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# **DEVELOPMENT OF NEW RSCM PROCESSES**

A THESIS PRESENTED IN PARTIAL FULFILLMENT  
OF THE REQUIREMENTS FOR THE DEGREE OF  
MASTERS OF TECHNOLOGY IN FOOD TECHNOLOGY  
AT MASSEY UNIVERSITY, PALMERSTON NORTH,  
NEW ZEALAND

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2007

## ABSTRACT

All concentrated milks thicken with storage time and the degree of thickening is highly dependent on the storage temperature. The aim of the current research project was to investigate this phenomenon in reconstituted concentrated milk (RCM) and recombined sweetened condensed milk (RSCM) and to investigate a method for overcoming the quality defect. RCM was initially investigated as this system had been extensively documented by previous works at Massey University, New Zealand. The RCM system was chosen to provide an opportunity of learning all about time dependent rheology. It was observed that reshearing of age thickened RCM samples destroyed the ability to age thicken again in subsequent storage. RSCM was then investigated to assess the effect of shear and temperature on age thickening during storage. Two shear levels of 900 and 31,000s<sup>-1</sup> were applied during the recombination stage in the process of producing RSCM. Samples of RSCM produced using both shear rates were then stored at temperatures of 30, 40 and 50°C for a period of 12 weeks. Triplicate samples from each storage temperature were analysed weekly for apparent viscosity, particle size distribution and colour. The RSCM samples stored at 50°C gelled by the 7th week while RSCM samples stored at 30 and 40°C did not gel even by the 12th week. The results of particle size distribution were consistent with the age thickening results. The particle sizes of samples stored at 30 and 40°C almost did not change with storage time but the particle sizes of samples stored at 50°C increased with storage time until they gelled. The colour of RSCM became darker with increased storage temperature and time. This was particularly noticeable at 50°C.

The study showed that the commonly observed quality defect in RSCM could be overcome for samples stored below 40°C for at least 12 weeks by the application of shear rates in excess of 900s<sup>-1</sup> during the manufacture of the product.

## ACKNOWLEDGEMENT

I gratefully acknowledge my supervisor, Dr. Khanh Tuoc Trinh, and my co-supervisor, Dr. Brian Wilkinson, for their supervision, guidance, advice and support throughout this study.

I also would like to express my thank to the following people;

Binh Trinh for training with the recombination rig and help in basic rheology.

Byron Mckillop and Garry Redford for their assistance in the pilot plant.

Steve Glasgow and Michelle Tamehana for their assistance in the laboratory.

Matt Levin and Peter Jeffery for IT support.

Helen and John Weber, my kiwi mum and dad, for their warm hospitality, for teaching me how to be a kiwi, and appreciate BBQ, potato and rugby.

Richard Croy and Mark Downey, my kiwi friends, for their friendship and their suggestion and support both study and life.

Duljira Sukboonyasatit and Angkana Noisuwan, my best sisters, for their friendship, love, help and support when I faced difficult situations. We share good and bad times together.

Thai friends for the good times we spend together here in Palmerston North especially fun activities in Thai Students' Association.

Most importantly, thank to dad and mum for their love, understanding and financial and mental support. Without them, I would not be here and done this degree.



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## CHAPTER 1 INTRODUCTION

Recombined Sweetened Condensed Milk (RSCM) is a concentrated dairy product that incorporates abundant sugar to allow a long shelf life without the need for refrigeration. In this respect, it is similar to Sweetened Condensed Milk (SCM) but the difference between those two products lies in the manufacturing process. SCM is made by evaporating fresh milk to a specific solids content and adding sugar before canning. RSCM is made from milk powder and therefore it is preferred in countries which lack local fresh milk. The main uses of RSCM are to make desserts and confectionary. In South-East Asian countries, RSCM is also popular for mixing with beverages to give a creamy texture and a sweet flavour.

The world market for RSCM is large and this is important for New Zealand which is one of the largest exporters of milk powder.

However, all concentrated milk products including RSCM have a basic weakness because they thicken with storage time. This phenomenon is called “age thickening”. This poses a problem to manufacturers of RSCM because the textural and functional properties perceived by the customer are variable and dependent on the time from manufacture. Customers do not expect products manufactured on a large scale to show this inconsistency. This problem has been investigated for more than four decades. But it is not completely understood yet. This research tests a new manufacturing process involving high shear that may delay the age thickening of RSCM.

### **Project aims**

- To test a process aimed at delaying the age thickening in RSCM.
- To study the changes in the properties of RCM (Reconstituted Concentrated Milk) and RSCM during storage trials.

**Objectives**

- To learn rheometry.
- To study time dependent rheology of recombined concentrated milk products.
- To assemble equipment for small scale production of RSCM.
- To Process RCM and RSCM at different shear rates.
- To investigate the effect of shear and temperature on the age thickening of RCM and RSCM during storage.
- To study the effect of temperature on colour of RSCM during storage.

The literature review in chapter 2 gives the background to the research topic. Chapter 3 describes the materials, equipment and methods used to manufacture the products studied and to analyse their samples. The results and discussions are presented in chapter 4. Finally, conclusions and suggestions for further works are presented in chapter 5.

## CHAPTER 2 LITERATURE REVIEW

This review discusses the state of Recombined Sweetened Condensed milk (RSCM) technology and traces the advances that have been made through out the years. Because of the similarities between Sweetened Condensed milk (SCM) and RSCM, the understanding of the two processes is often in linked and the manufacture of SCM will also be discussed where relevant. In *section 2.1*, a general background to the literature on RSCM, including a definition of RSCM is presented. This section also includes a discussion on the advantages and uses of RSCM together with a brief summary of its history and present standards. *Section 2.2* reviews the methods of selection of ingredients used in the manufacture of RSCM. *Section 2.3* discusses first the principle of the process for making RSCM and then the issues of manipulation of the operations in the process that have been targeted by numerous investigations. *Section 2.4* describes the rheological properties of Reconstituted Concentrated Milk (RCM) and RSCM including their apparent viscosities and the important phenomenon of age thickening. Finally, *section 2.5*, reports the most common and possible defects of RSCM.

