be poly(EDOT).

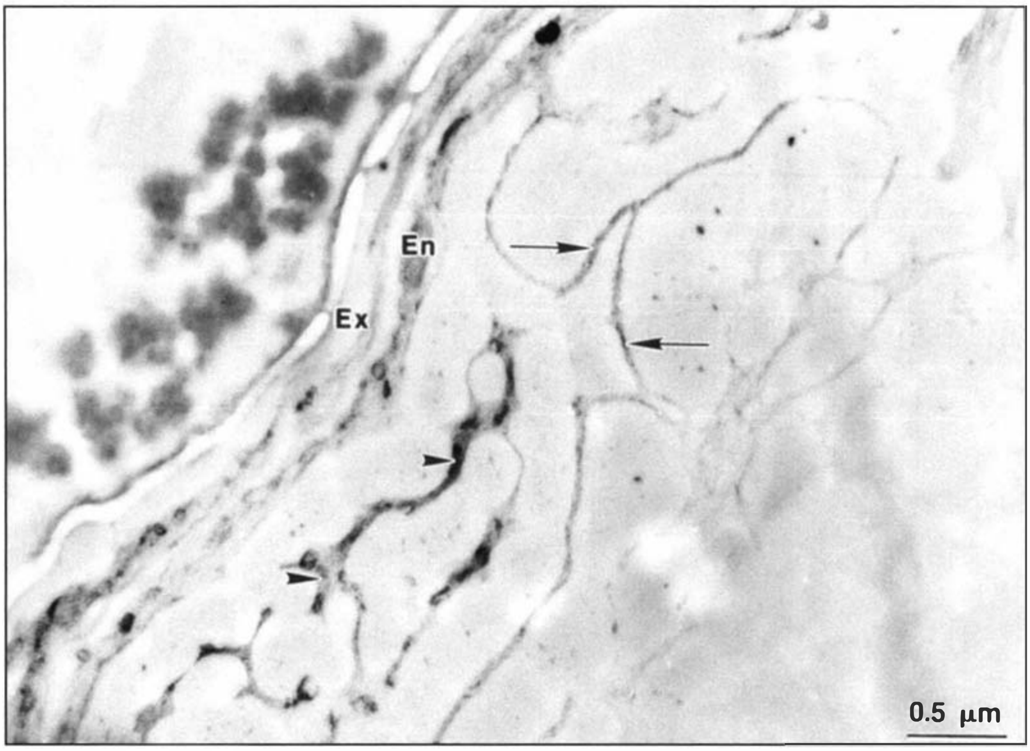


Figure 8.47. TEM: W60 x 1, poly(EDOT) on wool (magnification 30,950x).

These TEM images suggest that polymer formed inside the wool fibre. With the longer impregnation time, deposition was heavier, and slightly deeper. Presumably this was the case because the polymerisation solution penetrated into the interior of the fibre, and the longer this impregnation proceeded, the further into the fibre it penetrated. Polymer formed when the solvent escaped from the fibres during drying, in the same way that it was formed on the outside of the fibres. It is interesting to note that the polymer appeared to form on the surface of the fibres, in the endocuticle, and in the outer-most cortical cells, but to a much lesser extent in the exocuticle. Differences in the physical properties of these different regions were probably responsible for this.

The very different structure of polyester fibres can be seen in Figure 8.48: a smooth surface, and almost perfectly circular cross-section. The dark specks inside the fibre were probably inorganic delustrant particles, commonly applied to synthetic fibres to alter their reflective properties. The dark shading on the right hand side of the image (indicated with an arrowhead) is thought to be a sectioning artefact.

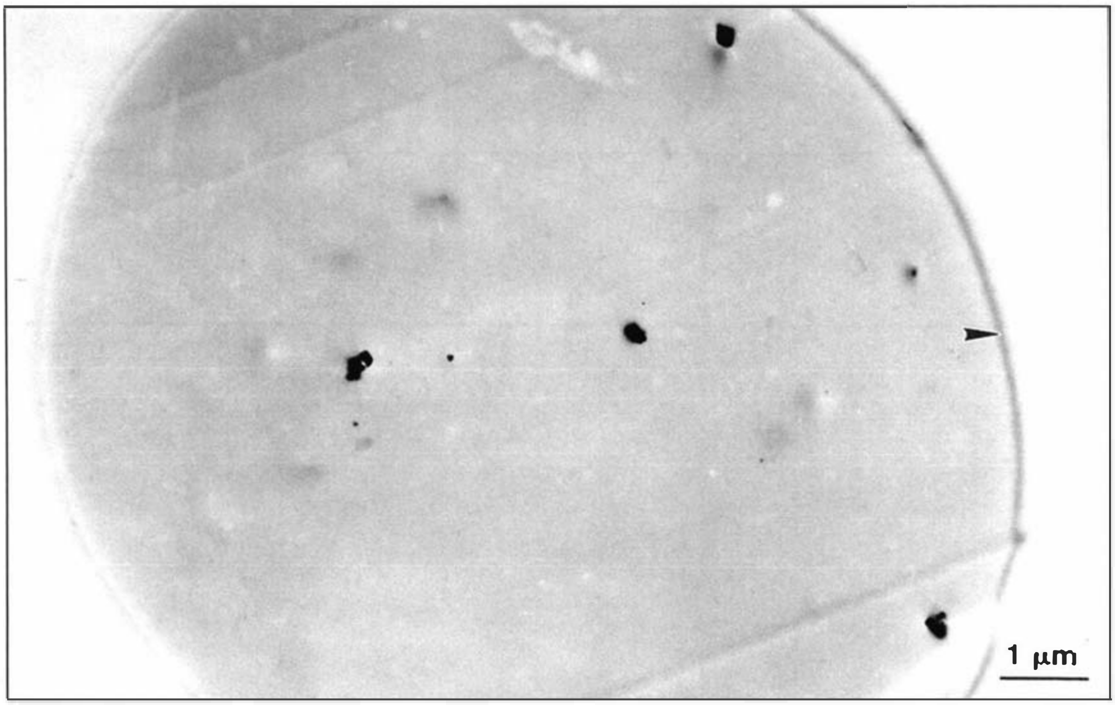


Figure 8.48. TEM: PC, untreated polyester (magnification 13,500x).

The poly(EDOT) coating deposited onto the surface of the polyester fibre can be clearly observed in Figure 8.49. Almost all the fibres examined had complete coatings around their circumference, with a coating thickness of perhaps ~0.1 µm. This often seemed to have two components, which can be clearly seen on the upper image – a thin layer (appearing darker on the image) adjacent to the fibre, with a less electron-dense (appearing lighter) layer outside it. This bi-component structure is also visible at lower magnification on the lower image, along with material that appeared to be only loosely adhering to the fibre surface (the thick diagonal line on this image is a sectioning artefact). The light microscopy indicated formation of a thin layer on the fibre surface, with loose material also accumulated on top of this. The TEM images confirm this morphology. Clearly there was no polymer formed inside the polyester fibres: their internal structure was unchanged from the untreated fibre.

With the longer impregnation time, the fibres were also well coated, with polymer forming a continuous layer around almost all the fibres examined. Generally the coating of the P60 specimens was thicker than that found on P4. A typical image of the structure of the coating is shown in Figure 8.50.