The literature on the rheology of RCM has been fully reviewed in Binh Trinh's PhD thesis (2006) and the interested reader should consult that work. The main emphasis of this chapter is literature pertaining to RSCM, its manufacture, and properties.

### 2.1 GENERAL BACKGROUND TO RSCM LITERATURE

#### 2.1.1 Definition

Recombined sweetened condensed milk (RSCM) is basically a recombination product of milk powder and/or fat, in an almost saturated sugar solution. The quantity of water is then reduced to concentrate this product to the desired total solids content. Sweetened condensed milk (SCM) is made by concentrating fresh milk and adding sugar to it. It has properties similar to RSCM. The differences between SCM and RSCM lie in the processes and the raw materials used (Table 2.1). Thus, it can be said

that RSCM is derived from SCM. Normally, SCM and RSCM contain approximately 8-9% fat, 20-22% milk-solids-non-fat (MSNF), 43.5-45.4% sugar and 25.5-26.6% moisture (Table 2.2). SCM can be classified, based on the compositional requirement, into four types: sweetened condensed milk; sweetened condensed skimmed milk; sweetened condensed partly skimmed milk; and sweetened condensed high-fat milk (Codex 1999). The fat and/or protein contents are adjusted to achieve the compositional requirements by the addition and/or withdrawal of milk constituents but adjustment of the whey protein to casein ratio of the milk is not allowed (Codex 1999).

Table 2.1 Differences between SCM and RSCM.

| Differences                    | SCM                              | RSCM   |
|--------------------------------|----------------------------------|--|
| 1. Raw materials               | - Raw milk<br>- Sugar<br>- Water | - Milk powder<br>- Fat<br>- Sugar<br>- Water |
| 2. Processing                  |                                  |  |
| • Reconstitution/Recombination | --                               | Yes  |
| • Evaporation                  | Yes                              | --   |

Table 2.2 SCM and RSCM compositions (adapted from Jensen and Nielsen 1982).

| Compositions               | EU Standard<br>(Minimum w/w) | US Standard<br>(Minimum w/w) |
|----------------------------|------------------------------|------------------------------|
| Fat                        | 9.0%                         | 8.0%                         |
| Milk-solids-non-fat (MSNF) | 22.0%                        | 20.0%                        |
| Total milk solids          | 31.0%                        | 28.0%                        |
| Sugar                      | 43.5%*                       | 45.4%*                       |
| Total solids               | 74.5%                        | 73.4%                        |
| Moisture content           | 25.5%                        | 26.6%                        |

\*Based on a sugar ratio of 63%



### 2.1.2 Advantages and Uses of RSCM

The major advantage of RSCM is its long shelf life at ambient temperature. The relatively low water content and high sugar content give the product a high osmotic pressure (Carić 1993; Early 1998; Speer 1998 and Varnam and Sutherland 2001), and thus reduces the water activity,  $a_w$ , to 0.83 (Early 1998 and Walstra *et al.* 1999) which means that the growth of most spoilage microorganisms is inhibited thus resulting in an extended shelf life at ambient temperatures.

The second advantage of RSCM is that it can be made from dry dairy ingredients such as skim milk powder (SMP) and whole milk powder (WMP) making it available in countries that do not have a supply of fresh milk. In that sense, RSCM is fundamentally different from SCM, which is made by evaporating fresh milk.

The third advantage of RSCM is its low cost. In tropical areas, RSCM is frequently made using local vegetable fats and oils instead of milk fat. This lower-cost alternative recombined product is called “filled” RSCM (Nieuwenhuijse 2003 and Tong 2003). The filled RSCM is cheaper than the conventional product (Clarke 1999). Palm oil is most frequently used in filled RSCM (Nieuwenhuijse 2003) and coconut oil is also used (Choat 1979). The advantage of palm oil in some countries comes from its local abundance and low price. Although palm oil can give a good quality filled RSCM, a very low residual lipase activity can mean that free fatty acid levels gradually increase with time resulting in a soapy taste to the product. Coconut fat also has a weak point because of its high content of lauric acid, which has a very low flavour threshold.

RSCM is normally used as a whitener in coffee and tea when consumers also want a sweetened beverage. Because it can be stored without refrigeration, it is used on the move by sports people and hikers. In older days, it was sometimes used in Asia in diluted form as a milk drink, but this use is now being replaced by UHT milk. However, the diluted RSCM is not recommended for use as a baby food due to its poor nutritional value (Walstra *et al.* 1999). RSCM is not only used as a consumer product, but also as an ingredient in confectionary manufacture such as toffee, caramel and fudge (Clarke 1999 and Early 1998).

The main consumer markets for RSCM are the former Soviet Union, East Asia, Africa and Central America (Nieuwenhuijse 2003). In many tropical regions, such as South East Asia, the Middle East and South America, RSCM is used because of a shortage of fresh milk (Tong 2003).

RSCM sold in the retail market is usually packed in wide-mouthed jars, cans, tubes, and plastic packs while products used by process industries are packed in metal barrels, metal cylindric drums or similar large containers (Carić 1993).

### **2.1.3 History**

In 1810, the first report of adding sugar to preserve milk appeared in an English patent by De Heine (Nieuwenhuijse 2003). A mixture of milk and sugar was heated in an open vessel to remove water. This concentrated product was called sweetened condensed milk (SCM). The first manufacturing process of SCM was patented by Gail Borden in 1856 in the USA and England. The milk was concentrated by using a vacuum pan (Carić 1993; Hunziker 1949 and Nieuwenhuijse 2003) but the enterprise was not commercially successful. The first commercially successful SCM plant was operated by the Anglo-Swiss Condensed Milk company in Switzerland in 1866 (Choat 1979; Hunziker 1949 and Newstead 1982). Later, this company became Nestlé.

During the past 150 years or so, many techniques for the production of milk powder have been developed (Early 1998). Undoubtedly the most important technique today is spray drying. Although the concept of spray drying existed in the late 19th century, it never ousted drum drying as a principal method of milk powder production until the middle of the 20th century. At about this time, the recombination of milk powder was chosen as an alternative way to produce a new product called recombined sweetened condensed milk (RSCM).

During the 1950s many developing countries embarked on a programme to raise the nutritional status of their population. Milk was seen as an ideal food to accomplish some of these nutritional improvements. Many of these countries did not have a fresh dairy milk industry and so set up a milk industry based on imported whole and SMP.

The recombined milk was produced at local recombination plants and used local labour to man the plants (Clarke 1999). Moreover, the local RSCM plants opened up opportunities for local products such as sugar, vegetable oil and containers (Sayce and Park 1971). In the late 1950s the first RSCM plant was built in South East Asia by Dutch and American companies (Newstead 1982). In 1960, the Australia Dairy Produce Board (ADPB) was entrusted to build recombination plants in Singapore, Bangkok and Manila (Sayce and Park 1971). Before 1961, all of the SCM in South East Asia was imported from milk-producing countries such as the Netherlands, Britain and Australia. ADPB partially financed the construction of plant and equipment for many recombination plants over a 15-year period with the proviso that these plants had to purchase their raw materials, such as SMP and butter oil, from Australia. The 1960s and 1970s marked a critical phase in the development of the recombining industry in South East Asia region (Newstead 2004). During this period considerable effort was focussed on solving the technical problems associated with the production of RSCM. Unfortunately, little information is available on the development of RSCM in other regions such as Latin America and the Middle East.

#### **2.1.4 Standards**

The Codex Alimentarius Commission was created in 1963 by the Food and Agriculture Organisation (FAO) and the World Health Organisation (WHO) to develop food standards, guidelines and related texts such as codes of practice under the Joint FAO/WHO Food Standards Programme (Codex 2004). The Codex food code has become the seminal global reference point for consumers, food producers and processors, national food control agencies and the international food trade. According to Codex, “sweetened condensed milks (SCM) are milk products which can be obtained by the partial removal of water from milk with the addition of sugar, or by any other process which leads to a product of the same composition and characteristics”. The compositional requirement of SCM is a minimum 8% w/w of milk fat, a minimum 28% w/w of milk solids and a minimum 34% w/w of milk protein in milk solid non fat (Codex 1999). This food code does not recommend a minimum sugar content for these products. However, it was quoted in the Codex standards that “For all sweetened condensed milks the amount of sugar is restricted by

Good Manufacturing Practice (GMP) to a minimum value which safeguards the keeping quality of the product and a maximum value above which crystallization of sugar, may occur". The sugar content in this product is discussed in *section 2.2.3*.

Many national SCM standards have been adapted from the Codex food code such as in Canada law (Blais *et al.* 1985), EU Standards (Table 2.2), US Standards (Table 2.2), Australia Standards (Early 1998) and New Zealand Food Standards (Food Standards Australia New Zealand 2004)

It is noted that in the USA, the standards may vary from state to state with fat and total milk solids in the range between 7.7-8.5% and 25.9-28.0%, respectively (Early 1998). Some of them are out of range of the Codex standards.

Unfortunately, there is no standard for RSCM. However, because RSCM is derived from SCM, it can be assumed that standards for SCM can apply to RSCM.

## 2.2 SELECTION OF RSCM INGREDIENTS

The main ingredients used in the manufacture of RSCM are milk powder, fat, sugar, water and lactose. An emulsifier is an optional ingredient. The types and quality of ingredients can have a significant effect on the properties of the RSCM produced. The criteria for selection of these ingredients are discussed in this section.

### 2.2.1 Milk Powders

Milk powders provide the main source of protein in RSCM and have a major influence on the nutritional quality of the product. Milk powders are also the main factor that determines the viscosity of the final product which changes with storage time. These textural attributes are considered prime indicators of RSCM quality (Lawrence *et al.* 2001).

Milk powders should be as free flowing as possible, free from lumpiness (Choat 1979). Lumpiness is caused by excessive moisture content and/or unsuitable storage

conditions. The powders should be free from scorched particles and from extraneous matters and have good solubility (Horan 1982).

Milk powders have been classified into three groups according to the preheat treatment (low-, medium- and high-heat) received during manufacture. Jensen (1990) stated that both medium- and low- heat SMP were suitable for RSCM manufacture. But Choat (1979) proposed that medium-heat and sometimes high-heat SMP were more suitable for RSCM manufacture depending on the viscosity characteristics desired in the product. Early (1998) and Sanderson (1979) also agreed on the use of medium-heat SMP to produce RSCM. The full details on the effect of heat treatment level of milk powder on RSCM viscosity and age thickening are discussed in *section 2.4.5 (2)*.