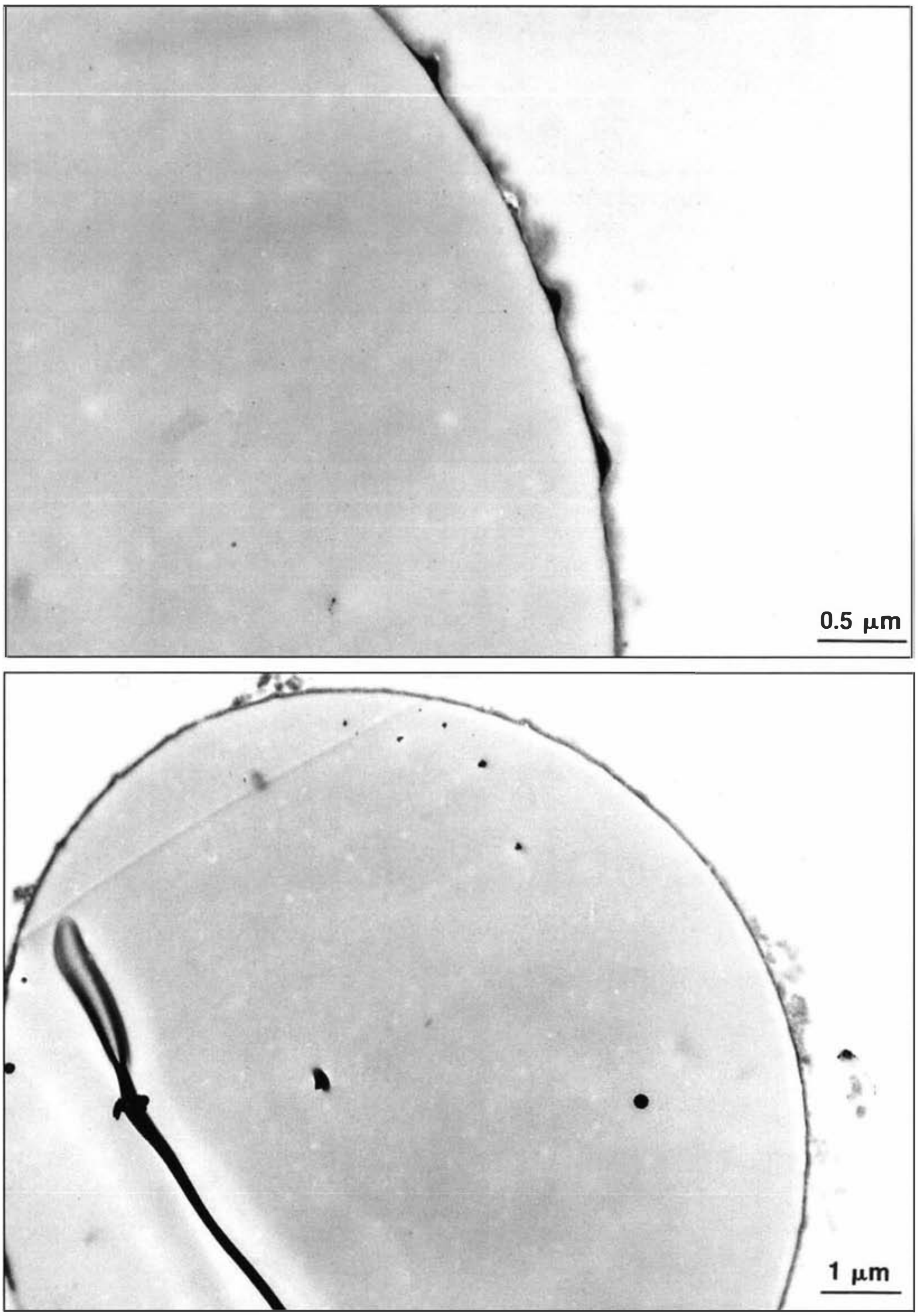


Figure 8.49. TEM: P4 x 1, poly(EDOT) on polyester (top image magnification 30,950x, bottom image 13,500x).

The P60 polymer coating seemed to consist of more loosely-adhering, lighter shaded material than was the case for P4, but there was still no polymer formed inside the fibres (the dark lines across the image are again sectioning artefacts).

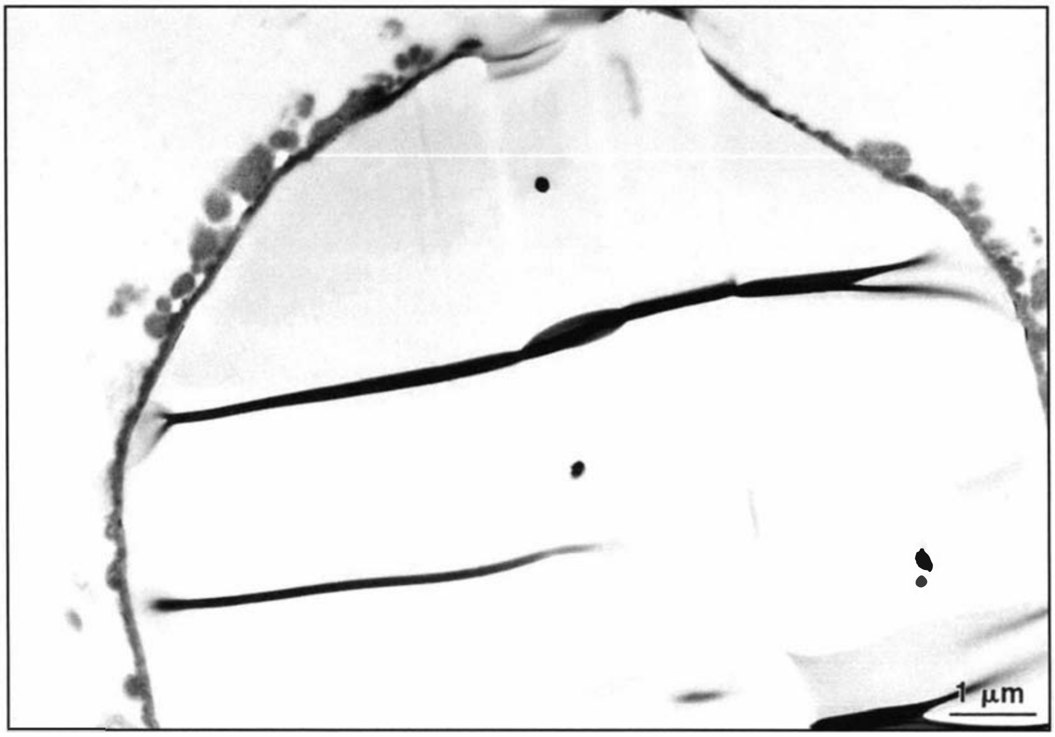


Figure 8.50. TEM: P60 x 1, poly(EDOT) on polyester (magnification 13,500x).

8.12.1.4 Conclusions.

This series of experiments was successful in determining the thickness of the polymer coating deposited onto fibres by the single-dip method, and in examining whether the polymer was also formed inside the fibres. By measuring the fibre diameter of wool and polyester fibres before and after five treatments with poly(EDOT), the thickness was calculated to be approximately 200 nm, or 0.2 µm.

The associated microscopy work was not able to positively confirm the coating thickness calculated from the fibre diameter measurements, because it revealed a substantial degree of variability in the polymer deposition along and between fibres. As far as it was possible to tell from the relatively small number of measurements possible, the TEM images indicate that the thickness coating was of the order of 0.1-0.2 µm, which is roughly consistent with fibre diameter data. This variability of polymer deposition may have been a result of the formation of a secondary polymer layer on top of a thin primary layer more closely associated with the fibre surface (perhaps forming epitaxially on that surface). The secondary layer seemed to be loosely adhering, and has possibly accumulated from polymer that formed in an uncontrolled manner in solution.

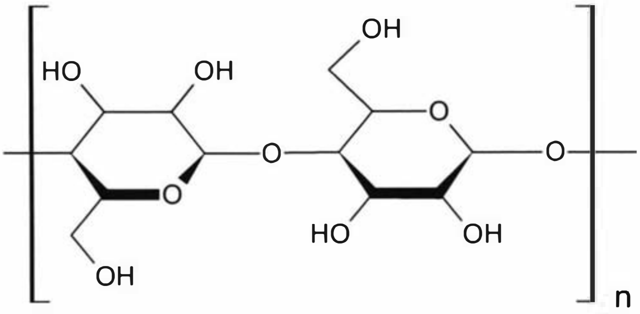
The wool fibres appeared to have a small amount of polymer deposition occurring inside the fibre. This was observed as visible fibre ultrastructure, particularly in the endocuticle and in the intermacrofibrillar regions of the outermost cortical cells. The longer reagent impregnation time did not appear to generate polymer much further into the fibre, but increased the amount formed in the same regions. No polymer was formed inside the polyester fibres, and a smoother, more uniform coating appeared to have been formed in comparison to that of wool. More controlled surface deposition may occur in the absence of reagent absorption into the fibre. It may also be that the irregular surface morphology of the wool fibre hinders the formation of a uniform coating. It was previously observed in a direct comparison of different fibre types (with other variables minimised as far as possible), that polyester had a lower surface resistance than wool. This could well be the result of more uniform formation of the conductive polymer layer on the surface of the fibres in the absence of absorption. Cotton, which is very absorbent, had an even higher resistance than wool.

8.12.2 Elemental Analysis of Textile-Poly(EDOT) Composites.

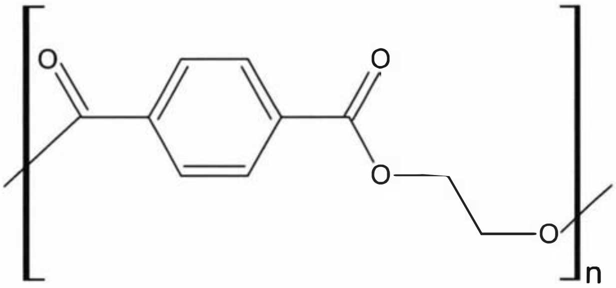
8.12.2.1 Background.

The chemical composition of the intrinsically conductive polymers prepared in this work has been assumed to be close to a simplified situation of multiple heterocyclic precursor units with associated dopant anions. However there are other components in the polymerisation system that could be incorporated into the polymer; in particular, the metal cation from the oxidising agent. There is also the potential for impurities from substrates and reagents to be incorporated. Some effort was made to prevent this, by using a solvent rinse to remove lubricants and finishes from the fabrics, and using de-ionised water. Also, where available, reagents of a grade higher than general purpose have been used. Regardless, it is still valuable to try to determine the actual composition of the ICP formed.

The obvious difficulty with elemental analysis of the ICPs prepared in this work was the presence of the textile substrate. Typical textile-poly(EDOT) composites had only a few percent poly(EDOT) content, so elemental analysis of these composites would mostly reflect the composition of the substrate and might not provide useful information about the ICP. The choice of substrate is also important in allowing a clear analysis of the ICP to be made; it must not mask any unique chemical signatures that come from the ICP. This requires a substrate without sulphur (by which thiophene would be detected), nitrogen (pyrrole or nitrate-doping), chlorine (chloride-doping) or iron (residue from oxidant). Only three of the textile polymers used in this work fulfil these criteria: polypropylene, polyester and cotton. Nylon (polyamide) and acrylic (polyacrylonitrile) were ruled out because of the presence of nitrogen, while wool has both nitrogen (from peptide linkages) and sulphur (from the amino acid cystine/cysteine). Polyester and cotton were chosen as they were at the extremes of electrical properties, with polyester typically the most conductive and cotton the least, thus making a potentially valuable comparison. Polyester and cotton (illustrated in Figure 8.51) are comprised of carbon, hydrogen and oxygen (poly(ethylene terephthalate) and poly(1,4β-anhydroglucose), respectively). With these two substrates, any sulphur, chlorine, nitrogen or iron detected can be assumed to be in the ICP component of the composite. Polypropylene (a pure hydrocarbon) could also have been used, but was somewhat different in fabric structure to the others (as has been discussed elsewhere), so was excluded.



Cotton: Poly(1,4β-anhydroglucose), i.e. cellulose.



Polyester: Poly(ethylene terephthalate).

Figure 8.51. Suitable polymer substrates for elemental analysis.

As well as simply determining the chemical composition of the ICP, elemental analysis can be used to determine the degree of doping of the conductive polymer by providing an indication of the ratio of sulphur to chlorine atoms. Each EDOT unit has one sulphur in the thiophene ring, so the molar ratio of sulphur to chlorine indicates how many monomer repeats there are per chloride ion. The perchlorate ion (ClO_4^-) also contains only one chlorine, so the same approach can be used for perchlorate-doped ICPs. The nitrate ion (NO_3^-) has one nitrogen, so with nitrogen analysed, the situation for nitrate-doped ICPs can be determined. It is thought that the dopant ratio in fully oxidised (i.e. conducting) ICPs is about one anion to 2.5-3 monomer units [68]. It follows that higher conductivity ICPs should have a higher number of dopant anions present (hence more capacity for the movement of electrical charge) than less conductive ones. This would be manifested in a lower surface resistance measurement for more highly doped textile-ICP composites. A significant negative correlation should be seen between the chlorine-to-sulphur ratio and the surface resistance; i.e. a high chlorine-to-sulphur ratio should correspond to low resistance.

8.12.2.2 Test Method.

Samples were prepared as described below, then sent to the Campbell Microanalytical Laboratory at the University of Otago, Dunedin, NZ. The proportion of each element in the composite was determined by a microanalytical procedure. Two replicates of each analysis were carried out.

8.12.2.3 Polymer Deposition.

Specimens were cut from the cotton and polyester standard fabrics at 35 x 35 mm, which was frayed back to 30 x 30 mm. With these fabrics having a weight of ~130 g/m^2, this gavc a sample mass of ~0.13 g, which increased slightly after poly(EDOT) deposition. This was sufficient for elemental analysis. The specimens were carefully prepared for polymer deposition by the usual method, except distilled water was used to improve the purity of the system. Two specimens of each fibre type were prepared; one was retained as a control for the elemental analysis, while the other was poly(EDOT) coated.

The specimens were treated with five successive depositions of poly(EDOT), to increase the poly(EDOT) content of the composite to approximately 4-5% (the intention was to make the chemical profile of the ICP detectable above the background composition of the substrate). Each poly(EDOT) treatment was carried out by the usual single-dip routine, as described in Section 4.4.4.The oxidants were iron (III) chloride, perchlorate and nitrate, at either 1.0 or 0.8 mol/L concentration in methanol.

A. Cotton and polyester fabrics, 1.0 mol/L iron (III) chloride.

These were prepared to determine if the elemental analysis technique could be successfully applied to textile-ICP composites, and to determine if there were any differences in composition that could explain the substantial difference in surface resistance between cotton and polyester substrates.

B. Polyester fabric, 0.8 mol/L iron (III) chloride, perchlorate and nitrate.

These were prepared to allow comparison of the elemental composition of poly(EDOT) polymerised using different oxidants. The counter-ion is incorporated into the polymer, so should be detectable in the elemental analysis. Previous experiments indicated that perchlorate-doped poly(EDOT) had a lower surface resistance than chloride-doped, and it would be valuable to determine if this was reflected in the elemental composition. The lower oxidant concentration used here was because iron (III) nitrate is less soluble in methanol than the other two oxidants, which are soluble to 1.0 mol/L and above. All three oxidants were prepared at the lower concentration for this work, to allow an unbiased comparison.

8.12.2.4 Results.

A. Cotton and polyester fabrics, 1.0 mol/L iron (III) chloride.

The polymer mass add-on and surface resistance of the specimens was assessed; the latter as a means of confirming that the textile-ICP composites prepared here were comparable to those produced previously. The surface resistance measurements were made by the same non-destructive technique used on the specimens prepared for bending and strength testing (see Section 8.10). These results are provided in Table 8.44.

Table 8.44. Mass add-on and approximate surface resistance – elemental analysis specimens (Cl-doped poly(EDOT)-coated polyester and cotton).

Fibre type (fabric code)	Polymer mass add-on	Surface resistance (Ω/sq)
Polyester (D)	+ 4.20%	165.3
Cotton (C)	+ 4.80%	201.5

The mass add-on levels were in the target range of 4 to 5 %. The surface resistance values reflected the multiple coatings, a relationship that was explored in detail in Section 8.9. Unfortunately, with multiple coatings, the difference in resistance between cotton and polyester diminished, meaning that elemental analysis of these specimens might be unable to explain the differences observed with one coating.

Tables 8.45 and 8.46 contain the results of the elemental analysis on these specimens and the untreated controls. The percentage content by mass is given in Table 8.45, and adjusted in Table 8.46 for the molecular weight of each element (this can be used to determine the molar ratios of the elements). It is essential to consider the uncertainty or error that could be present in this elemental analysis, especially as the elements of interest are present in such small quantities in the composite. For this purpose, the 95% confidence interval for each mean value is also provided (in parentheses), although any statistical analysis of this data is somewhat hampered by the small number of replicates used. However, in most situations this confidence interval is quite small (relative to the average value), giving some confidence that the values obtained are reasonably representative of the specimen as a whole.

Table 8.45. Elemental analysis (g/100 g) of Cl-doped poly(EDOT)-coated polyester and cotton fabrics.