Milk powders have also been classified in to two groups: whole milk powders (WMP), also known as full cream milk powders and skim milk powders (SMP), from which fat has been removed. Most of the discussions in the literature on the contribution of milk powders to the viscosity of RSCM have been based on the properties of SMP (see *section 2.4.5 (2)*) which were the only milk powders used until recent attempts to introduce WMP as an alternative ingredient. Lee (1959) observed that WMP could not be used because it produced RSCM of relatively poor flavour and with a very high viscosity. WMP can develop oxidised or rancid flavours on storage which reduce its shelf life (Blais *et al.* 1985; Early 1998; Kiesecker *et al.* 1984 and Sanderson 1970). Before the 1980s, the techniques of manufacturing and packing WMP were ineffective. With the overall improvement in the use of modern milk drying technology, it is now possible to produce WMP with improved flavour and storage stability characteristics (Kiesecker *et al.* 1984). Kiesecker *et al.* (1984) also showed that RSCM made from WMP had higher viscosity than RSCM made from SMP

### **2.2.2 Fat**

Fat is added to RSCM to achieve the standard on composition. The fat sources used in RSCM can be both milk fat and vegetable fat. At present, the popular source of milk fat is AMF (Anhydrous Milk Fat) or FFMR (Fresh Frozen Milkfat for Recombining). AMF and FFMR have the same composition of fat 99.9% and moisture < 0.1%

(Fonterra product bulletin 2005a,b). AMF/FFMR should be packed in an airtight and lightproof container that has been flushed with nitrogen. The differences between AMF and FFMR are its packaging and storage conditions. AMF comes in 210kg drums and 1,000kg/1,250kg bulk containers and can be stored without refrigeration. However, the recommended storage is in a cool dry place. FFMR is in 25kg cartons and stored frozen. The major advantage of AMF/FFMR is their relative stability to oxidation during distribution and storage (Kieseker *et al.* 1984).

Sometimes, in tropical countries, vegetable oils such as palm oil and coconut oil are used to replace milk fat. Although vegetable oil is cheaper than milk fat, there is a disadvantage: product containing coconut or palm kernel oil may develop a rancid off-flavour (Nieuwenhuijse 2003).

AMF used for recombined dairy products should be manufactured to the following minimum standard (IDF standard 68A: 1977) (Sanderson 1979). The peroxide value (PV), colour and odour are characteristics of the AMF which often cause a problem in recombined products (Horan 1982). A PV of 0.7-1.0 milli-equivalents is often chosen. A PV of 0.2 milli-equivalents is the best but not always easy to obtain and fetches a premium price. It is wise to request provision of samples before ordering supplies.

### **2.2.3 Sugar**

Sugar is the ingredient that promotes high osmotic pressure to prevent the growth of microorganisms in RSCM.

Usually the preferred sugar for manufacturing RSCM is sucrose, although glucose, dextrose, or others could also be used, particularly when the product has special applications such as diabetic diets (Carić 1993, 1994). The key advantages of sucrose over other sugars are its good solubility and customer preference. Sucrose must be microbiologically safe, with no acids or invert sugar present. Also it should be free from extraneous matters (Horan 1982).



Sugar should be refined, granular and white in colour (Choat 1979). This is because sugar will influence the colour of the final product. Brown sugar is not suitable as a raw material because it produces a brown coloured final product.

The sugar number, also-called the sugar index (Carić 1994) or sugar/water concentration ( $C_{S/W}$ ) (Speer 1998) or sugar ratio (Varnam and Sutherland 2001) is very important for inhibiting the growth of microorganisms (Speer 1998). The sugar ratio should be in the range of 62.5-64.5% (Carić 1994; Early 1998 and Varnam and Sutherland 2001). If the ratio is lower than 62.5%, it may result in bacterial-induced defects in the final product (Carić 1994; Choat 1979; Clarke 1999 and Fluck 1976). On the other hand, if the sugar ratio is greater than 64.5%, lactose crystallisation may occur at low temperatures, which results in a gritty mouth feel. The sugar ratio is calculated on the basis of dry matter and sugar contents of the product as shown in Equation 2.1:

$$\text{Sugar ratio (\%)} = \frac{S}{S + W} \times 100 \quad (2.1)$$

Where S is the percentage of sucrose content in the product and W is the percentage of moisture content (Carić 1993, 1994; Clarke 1999; Early 1998 and Speer 1998).

#### 2.2.4 Water

The water used in the manufacture of RSCM should neither contain bacteria nor a high level of calcium (Choat 1979 and Newstead 1982). The use of hard water or alkaline water may affect the solution rate of milk powders and tend to give a chalky defect in the product due to a reaction between calcium ions from the water and phosphate groups in the milk.

### 2.2.5 Lactose

Seeding lactose is added to control the size of lactose crystals in RSCM to avoid large crystals causing sandy mouthfeel defect (see *section 2.5.1*).

Lactose seed is derived from whey solutions high in lactose (Choat 1979) and made by spray-drying. After spray-drying the amorphous lactose powder is left to absorb just enough water (at  $a_w \sim 0.4$ ) to allow crystallisation, which gives extremely small crystals ( $<1\mu\text{m}$  length) embedded in amorphous lactose (Walstra *et al.* 1999). Newstead (1982) stated that lactose powder should be very finely ground to less than  $10\mu\text{m}$  (Choat 1979) or around 300 mesh and must conform to high microbiological standards. Lactose powder is sometimes not added directly in crystalline form, but suspended in a small amount of SCM, which is more easily dispersed (Carić 1994).

### 2.2.6 Emulsifier

An emulsifier such as glycerol monostearate (GMS) is an optional ingredient. Pont (1960) suggested that GMS be added at the rate of 2-5% of the fat. GMS gives a less viscous mix by minimising air intake and permitting slightly higher homogenisation pressures and minimises fat separation. It has no effect on flavour or texture of the finished product. In 1982, Eggers reported that the addition of emulsifiers, carrageenan and GMS helped to reduce foam in RSCM. However, later experiments by Sinha and De (1972) were in disagreement with Pont's findings. They reported that GMS had no effect on the properties of RSCM

## 2.3 PROCESSING OF RSCM

Although the process of producing RSCM varies widely from factory to factory, the basic principles are the same everywhere. The conventional process of RSCM manufacture consists of the following stages – mixing, preheating, filtration, deaeration, homogenisation, pasteurisation, cooling then seeding with lactose, and finally canning (Choat 1979) as shown in Figure 2.1.



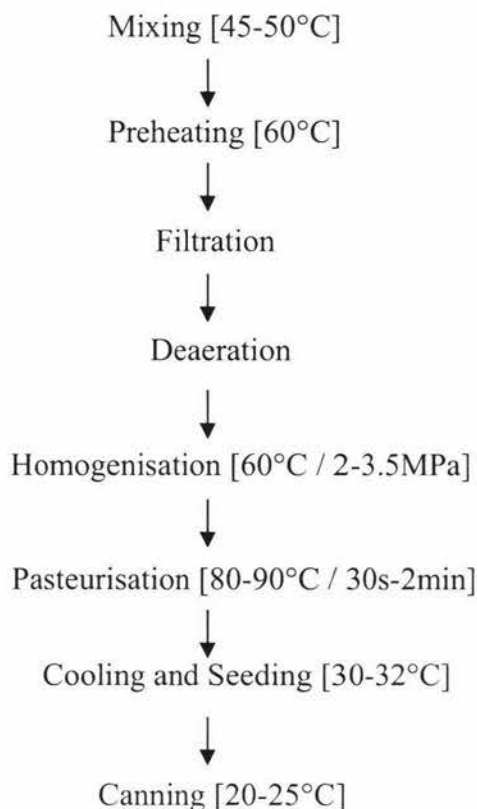


Figure 2.1 Flowchart of RSCM process (Adapted from Choat 1979)

The first stage in the conventional process is a recombination of the raw materials, which are milk powder, and/or fat, sugar, and water. Milk powder is dispersed in water at 45-50°C. A high shear mixer is used to agitate the mixture. The mixture temperature is kept constant throughout the dispersion process. After the milk powder is completely dissolved, the reconstituted milk is hydrated without agitation for 10-15 minutes to allow milk proteins to fully rehydrate. Sugar is subsequently added and dissolved in the mixture with continued agitation. If SMP is used as a main ingredient, fat is melted at the same temperature as the mixture to prevent a drop in temperature of the mixture upon the addition of the fat.

The mixture is then heated to 60°C to prepare for homogenisation. The mixture is first sent to filters to remove undesirable objects, such as big lumps of milk powder. The mixture is then homogenised and care is taken to avoid cavitation which may result in

the incorporation of air into the mixture. Homogenisation is carried out at 2-3.5 MPa to avoid fat separation in the final product. The next step is pasteurisation at 80-90°C for between 30 seconds to 2 minutes to destroy most microorganisms including osmophilic yeast. The mixture is cooled down to 50°C before it leaves the pasteuriser and further cooled to 30-32°C for lactose seeding. Because the mixture is supersaturated with lactose, if crystallisation is not carefully controlled then large crystals created to the product. Next the mixture is cooled down to a suitable temperature for filling into cans at 20-25°C. The filling and canning process should be under aseptic conditions to avoid recontamination with microorganisms.

The following sections review the details of each step of processes.

### **2.3.1 Recombination of Powder**

#### **(1) Recombination temperature**

Many authors have reported different recombination temperatures for RSCM manufacture such as 100°F or 37.78°C (Lee 1959), 30°C (Pont 1960), 45-50°C (Choat 1979 and Jensen and Nielsen 1982) and 40-50°C (Newstead 1982).

According to the review of Clarke (1999), the temperature during the recombination of the powder has an influence on its solubility and the production of undissolved powder as shown in Figure 2.2. Increasing the temperature causes a reduction in the insolubility index. On the other hand, the weight of undissolved powder increases with temperature. Clarke (1999) suggested that the optimum recombination temperatures of powder are around 45-50°C, as also proposed by Choat (1979) and Jensen and Nielsen (1982).

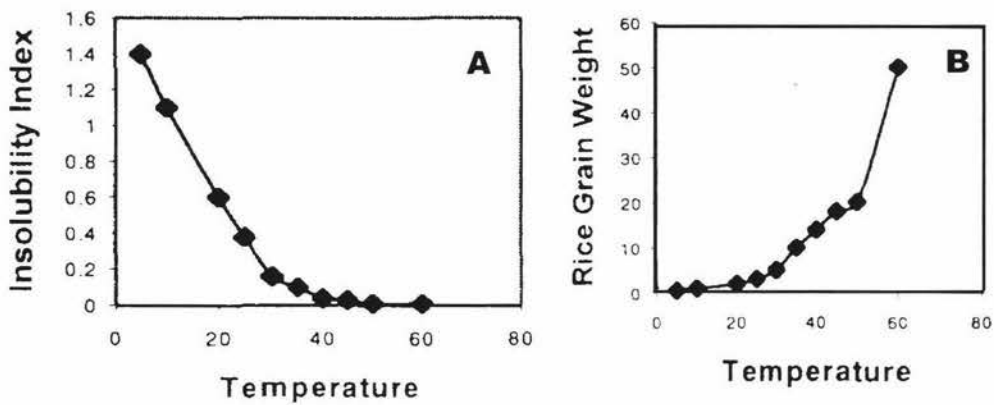


Figure 2.2 Relationship of the temperature and insolubility index (A) compared with the relationship of rice grains (undissolved powder formed) weight (B) at the same temperature, 0-80°C (Clarke 1999).