	Amount of each element (g/100 g) with 95% confidence interval					
	C	H	Cl	S	Fe	O[1]
Cotton – control	41.52 (± 0.10)	5.69 (± 0.06)	Nil	Nil	Nil	52.79 (± 0.16)
Cotton – 5 x poly(EDOT)	41.64 (± 0.04)	5.84 (± 0.16)	0.21 (± 0.04)	0.86 (± 0.06)	0.10 (± 0.00)	51.35 (± 0.14)
Polyester – control	61.62 (± 0.15)	4.21 (± 0.03)	Nil	Nil	Nil	34.18 (± 0.18)
Polyester – 5 x poly(EDOT)	60.63 (± 0.08)	4.11 (± 0.21)	0.23 (± 0.03)	0.72 (± 0.03)	0.05[2] (± 0.00)	34.28 (± 0.23)

Notes:

1. Oxygen content determined by difference; i.e. the residue after determining content of C, H, Cl, S and Fe is assumed to be O.
2. In fact it is lower than 0.05, as the two readings for iron on this sample were 0.05 and <0.05. In other words, in one of the two samples no iron was detected, but it cannot be assumed to be absent.

Table 8.46. Elemental analysis (mol/100 g) of Cl-doped poly(EDOT)-coated polyester and cotton fabrics.

	Amount of each element (mol/100 g)					
	C	H	Cl	S	Fe	O
Cotton – control	3.4568	5.6454	Nil	Nil	Nil	3.2996
Cotton – 5 x poly(EDOT)	3.4668	5.7942	0.0059	0.0268	0.0018	3.2096
Polyester – control	5.1299	4.1720	Nil	Nil	Nil	2.1364
Polyester – 5 x poly(EDOT)	5.0479	4.0728	0.0063	0.0223	0.0009	2.1423

Considering first the untreated fabrics. The most encouraging result was the absence of chlorine, sulphur or iron in the two fibre types. This means that the presence of these elements in the treated specimen was solely due to the addition of poly(EDOT). Based on the chemical structures given in Figure 8.54, it is possible to calculate the molar ratios of the constituent elements, and compare them with the molar ratios obtained through elemental analysis (using the average values from Table 8.46). For cotton, the chemical formula as drawn is $[C_{12}H_{20}O_{10}]_n$, while for polyester it is $[C_{10}H_8O_4]_n$. Theoretical and calculated molar ratios for cotton and polyester are compared in Table 8.47, with the data normalised to carbon.

Table 8.47. Molar ratio of constituent elements for untreated cotton and polyester.

	Measured (elemental analysis)			Calculated (theoretical)		
	C	H	O	C	H	O
Cotton	1	1.63	0.95	1	1.67	0.83
Polyester	1	0.81	0.42	1	0.80	0.40

The only substantial discrepancy between the measured and theoretical values is that of oxygen in cotton, with slightly more present in the elemental analysis than would be expected. Cotton is not absolutely pure cellulose, but also has very small percentages of other substances (waxes, pectin and proteins), which could alter the measured composition. Generally, the good agreement between the measured and calculated molar ratios and the absence of Cl, S and Fe in the untreated controls indicated that elemental analysis would be a useful tool for the treated specimens.

The elemental analysis results for the poly(EDOT)-coated specimens showed the presence of chlorine, sulphur and iron, presumably either from the ICP coating itself, or absorbed during the single-dip process. The iron content was very low – just on the threshold of what was detectable. Armes [3] concluded that in iron (III) chloride-polymerised polypyrrole, the presence of iron (assumed from the presence of a significant proportion of mineral ash in his microanalysis) indicated that the polypyrrole was in fact doped with the $FeCl_4^-$ anion. For that to be the case here, we would expect the ratio of iron to chlorine to be approximately 1:4, and while this could be the case for cotton (Fe:Cl is 1 : 3.28, taking average values for molar composition from Table 8.46), it is unlikely to be so for polyester (Fe:Cl is 1 : 6.00). The higher iron content for cotton could have been due to absorption of iron into the cotton fibre during the polymerisation, rather than any difference in poly(EDOT) composition. There does not appear to be a compelling reason to assume that the dopant anion was that claimed by Armes, and not simply Cl^-.

The ratio of sulphur to chlorine indicates the degree of doping that was present in the polymer. For poly(EDOT) deposited onto cotton, the Cl:S ratio was 1 : 4.54, which indicates a level of doping somewhat lower than what is assumed to be the fully doped condition. With polyester as the substrate, the Cl:S ratio was 1 : 3.54, which indicates a higher level of doping than for cotton, and is quite close to the (assumed) fully doped state of 1 : 3. However, the implications of the error in the elemental composition measurements should be considered at this point. For the cotton specimen with five layers of poly(EDOT), the 95% confidence interval of the average mass composition is 0.17 – 0.25 g/100g for chlorine and 0.80 – 0.92 g/100g for sulphur. This gives a maximum range for the molar ratio of 3.54 – 5.98 (taking the highest value for chlorine with the lowest for sulphur, and vice-versa). For the polyester specimen, the range for the molar ratio (calculated in the same way) is 2.94 – 4.15. There is a clear overlap between these intervals, and while this does not mean that the difference between them is not statistically significant, it serves to indicate the caution that should be used when interpreting many of the elemental analysis results presented in this section

With five layers of poly(EDOT) deposited onto these substrates, there was very little difference in surface resistance, but with only one layer, polyester's resistance was very much lower. Assuming that the same level of doping applied with only one layer present, then the lower level of doping for cotton may explain its higher resistance. It seems that, with multiple layers, the difference in resistance is diminished, probably because poly(EDOT) is increasingly being deposited onto poly(EDOT) and not the fibre surface (hence the influence of fibre type is decreased). This may of course mean that the composition of subsequent layers becomes similar for cotton and polyester, so the difference in composition observed here may reflect a substantial difference between the fibre types for the first layer, followed by subsequent depositions that were more alike. If this was the case, the doping in the first layer on a cotton substrate may be very much lower than has been found here, which would explain the substantial difference in surface resistance observed with one poly(EDOT) layer.

The proportions of elements specifically from the poly(EDOT) component of the composite were, of course, very low. This is because the poly(EDOT) formed only a small percentage of the mass of the composite. In the case of the cotton fabric, the 4.80% add-on means the composite was 4.58% poly(EDOT) by mass, and the polyester-based composite (add-on of 4.20%) was 4.03% poly(EDOT) by mass. If we consider an idealised form of Cl-doped poly(EDOT) with a chemical formula (assuming a doping of one Cl for every three S atoms) of $[C_6H_4O_2SCl_{1/3}]_n$, then it is possible to calculate the mass percentage of each element in the polymer. These can then be compared with the measured mass percentage (average data from

Table 8.45). This comparison is provided in Table 8.48 (these values are mass percentages so they do not directly indicate the mole ratios of the elements).

Table 8.48. Percentage (by mass) of poly(EDOT) specific elements in composite.

	Calculated (%)		Measured (%)	
	S	Cl	S	Cl
Cotton	0.97	0.36	0.86	0.21
Polyester	0.85	0.31	0.72	0.23

The measured results were reasonably close to the calculated results, which gives confidence that the conductive polymer formed was in fact Cl-doped poly(EDOT), in approximately its idealised form. One reason for the small deviations was the higher Cl:S ratios; in other words, the incomplete doping of the poly(EDOT). The percentages were a little lower than for the idealised form – the calculation doesn't allow for elements other than C, H, O, Cl and S to be present in the poly(EDOT), and some of the mass may have been an element not considered in the calculation (such as iron).

B. Polyester fabric, 0.8 mol/L iron (Ill) chloride, perchlorate and nitrate.

As for the previous set of specimens, these were assessed for mass add-on and surface resistance, before undergoing elemental analysis. The non-destructive surface resistance test method used tends to give slightly lower surface resistance readings than the full method. These results are given in Table 8.49.

Table 8.49. Mass add-on and approximate surface resistance – elemental analysis specimens (Cl, ClO_4 and NO_3-doped poly(EDOT)-coated polyester).

Dopant anion	Polymer mass add-on	Surface resistance (Ω/sq)
Chloride	+ 3.85%	150.0
Perchlorate	+ 6.39%	64.6
Nitrate	+ 3.62%	98.9

The Cl-doped specimen here did not correspond to the treated polyester specimen from the previous experiment, as they were prepared at different oxidant concentrations. The mass add-on was lower for this specimen (as would be expected for the lower oxidant concentration), although they did have similar surface resistance values. The perchlorate and nitrate-doped specimens had lower resistance than chloride-doped, as was observed for single layers. In fact the surface resistance of the perchlorate-doped poly(EDOT) specimen prepared here was the lowest surface resistance that was achieved anywhere during this work (it is the same specimen as in Section 8.9.4).

Elemental analysis was carried out in the same way as for the other specimens. These results are presented in mass and mole terms in Tables 8.50 and 8.51, with 95% confidence intervals also given for each average value. As for the previous specimens, the analysis appeared to have been successful; the expected elements were detected, with the exception of nitrogen in the nitrate-doped specimen (possible reasons for this are discussed in detail below). The perchlorate and nitrate-doped specimens were very low in iron; on the threshold of what is detectable for perchlorate and below it for nitrate. The iron content of the chloride-doped specimen was similar to that of the equivalent specimen analysed in the first experiment. It appeared that less iron was trapped in the specimen with perchlorate and nitrate as dopant anions, but the values were so low, and the potential for error so large, that caution must be used in drawing this conclusion. Polymerisation was faster with iron perchlorate and iron nitrate than for iron chloride, so perhaps this faster polymerisation resulted in less iron being trapped in the specimen. The chlorine and sulphur amounts were less for this chloride-doped specimen than for the previous one. This is probably an outcome of the lower mass add-on for the chloride-doped specimen on this occasion.

Table 8.50. Elemental analysis (g/100 g) of Cl, ClO_4 and NO_3-doped poly(EDOT)-coated polyester.

	Amount of each element (g/100 g) with 95% confidence interval					
	C	H	Cl or N[1]	S	Fe	O[2]
Chloride	61.09 (± 0.26)	4.30 (± 0.14)	0.20 (± 0.03)	0.64 (± 0.06)	0.07 (± 0.01)	33.72 (± 0.32)
Perchlorate	60.48 (± 0.09)	4.47 (± 0.19)	0.43 (± 0.25)	0.95 (± 0.02)	0.02 (± 0.00)	33.67 (± 0.32)
Nitrate	61.17 (± 0.12)	4.53 (± 0.20)	Nil	0.65 (± 0.22)	Nil	33.65 (± 0.29)

Notes:

1. For chloride and perchlorate the analysis was for chlorine, for nitrate it was for nitrogen.
2. Oxygen content determined by difference, i.e. the residue after determining content of C, H, Cl/N, S and Fe is assumed to be O.

It was impossible to determine the extent of doping in the nitrate-doped specimen (because of the nil reading for nitrogen), while the reading for chloride-doped was similar to that from in the previous experiment, with a Cl:S ratio of 1 : 3.64. The result for the perchlorate-doped specimen was remarkably low, with a Cl:S ratio of 1 : 2.47. In other words, there were 2.47

sulphur atoms to every chlorine atom, suggesting a much higher level of doping than for chloride. This result may explain the much lower surface resistance of composites prepared with perchlorate-doped poly(EDOT) than with chloride-doped poly(EDOT), which has been consistently observed in this research. However, calculating a maximum range for these molar ratios emphasises the uncertainty in these measurements; for chloride-doped it is 2.79 – 4.55, while for perchlorate-doped it is 1.51 – 5.96. The latter is a very wide range, and was caused by the large 95% confidence interval for the amount of chlorine in this specimen.

Table 8.51. Elemental analysis (mol/100 g) of Cl, ClO_4 and NO_3-doped poly(EDOT)-coated polyester.

	Amount of each element (mol/100 g)					
	C	H	Cl or N	S	Fe	O
Chloride	5.0858	4.2663	0.0055	0.0200	0.0012	2.1073
Perchlorate	5.0350	4.4300	0.0120	0.0296	0.0004	2.1042
Nitrate	5.0928	4.4945	Nil	0.0203	Nil	2.1033

The apparent absence of nitrogen in the nitrate-doped specimen warrants further consideration. By carrying out the same calculation to determine the amount of poly(EDOT)-specific elements as was used for the polyester and cotton specimens from the previous trial, it is possible to determine how much nitrogen should be present with idealised poly(EDOT) formulae, as shown:

Chloride-doped: $[C_6H_4O_2SCl_{1/3}]_n$ (i.e. one chlorine for every three sulphur atoms).

Perchlorate-doped: $[C_6H_4O_{10/3}SCl_{1/3}]_n$ (i.e. same as chloride-doped except 1 1/3 additional oxygen atoms per sulphur atom).

Nitrate-doped: $[C_6H_4O_3SN_{1/3}]_n$ (i.e. same as chloride-doped, except chlorine replaced by nitrogen and 1 extra oxygen atom per sulphur atom).

The results of this analysis (i.e. the calculated and measured percentage (by mass) of each poly(EDOT) specific element for all three specimens), are given in Table 8.52. These values are mass percentages, and do not directly indicate the mole ratios of the elements.

Table 8.52. Percentage (by mass) of poly(EDOT) specific elements in composite.

	Calculated (%)		Measured (%)	
	S	Cl/N	S	Cl/N
Chloride	0.78	0.29	0.64	0.20
Perchlorate	1.11	0.41	0.95	0.43
Nitrate	0.65	0.09	0.65	nil

There is reasonable agreement between the calculated and measured values, and a possible reason for the nil reading for nitrogen is immediately apparent. The calculated percentage by mass of nitrogen in the composite is extremely low, at 0.09 % (roughly the minimum level an element was detected at in this work). Also, it was previously observed that the measured mass percentage was lower than the calculated, so it is likely that the true situation is not an absence of nitrogen, but simply too little to measure. This was not a problem for chlorine, because its molecular weight is high enough that its percentage by mass in the composite was able to be detected. In other words, the nil reading for nitrogen was an artefact of its low molecular weight (although the nitrate anion is relatively large, the detection of it was via the small nitrogen atom). Given the low surface resistance of the nitrate-doped specimen, it is likely that it was in fact doped with nitrate, and there is no evidence to suggest that an alternative conductivity mechanism was present.

8.12.2.5 Summary and Conclusions.

The microanalysis techniques used for this work provided valuable information regarding the composition of chemically polymerised poly(EDOT), the level of doping present, and the extent to which iron is trapped in the polymer. Despite the necessary considerations of the potential error in these measurements, it is possible to have some confidence in the results, as there was good agreement between measured and predicted values when the elemental analysis was carried out on the substrate fabrics (for which the chemical composition is well defined). Similarly, when analysis of the likely proportions of poly(EDOT)-specific elements was carried out, there was also reasonably good agreement between the calculated values (from the mass add-on and an idealised poly(EDOT) structure) and those obtained from elemental analysis.

In general, the results suggest that a small amount of iron was present in the ICPs. This is not unexpected, as it is hard to imagine that during the (fairly uncontrolled) polymerisation process, none of the iron from the iron (III) salt oxidising agent gets trapped. It could be in the reduced form as iron (II), or as iron (III), but it is unclear what effect it would have on the properties of the composite. In the presence of sufficient moisture, iron cations would provide a degree of conductivity (as an ionic solution). Alternatively, as elemental iron it would of course be conductive as a metal. It is unlikely that sufficient iron or moisture would be present for the former to be the case (although a very low level of conductivity was observed for an 'oxidant only' specimen of cotton in Section 8.7.5), and the latter is not supported by any experimental observation.

The level of doping, as measured by the ratio of chlorine to sulphur (or nitrogen to sulphur, in the case of nitrate-doped specimens), appears to correspond quite well with the surface resistance measurements. The specimen prepared using a cotton substrate had higher surface resistance than one prepared using polyester, and also had a lower chlorine-to-sulphur ratio. Similarly, the specimen prepared using iron (III) chloride as the oxidant had a higher surface resistance than one prepared using iron (III) perchlorate, and also had a lower chlorine-to-sulphur ratio. The single chlorine atom in the perchlorate anion was used to detect the presence of perchlorate in the polymer, but the nitrogen atom in the nitrate anion was present in too small a quantity (by mass) to be detectable. Analyses of hypothetical poly(EDOT) formulae for the various differently-doped versions were used to determine the likely composition of the polymer, and reasonably good agreement with measured values was found. In particular, a probable explanation for the apparent absence of nitrogen in nitrate-doped poly(EDOT) was identified, being that its low molecular weight rendered its percentage of the poly(EDOT) by mass below the detection threshold of the microanalysis. One solution to this problem would be to repeat the experiment with a much higher loading of poly(EDOT), to boost the level of nitrogen to a detectable level.

These experiments have confirmed the suitability of elemental analysis as a tool to investigate the composition of textile-ICP composites, provided the substrate is carefully chosen to highlight the poly(EDOT)-specific elements. The small proportion of ICP in the composites means that the data obtained for some components has a large error, but this could be reduced by using more replicates than were employed here.