## (2) Air incorporation

During agitation, especially vigorous stirring, air is quickly incorporated in the mixture (Pont 1960). Care should be taken at this stage to avoid the formation of air bubbles, which must be limited as much as possible in the mixture (Lee 1959). It is important that the type of batch mixer be designed so that a vortex is not drawn from the water surface as this results in the incorporation of air and leads to considerable problems (Sanderson 1970). Not only do air bubbles cause a problem to the homogeniser, but air is also undesirable in the final product (Eggers 1982 and Pont 1960). For example, if the final product contains air bubbles, these could, partly at least, rise to the top of the can and cause surface froth and excessive headspace (Pont 1960).

## (3) Shear during RSCM recombination

As RSCM is a shear-dependent product, the rate of shear during recombination is one of the most important parameters to consider during the manufacture of RSCM. Many authors argue that high shear is developed in especially designed agitators such as the S.S. spoon (Sinha and De 1972) and the Cowles dissolver (Lawrence *et al.* 2001 and Newstead 1982). However, none of the authors gave a numerical estimate of the shear

rate developed in their equipment. Trinh *et al.* (2003) applied a range of shear rates during the reconstitution of RCM by forcing samples through capillary tubes of varying diameter. They showed that high shear rates (above  $10,000\text{s}^{-1}$ ) were able to slow down the age thickening of RCM.

#### **(4) Sugar addition**

Sucrose is added either in crystal form or as a solution. In the latter case, the sugar is dissolved in water at  $95^{\circ}\text{C}$ , the solution is heated to pasteurise and deactivate microorganisms (Carić 1993, 1994). The sugar involved should be devoid of invert sugar to prevent accelerated browning of the product due to Maillard reaction (Nieuwenhuijse 2003 and Walstra *et al.* 1999). The presence of sugar increases the boiling point of the mixture and decreases the coefficient of heat transmission due to the high viscosity of the mixture.

#### **2.3.2 Homogenisation**

If the RSCM is viscous enough and the fat is sufficiently emulsified by high shear mixing, then homogenisation may not be necessary to prevent fat separation (Sanderson 1970). However homogenation is normally used in the manufacture of RSCM to control the viscosity of the emulsion and to achieve better fat dispersion.

Different authors have reported different pressure settings for the first and second stages of the homogenisation of RSCM.

Muller and Kieseker (1965) stated that homogenisation at 2.1-2.8 MPa was optimum for control of fat separation and product viscosity. Krüger (1970) reported that better control of product viscosity could be obtained if homogenisation was carried out in two stages at up to 10 MPa after pasteurisation. However, this would require virtual aseptic operation of the homogeniser to avoid contamination of the product after pasteurisation. In their reviews, Choat (1979) and Newstead (1982) gave a popular range of 2-3.5 MPa and occasionally up to 7 MPa. Early (1998) stated that the range of about 7-10 MPa was often used to control the viscosity of product. However, other

authors have suggested intermediate homogenisation pressures: Walstra *et al.* (1999) at 2-6 MPa and Nieuwenhuijse (2003) at 5-10 MPa. It appears that the most common homogenisation pressures were relatively low in the 1970s and 1980s but became higher in the 1990s and 2000s because of a new focus on viscosity control.

### 2.3.3 Pasteurisation

The aims of pasteurisation are to destroy pathogens plus osmophilic and thermophilic microorganisms and to inactivate all enzymes particularly lipases and proteinases (Carić 1993, 1994; Nieuwenhuijse 2003 and Walstra *et al.* 1999). Pasteurisation also decreases milk fat separation and inhibits oxidative changes.

During milk powder manufacture most pathogens are destroyed and most of the enzymes are deactivated during the preheat treatment and concentration steps of the process. Pasteurisation is used in the RSCM process to destroy any new pathogens introduced during processing and possibly to destroy any thermophilic bacteria and spores that may have germinated subsequent to spray drying.

Again, the reports of different authors differ in the details but agree in general on the gross heat treatment required: Muller and Kiesecker (1965) suggested a temperature/time regime of 91°C for 30 seconds; Sinha and De (1972) suggested 75°C for 3 minutes and Choat (1979) and Newstead (1982) at 80-90°C for 30 seconds up to 2 minutes.

### 2.3.4 Seeding lactose

After pasteurisation, lactose crystals begin to form in the SCM/RSCM solutions which are supersaturated. The process must be controlled in such a way as to ensure that only very fine crystals are formed during this stage (Carić 1993). The final size of lactose crystals must not exceed 10µm (Blais *et al.* 1985; Carić 1994; Early 1998 and Newstead 1982).

In addition, large sucrose crystals can also be formed if too much sucrose has been added or if the milk has been concentrated too far, and the SCM is kept at low temperatures. In these cases the level of sucrose supersaturation is generally low and large sucrose crystals are generally formed, thus producing a decidedly sandy texture (Walstra *et al.* 1999).

Speer (1998) reported that the effects of the unavoidable crystallisation of lactose and sucrose could be minimised by:

- (1) Rapid cooling of the mixture to optimal crystallisation temperature of lactose.
- (2) Inoculation with crystal nuclei by adding finely milled and pulverised lactose after cooling to crystallisation temperature.
- (3) Constant low stirring of the product (too strong mechanical stress inhibits crystal formation).

Seeding with very fine lactose crystals is to prevent the formation of large lactose crystals by providing a large number of nuclei (Nieuwenhuijse 2003). This can be done only at a temperature at which SCM/RSCM is supersaturated with respect to lactose otherwise the seeding lactose crystals have no effect (Nieuwenhuijse 2003 and Walstra *et al.* 1999). The optimum crystallisation temperature is reported in the range of 30-32°C (Carić 1993,1994; Choat 1979 and Early 1998). After seeding, further cooling should be continued to crystallise the lactose (Walstra *et al.* 1999). However, large crystals cannot be avoided entirely.