Finally, and leaving aside error considerations, the results suggest that the lower surface resistance for composites prepared from iron (III) perchlorate could be linked to higher levels of doping in this version of poly(EDOT) than for those prepared using iron (III) chloride. The level of doping in poly(EDOT) also appeared to be dependent on the substrate, as cotton-poly(EDOT) was doped at a lower level than polyester-poly(EDOT). This further reinforces the important role of the substrate in the polymerisation process.

8.13 Summary and Conclusions.

8.13.1 An Optimum ICP Deposition System.

In concluding this chapter, it is worthwhile to summarise the findings by defining an optimised 'single dip' ICP deposition system, taking into account all of the parameters investigated.

8.13.1.1 Precursor.

3,4-Ethylenedioxythiophene (EDOT) was far superior to both 2,2'-bithiophene and pyrrole as an ICP precursor to use with this method. It is sufficiently reactive to polymerise into what appears to be a fully-doped, conductive state (whereas bithiophene appeared not to be), but not so reactive that polymerisation occurs away from the fibre surfaces, in the polymerisation solution (as pyrrole appeared to).

The optimum precursor concentration found for EDOT (established in Section 8.2) was between 0.02 and 0.04 g/10 mL of polymerisation solution. Throughout most of the work, 0.03 g/10 mL was taken to be the optimum concentration. It is not clear exactly why this quite low concentration created composites with superior electrical properties to those prepared at higher concentrations (that resulted in higher polymer mass add-on). The most likely explanation is that polymerisation is more controlled, and polymer deposition more ordered, at a low precursor concentration.

8.13.1.2 Oxidant.

Of the four oxidants used in these investigations, iron (III) perchlorate was the most effective. The potentially dangerous reactivity of perchlorates is a disadvantage to their use, so iron (III) nitrate offers an alternative, as it was also superior to the more commonly-used iron (III) chloride. Note that in all cases, the hydrated forms of these iron (III) salts were used (described in Sections 8.4 and 8.11). As discussed in Section 8.4, the iron (III) salt of *p*-toluenesulphonate was disappointing, providing neither lower resistance nor improved durability (the latter was expected from its large counter-ion).

As reported in Section 8.3, the oxidant concentration needed to be as high as possible when iron (III) chloride was used. This in turn means that the choice of solvent (see Section 8.13.1.3) becomes critical, in that it needs to allow a high concentration (ideally 1.0 mol/L) to be reached. This relationship was not as clear for iron (III) perchlorate, where the optimum oxidant concentration for surface resistance was approximately 0.75 mol/L in methanol. This corresponded to a minimum surface resistance value but not a maximum mass add-on (reminiscent of the situation for the precursor). The surface resistance for composites prepared with iron (III) perchlorate at 0.75 mol/L was lower than that with the highest possible concentration of iron (III) chloride, while the mass add-on values were approximately the same.

8.13.1.3 Solvent Type.

Both methanol and ethanol produced composites with the best electrical properties, particularly at the optimal (high) oxidant concentrations used. The lower dissociation of the ionic oxidant salt in ethanol (compared with methanol, which is more polar) was compensated for by a lower volatility, which resulted in slower (and possibly better ordered) polymerisation. In some circumstances acetonitrile was a very effective solvent, but at the high oxidant concentrations that were favoured, the two simple alcohols were as good, or better. As acetonitrile is a more hazardous chemical to use, methanol or ethanol were preferred. Full details are provided in Section 8.5.

8.13.1.4 Substrate (Fibre Type).

For poly(EDOT) (being of the greatest interest in this work), polyester was found (as described in Section 8.7) to be the best substrate, with a moderate polymer mass add-on at the lowest surface resistance. Acrylic and wool were also good substrates; polypropylene was reasonable; but cotton and nylon were poor.

For polypyrrole, nylon was the best substrate in terms of surface resistance, but polyester was the second best, with a much lower polymer mass add-on. Acrylic and polypropylene were reasonable, but wool and cotton were poor.

8.13.1.5 Multiple Treatments.

The surface resistance of textile-poly(EDOT) composites reduced with successive treatments until six treatments had been carried out, at which point it levelled off (as reported in Section 8.9). The mass add-on at this point was about four to five percent; a level that did not have any adverse effect on fabric mechanical properties. The latter was established via tests of fabric bending behaviour (related to drape), and strength.

8.13.1.6 Miscellaneous Parameters.

A solution impregnation time of less than four minutes was sufficient on synthetic fibres, while there was (as reported in Section 8.8.2) an indication that longer times might be beneficial for the more absorbent natural fibres.

The length of time needed for solvent evaporation was found to be at least 30 minutes for the standard woven fabrics and polyester interlock used in this work (see Section 8.8.3). For other fabric types (thicker structures, for example) a longer time may be necessary.

It was found in Section 8.8.5 that polymerisation solutions are best prepared just before use, as they deteriorate over time. Approximately one gram of textile can be treated in 10 mL of polymerisation solution with no statistically significant change in the resultant composite's electrical properties (see Section 8.8.4).

8.13.1.7 Summary.

The optimum conditions for the preparation of textile-ICP composites by the single-dip method are summarised in Table 8.53.

Table 8.53. Summary of optimum polymerisation conditions for the preparation of textile-ICP composites by the single-dip technique.

Parameter	Optimum condition	Notes
Precursor type	3,4-Ethylenedioxythiophene (EDOT)	
Precursor concentration	0.03 g/10 mL	For EDOT.
Oxidant type	Iron (III) perchlorate	
Oxidant concentration	0.75 mol/L	For iron (III) perchlorate.
Solvent	Methanol or ethanol	
Substrate	Polyester	For poly(EDOT).
Number of treatments	6	For poly(EDOT) on polyester.
Solution impregnation time	4 minutes	For poly(EDOT) on polyester.
Solvent evaporation time	30 minutes	For standard woven fabrics and polyester interlock fabric used in this work.
Amount of textile	1 g/10 mL polymerisation solution.	For poly(EDOT) on polyester.

8.13.2 Conclusion.

The results of the experiments described in this chapter are extremely encouraging. The low surface resistance possible when the optimum conditions (described in Table 8.55) were employed, and the extremely good durability of textile-poly(EDOT) composites, are particularly exciting. The durability of conductive polymers has long been a major limitation to their use in many applications, with the most readily prepared example (polypyrrole) being quite poor. The very simple technique used here allows a much more durable type of conductive polymer to be prepared. It is probable that many of the features that give polythiophenes better durability are also responsible for them being difficult to prepare. The system here uses a relatively new ICP precursor (EDOT), and controlled, strong oxidising conditions to make a conductive and durable textile-ICP composite, suitable for evaluation in a range of applications.

Late in this research project, an ICP deposition technique bearing some similarity to the single-dip process described in this chapter was discovered in the literature. In a now-expired patent, Japanese workers described a technique for casting films of conductive polymers based on aromatic heterocycles [163]. The method involved creating a solution containing the precursor, oxidant, and possibly an additional component to improve film mechanical properties. Removal of the solvent by evaporation resulted in polymerisation onto the substrate, which was then peeled off the substrate. The components in the film casting solution were carefully chosen to encourage polymerisation onto the substrate, and a subsequent doping step was used (such as exposure to iodine vapour) to dope the conductive polymer film. Substrates mentioned were generally inorganic materials such as glass and ceramic plates.

Also of note is the recent commercialisation (by Bayer, via spin-off company HC Starck) of Baytron®; a conductive polymer based on poly(EDOT) [164]. It is prepared from two components: 'Baytron M' (EDOT) and 'Baytron C' (iron (III) *p*-toluenesulphonate). Suggested applications for the product include anti-static coatings, OLEDs and thick-film electroluminescent materials. The use of *p*-toluenesulphonate is interesting, as despite its predicted suitability for oxidative polymerisation of EDOT, it was found in this work to perform much worse than other iron (III) salts, with higher resistance and poorer durability (Section 8.4).

Despite these two recent findings, the use (and refinement) of such a system to deposit relatively conductive ICPs onto textiles, rather than as a means of casting films, is novel. In addition, the clarification of the influence of a wide range of process parameters is valuable, and the verification of the physical and durability properties of textile-poly(EDOT) composites confirms the suitability of the system for evaluation in various applications.

Chapter 9 Summary and Comparison of Techniques.

9.1 Aqueous System (Milliken).

Investigations into this technique were reported in Chapter 5. Although it is well proven and very effective when used to polymerise pyrrole onto the surface of textiles, attempts to create thiophene-based textile-ICP composites via this route were unsuccessful. The only conductive composite produced was when EDOT was used, with acetonitrile in place of water as the polymerisation medium. However, it appeared that polymerisation had taken place not on the fibre surfaces, but in the solution, with the amorphous polymer particulate subsequently accumulating in the fabric interstices.

The influence of substrate fibre type was investigated for the standard polymerisation system with pyrrole in water. Synthetic fibres (nylon, polyester, polypropylene and acrylic) were all very similar, and produced lower resistance composites than natural fibres (wool and cotton). The latter are quite absorbent materials, and it is postulated that this absorbency hinders polymer surface deposition by favouring migration of reaction species into the fibres, rather than keeping them on the surface.

9.2 Vapour Deposition.

Investigations into this technique were reported in Chapter 6. Its suitability is well-established in the literature for pyrrole, as this precursor has relatively high volatility and reactivity. A simple and reproducible technique was used to establish the optimum conditions for pyrrole, but under the same conditions, deposition of poly(EDOT) and poly(2,2'-bithiophene) was unsuccessful. However, increasing the temperature at which the process was carried out resulted in conductive composites from both thiophene variants. At higher temperatures both the rate of reaction and the vapour pressure (and therefore the availability of precursor in the vessel) were increased.

The ideal conditions for polymerisation of EDOT were at room temperature for eight hours, with the highest possible oxidant concentration, and a small amount of additional dopant (NDSA). For 2,2'-bithiophene, the temperature needed to be greater than 50°C, for an eight hour process, with slightly less additional dopant used.

Surface morphology of the composites was irregular, with obvious deposits on and around the fibres visible under SEM. For bithiophene these deposits were protruding, needle-like growths, which could have been re-crystallised precursor or ICP. The mass of ICP added with EDOT was comparable to that with pyrrole (for a given surface resistance), while bithiophene needed much higher mass add-on. The preparation of conductive textile-poly(EDOT) and poly(2,2'-bithiophene) composites by vapour deposition carried out in this work is (as far as can be ascertained) the first time this has been reported.

9.3 Two-Stage Impregnation.

Investigations into this technique were reported in Chapter 7. It is the only technique to have been used in the literature for the *in situ* polymerisation of thiophene variants onto porous substrates, and its suitability was confirmed for both EDOT and bithiophene. The technique uses successive impregnations of a specimen in precursor and oxidant solutions, but polymerisation does not take place until after the specimen is removed from the latter and the solvent allowed to evaporate. Interestingly, the lowest surface resistance did not correspond with the highest mass add-on. In fact, although precursor concentration was directly proportional to mass add-on, it was not (inversely) proportional to surface resistance. An optimum precursor concentration of about 0.25 g /10 mL (for EDOT) or 0.40 g / 10 mL (for bithiophene) was established, above and below which the surface resistance increased.

Simple alcohols (methanol and ethanol) were preferred for the oxidant solution, with acetonitrile ideal for the precursor solution. Impregnation in precursor followed by oxidant was preferable to the reverse. The surface morphology of the specimens was examined by SEM, and showed a smooth coating around the fibres, with amorphous polymer also present as scattered particles. The quantity of these particles increased as the mass of polymer deposited increased.

The two-stage impregnation system's insensitivity to agitation during the second (oxidant) impregnation led to the development of the single-dip technique.

9.4 Single Dip Technique.

Investigations into this technique were reported in Chapter 8. It was established that ICP deposition could be achieved by combining oxidant and precursor impregnations in one step (a single 'dip' of the specimen into the polymerisation solution). This worked best with EDOT as the precursor, although polypyrrole and poly(2,2'-bithiophene) could also be deposited in the same way. Like the two-stage impregnation technique, there was an optimum precursor concentration that gave the lowest resistance composites. This was approximately 0.03 g/ 10 mL, above and below which the composite surface resistance increased. The preferred polymerisation medium was methanol or ethanol. Iron (III) chloride, nitrate and perchlorate all performed well as oxidants, with the lowest resistance occurring with perchlorate used at 0.75 mol/L. Iron chloride and nitrate were best used at their highest attainable concentrations, but did not produce composites with as low a surface resistance as those prepared using perchlorate.

Polyester fabric was the best substrate to use, and by applying multiple depositions of perchlorate-doped poly(EDOT), very low surface resistance could be reached at moderate mass add-on. The best was ~65 Ω/square at ~5% polymer mass add-on, achieved by carrying out five or six successive depositions. The mechanical properties (flexibility and strength) of the fabric were not adversely affected by multiple polymer depositions to this level. SEM examination showed a smooth coating, with increasing amounts of loose amorphous polymer accumulating in the fabric interstices as mass add-on increased. Light microscopy and TEM confirmed this structure, and suggested that there was a smooth, reasonably dense coating that surrounded the fibres, with an irregular layer of lower density material outside it.

The durability of perchlorate-doped polyester-poly(EDOT) composites was remarkably good. Ageing in standard conditions resulted in only a slight decrease in resistance over several months, while accelerated ageing (by exposing the specimen to dry heat at 100°C for one hour, 10 times) had almost no effect on resistance. By comparison, the high temperature ageing caused a factor of 11 increase for chloride-doped polypyrrole, and a factor of five increase for chloride-doped EDOT on the same substrate. Washing caused a 700-fold deterioration for chloride-doped polypyrrole, but only increased the perchlorate-doped poly(EDOT) specimen's resistance by a factor of 2.5 (perchlorate-doped polypyrrole could not be deposited onto a textile because it was not possible to control the polymerisation reaction). The conductivity of *p*-toluene-sulphonate-doped poly(EDOT) was low and its durability poor, despite its expected suitability for combined oxidation and doping of ICPs.

Elemental analysis indicated that the composition of the poly(EDOT) deposited onto textiles was close to that expected from its chemical formula. Doping levels were from 2.5 to 3.5 heterocyclic units to every dopant anion, the highest doping level being achieved with perchlorate.

9.5 Comparison of Techniques.

The best results obtained for each precursor (for a single deposition of ICP using each of the three successful techniques) are provided in Table 9.1. The results could, in some circumstances, be improved by optimising the treatment parameters. Bithiophene, for example, was not widely used with the single dip technique, and the result given in the table was from deposition onto a substrate that was probably not optimal.

Table 9.1. Summary of 'best results' for each precursor.

Technique	Property	EDOT	2,2'-Bithiophene	Pyrrole
Vapour deposition	Mass add-on (%)	4	8	1
	Surface resistance (Ω/sq)	700	100,000	1000
Two-stage impregnation	Mass add-on (%)	5	7	3
	Surface resistance(Ω/sq)	10,000	20,000	4000
Single dip	Mass add-on(%)	0.8	1.0	0.5
	Surface resistance(Ω/sq)	300	600,000	3000

The best result was accomplished by polymerising EDOT by the single dip technique. This provided the ideal combination of low surface resistance and low mass add-on. Composites of this type (for example, the perchlorate-doped version of poly(EDOT) on polyester from Section 8.11) also had excellent durability. When up to five coatings were used (to further reduce the resistance), the composite did not lose its inherent textile properties of drape and strength.

When 2,2'-bithiophene was used, the best properties resulted when the two-stage impregnation technique was used. However, the focus of the work reported in Chapter 8 (investigations into the single dip technique) was very much on EDOT, so the results for bithiophene were almost certainly not optimised. Although pyrrole provided good results in two-stage impregnation, it is so well-suited to both vapour deposition and the aqueous technique (due to its volatility and slight solubility in water, respectively) that its use wasn't explored in any detail with the single dip technique. When it was used under conditions that were optimal for EDOT, it had inferior conductivity and durability.

Chapter 10 Conclusions and Future Work.

10.1 Conclusions.

The primary aims of this research (as outlined in Chapter 3) have been met. Thiophene-based precursors were polymerised *in situ* on textile substrates by three approaches, including a new method (referred to in this thesis as 'single dip'), which was a refinement of the two-stage impregnation technique known from the literature [13]. Vapour-phase polymer deposition of thiophene-based precursors was also achieved, including from 2,2'-bithiophene, which is solid at room temperature. The two-stage impregnation and vapour deposition techniques were of less interest than the single dip approach, so were not as fully investigated or optimised.