## 2.4 RHEOLOGICAL PROPERTIES OF RCM AND RSCM

The rheological behaviours of RCM and RSCM are in many ways similar and the methods of measurement are common to both products. A critical problem for RCM and RSCM is age thickening. This section will define the rheological terms used to discuss the apparent viscosity of RCM and RSCM and fully review the age thickening of RSCM.

### 2.4.1 Rheology

The definition of rheology is “the study of the deformation and flow of matter” under the action of stress (Barnes *et al.* 1989; Steffe 1996 and Rao1999).

The simplest way to describe the flow properties of a fluid is to generate a shear stress-shear rate curve (flow curve). Examples of typical flow curves are shown in Figure 2.3.

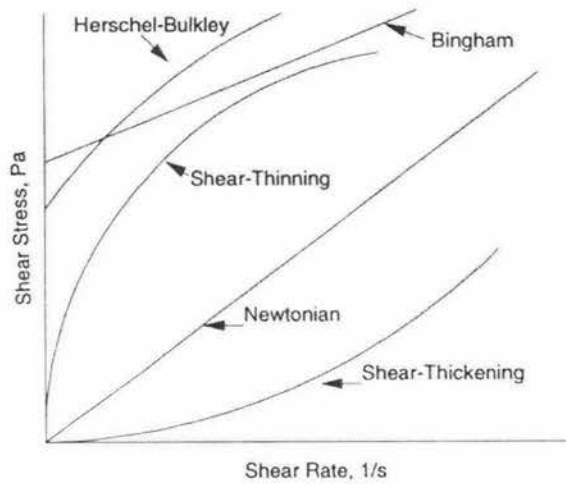


Figure 2.3 Curves for flow behaviour of fluids (Steffe 1996).

### 2.4.2 Viscosity

Viscosity ( $\mu$  in Pa s unit) is defined by the ratio of shear stress ( $\tau$  in Pa unit) to shear rate ( $\dot{\gamma}$  in  $s^{-1}$  unit) as shown in Equation 2.2.

$$\mu = \frac{\tau}{\left(\frac{d\gamma}{dt}\right)} = \frac{\tau}{\dot{\gamma}} \quad (2.2)$$

It measures the internal friction of the fluid or its tendency to resist flow (Barnes *et al.* 1989; Bourne 2002; Rao1999 and Viswanath and Natarajan 1989).

If the flow curve of a fluid is a straight line that passes through the origin then the viscosity is independent of shear rate and therefore a constant. Such a fluid is called a

Newtonian fluid after Sir Issac Newton's postulate (Barnes *et al.* 1989). Fluids with viscosities that change either with shear stress, shear rate or time are stated to be non-Newtonian. Their flow curves are represented by curved lines or straight lines not going through the origin as shown in Figure 2.3. The viscosity of a non-Newtonian fluid at any particular shear rate or shear stress is called the apparent viscosity (Barnes *et al.* 1989) and the shear stress or shear rate at which it is measure should always be quoted.

Many dairy products exhibit the phenomenon of shear thinning; the apparent viscosity decreases with increasing shear rate. If the change in viscosity occurs instantly when the shear rate is changed, the material is said to be time-independent. Time-independent-shear thinning fluids are called pseudoplastic. The changes in apparent viscosity with shear rate in complex fluids are usually associated with the change in structure of the dispersed phase (Steffe 1996). In many cases, that change in structure takes time, particularly when the fluid is moved from a region of high shear to a region of low shear, the fluid is said to be time-dependent and the viscosity is now a function of both shear rate and duration of shear. Time-dependent-shear-thinning fluids are said to be thixotropic. The slow build up of viscosity and structure when a fluid is stored at rest after processing is called age thickening.

Initial viscosities of RSCM before storage are quoted in the range of 30-40 poise (Kieseker *et al.* 1984 and Newstead 1982). Since RSCM is a non-Newtonian product, the shear rate or shear stress at which the apparent viscosity is measured should be reported which is unfortunately not always the case in the references quoted above.

It is important to control the viscosity of RSCM because the product is unacceptable if the apparent viscosity is too high or too low (Hunziker 1949; Newstead *et al.* 1982 and Tong 2003). If the product is too viscous, it can become difficult to remove from the container. During manufacture, a product is expected to be pumpable and flow easily. On the other hand, if the product is low in viscosity, defects in the final product may occur such as the rapid separation of fat and the sedimentation of crystals of lactose and calcium phosphate (Early 1998 and Newstead 1982). A thin product may also allow air to be entrained during production.



### 2.4.3 Age Thickening

Age thickening happens during storage of condensed milk products such as Evaporated milk (EM)/ Concentrated milk (CM) (e.g. de Koning *et al.* 1992; Harwalkar 1992; Harwalkar *et al.* 1983; Snoeren *et al.* 1982, 1984), SCM (e.g. Blais *et al.* 1985; Samel and Muers 1962a,b,c; Upadhyay 1998; Varnam and Sutherland 2001 and Walstra *et al.* 1999), RCM (e.g. Trinh 2006; Trinh and Yoo 1997 and Trinh *et al.* 2002a, 2003;) and RSCM (e.g. Kiesecker *et al.* 1984; Lawrence *et al.* 1963; Muller and Kiesecker 1965; Noda *et al.* 1978 and Rohm 1988). All these products are also shear thinning i.e. thixotropic. There are two definitions of age thickening. Samel and Muers (1962a) defined age thickening as “the gradual increase in viscosity, due to physico-chemical changes, which occurs during storage of condensed milk”. This definition has been adopted by several authors such as Carić (1993) and Upadhyay (1998). de Koning *et al.* (1992) proposed a second definition that described age thickening in two steps “1. Increase in viscosity and spotty lump formation observed during storage, while still uniform fluidity is reached after stirring; 2. Gelation, which takes place after this stage as an irreversible process accompanied by syneresis in rest and flocculation after stirring”. This definition was also quoted by several authors such as Varnam and Sutherland (2001) and Walstra *et al.* (1999).