Moderately conductive composites were made – in fact, by using multiple coatings and/or iron (III) perchlorate as the oxidant, quite low (< 100 Ω/square) resistances were reached at less than 5% mass add-on (making the composite ~4.8% ICP and ~95.2% textile, by mass). As expected at this mass add-on level, the flexibility (related to fabric drape) of the fabrics was not substantially adversely affected. It was also pleasing that fabric strength had not been decreased by the deposition of an ICP layer. Extensibility was not directly measured, as the fabrics that were assessed were the woven standard fabrics, and all have low extensibility. An alternative tensile deformation test method would be necessary to establish the suitability of knitted materials for strain gauge applications.

This resistance level is probably lower than is needed for sensing applications, but may allow other applications to be explored where a higher conductivity is more useful. In wearable electronics these might be in signal transfer applications, or as electrodes in electronic textile devices like switches. Textile-ICP composites were made that were reasonably durable – perchlorate doped poly(EDOT) showed only small changes when aged (even when this was accelerated by exposure to high temperatures), and only changed by a factor of two or three after 10 washes. If such a material had a sensory response to environmental stimulus of an order of magnitude or more, then it may not need to be re-calibrated during use (as would be necessary for materials that deteriorate to a greater extent). However, it is possible that in stabilising the resistance to this extent, the capacity of the material to act as a sensor may have been diminished.

The influence of fibre type on the polymerisation process and composite properties was found to be very complex. Polyester was clearly the best substrate to use, possibly because its low absorbency encouraged the reaction to take place on the fibre surface rather than inside the fibre, where polymerisation may be hindered by the internal molecular structure of the textile fibre polymer. There may also be some aromatic ring interaction between polyester and the precursor (during polymer formation), and with the ICP itself. Perhaps polyester provides a template for ICP formation – almost 'guiding' polymer formation into a more linear (more conductive) configuration.

The key polymerisation parameters such as reagent concentration, time, temperature, and additional dopants were established for all three polymer deposition techniques. The most interesting phenomenon was that observed for precursor concentration for the two-stage impregnation and single dip techniques. This has been fully discussed elsewhere (Sections 7.2 and 8.2), but it highlights the need to use conditions that encourage the formation of high 'quality' rather than large quantity ICP. This principle seems to hold for other techniques as well: a low temperature is recommended for the Milliken technique to encourage a more controlled and more conductive polymer deposition [12], while the use of low temperatures to slow vapour deposition has been demonstrated for polyaniline [61].

The three deposition techniques were compared, their suitability for use with textile substrates has been confirmed, and potential issues that relate to commercial scale-up have been noted where apparent. A possible means of adapting the single-dip method for continuous production of ICP-coated yarns or fabrics is described in Section 10.2.

Test methods were used to indicate the extent to which the desirable properties of the textile substrate were compromised by ICP deposition. Flexural rigidity and strength were measured, but extensibility was not, as discussed above.

The morphology of fibres coated with ICP by the various methods was assessed by SEM, with reasonably useful results. Some interesting phenomena were observed (such as the fine, needle-like, structures with vapour deposited poly(2,2'-bithiophene), shown in Figure 6.15), but more often a uniform coating with varying amounts of particulate ICP was apparent. At high mass add-on levels the amount of particulate was greater, which suggests that the fibre surfaces are only able to accept a certain amount of ICP in any single deposition process, and further polymerisation that occurs is not associated with the fibres. This may explain why multiple low-add-on depositions were better than a single high add-on deposition.

The elemental composition and level of doping were established for the single-dip system, and agreed quite well with the idealised form of the polymer/dopant system. The level of doping was calculated, and the lower resistance of perchlorate-doped poly(EDOT) thought to be due to a higher level of doping (higher Cl:S ratio). The presence of the substrate complicated this type of analysis, but careful selection of the substrates allowed useful information to be gathered. This work has shown that elemental analysis of ICPs can be useful even when specimens are not 'pure', i.e. when there is a component of them (the textile) that might mask the presence of substances of interest (the ICP/dopant system).

10.2 Future Work.

Opportunities for future research that would build on the work described in this thesis can be considered in terms of the deposition technique they relate to.

10.2.1 Vapour Deposition.

The evaluation of this technique could have been extended, in particular by optimising the system further for thiophene-based precursors. While it was demonstrated that they could be polymerised *in situ* on a textile substrate by vapour deposition, very little optimisation of the system was carried out. For example, increasing the temperature further (particularly for 2,2'-bithiophene) could be examined, as could the addition of other materials in vapour form. The fine, needle-like, structures on the surface of the fibres with vapour deposited poly(2,2'-bithiophene) also need further examination. Regardless of their composition (which would be very useful to know), this may be a useful way of growing nano-scale structures on surfaces.

A much more sophisticated technique could be developed with both temperature and pressure controlled. Use of an evacuated vessel for example (into which the textile substrate has been placed), with introduction of the precursor in vapour form, could be very effective at rapidly forcing the precursor into the fabric interstices.

10.2.2 Two-Stage Impregnation.

This technique evolved into the single dip approach that became the main focus of this work. It doesn't appear to have any particular advantages over the single dip approach, except that the lowest resistance composite prepared using poly(2,2'-bithiophene) was created via two-stage impregnation. However, relatively little work was carried out with bithiophene using the single dip system, so there is almost certainly room to optimise it further for that precursor, and the two-stage approach probably has no particular advantage. There seems to be little obvious value in investigating it further.

10.2.3 Single Dip Technique.

As discussed in Section 10.2.2, it would be worthwhile to optimise this technique for 2,2'-bithiophene, and any other ICP precursor variants that are of interest. Other than this, the system has been extensively investigated (as discussed in Chapter 8), so future research into it may be most usefully focussed on the development of applications for the composites produced. It was an initial intention of this research to assess the composites produced as textile-strain gauges, and this could be carried out in the future, as well as investigating their suitability as sensors for other environmental stimuli. The moisture and temperature sensitivity would be of primary interest, with gas sensing being a logical extension of that work.

Throughout this research, attempts have been made to relate the laboratory-scale polymer deposition processes to potential commercial scale-up. Issues relevant to this have been identified and discussed. The single dip technique in particular lends itself to a continuous polymer deposition approach, partly because of its simplicity. A possible system is illustrated in Figure 10.1, and could be used for fabric or yarn treatment. The latter would allow the creation of patterned conductive fabrics if conductive and untreated yarns were used in combination.

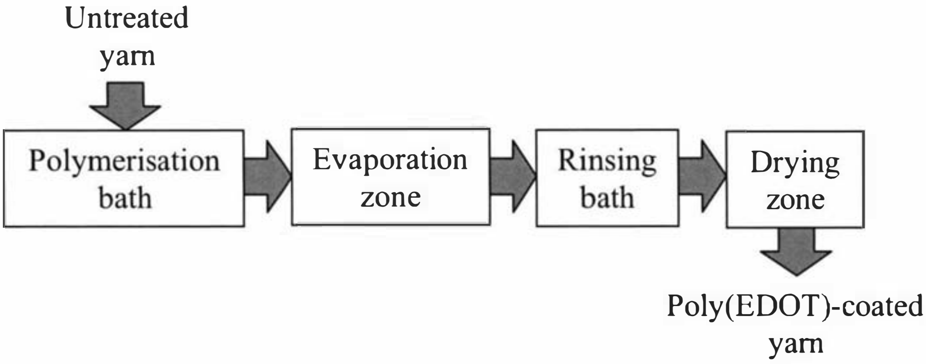


Figure 10.1. A possible continuous single-dip treatment for yarns (or fabrics).

In the system, the fabric (or yarn) would be run into a bath containing the polymerisation solution (oxidant and precursor in an appropriate solvent), then into an evaporation zone, which may need to be heated to get full polymerisation in a short time. Next the material would run through a rinse bath, probably with some liquor flow to improve rinsing. Two or more rinsing baths may be necessary, with the composite material getting cleaner as it progresses through the system. Finally it would be dried, then wound onto a package for use.

The development of this system would require several new parameters to be investigated, including the optimal rate of progression of the material through the system (controlling the impregnation, evaporation, rinsing and drying durations). The evaporation and drying temperatures would also need to be optimised.

10.3 Final Remarks.

A useful new technique for preparing robust ICP composite materials has been established and studied. This ‘single dip’ system allows thiophene-based precursors to be *in situ* polymerised onto textile (and probably other) substrates. The resultant composites have good conductivity, excellent durability, and retain the mechanical properties of the textile material. A range of fibre types have been assessed, with polyester the best substrate to use, giving a low electrical resistance and low polymer mass add-on. In the future, materials of this type will be useful in wearable electronic and smart textile devices.

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