Monitoring the changes in viscosity with storage time is common in the application of both definitions of age thickening, but monitoring the onset of gelation only occurs with the de Koning *et al.*'s definition.

The mechanism of age thickening of concentrated milks is still not fully understood (Bienvenue *et al.* 2003a). The most likely causes are changes in the milk proteins, especially casein micelles,  $\beta$ -Lactoglobulin and other particles and the interaction between these particles (e.g. De Felipe *et al.* 1991 and Harwalkar and Vreeman 1978, b). Samel and Muers (1962a) compared sweetened condensed whey and SCM and reported that sweetened condensed whey did not age thicken significantly in 13 days at 39°C whereas the apparent viscosity of SCM increased by a factor of 20 after just 3 days storage at 39°C. They concluded “whey proteins play no significant part, directly or in association with casein, in the age thickening process”. However, De Felipe *et al.*

(1991) examined three samples of commercial SCM after 45 days storage at 37°C and found filamentous appendages linking casein micelles and argued that “denatured whey proteins do participate directly in micellar aggregation and hence in the increase in viscosity”. Vélez-Ruiz and Barbosa-Cánovas (1997) concluded that the role of whey proteins in the physical change during age thickening was still not clearly understood. In their study of age thickening of concentrated skim milk stored at rest at 50°C, Bienvenue *et al.* (2003b) conducted SDS-PAGE tests in both reducing and non-reducing conditions. They found that “the increase in particle size and probably high-shear viscosity during storage did not involve formation of additional covalent bonds” which would involve  $\beta$ -Lactoglobulin. In their review, Samel and Muers (1962a) showed that at the same time that the viscosity increases, the sizes of casein particles also increase and their shapes changed during age thickening. It is known that the size and shapes of these particles in the dispersed phase have an effect on apparent viscosity (Eirich 1956 and Steffe 1996).

Newstead (1982) stated that in his experience the apparent viscosity of RSCM rose from an initial viscosity of 30-40 poise up to around 80-100 poise after 6 months storage. However, since the rate of age thickening is very dependent on the storage temperature, the values described by Newstead (1982) were not very helpful since he did not detail the temperature of storage and the shear rate and/or shear stress that the apparent viscosity was measured at. Nonetheless, these values apparently agreed with Kieseker *et al.* (1984) who reported that the viscosity in their experiment increase from 30-35 poise up to 70-80 poise over 6 to 8 months at 25°C. Unfortunately, Kieseker *et al.* (1984) did not quote the shear rate and/or shear stress of measurement. The initial viscosity of Kieseker *et al.* (1984) and the rate of age thickening appeared to agree with Samel and Muers (1962b) for storage between 20 and 30°C. Samel and Muers (1962b) measured the apparent viscosity at the shear rate of  $4.61\text{s}^{-1}$ .

Age thickening tends to occur when the initial apparent viscosity of the RSCM is high but it is difficult to predict age thickening characteristics based on the initial apparent viscosity alone (Kieseker *et al.* 1984 and Noda *et al.* 1982).

For a detailed discussion of the phenomena observed in the age thickening of RCM, the literature review of Trinh (2006) is strongly recommended.

The flow curves of RCM and RSCM obtained after various times of storage have been described with the Herschel-Bulkley (HB) model. This model is shown in Equation 2.3 (Rao 1999):

$$\tau = \tau_y + K\dot{\gamma}^n \quad (2.3)$$

where  $\tau$  is the shear stress [Pa],  $\tau_y$  is the yield stress [Pa] which is a stress required to achieve flow,  $K$  is the consistency index [Pa.s<sup>n</sup>],  $\dot{\gamma}$  is the shear rate [s<sup>-1</sup>] and  $n$  is the flow behaviour index [Dimensionless].

This model (Equation 2.3) is useful when dealing with a new fluid of unknown behaviour because it is a general model and incorporates estimates of  $\tau_y$  and  $n$ . Fluids are shear thinning when  $0 < n < 1$  and shear thickening when  $n > 1$ . This model degenerates to the useful power law model (Equation 2.4 Rao 1999) when  $\tau_y = 0$ ; the fluid has no yield stress.

$$\tau = K\dot{\gamma}^n \quad (2.4)$$

The power law model (Equation 2.4) has been found to apply to RCM of medium concentration about 23-42%TS (Trinh *et al.* 2002a and Vélez-Ruiz and Barbosa-Cánovas 1998, 2000). Alternately, when the fluid has a yield stress but the shear dependence is weak,  $n = 1$ , the model degenerates to the Bingham plastic model (Equation 2.5 Rao 1999):

$$\tau = \tau_y + \mu_B \dot{\gamma} \quad (2.5)$$

where  $\mu_B$  is the plastic viscosity [Pa.s].

This situation was observed by Trinh and Leslie (1997) during concentrate heating at low temperature (75°C) and by Bienvenue *et al.* (2003b) in their study of milk concentrate with different genetic variants of  $\beta$ -Lactoglobulin after evaporation and storage at 50°C. The full HB model applies to high concentrations above 42% TS (Trinh *et al.* 2002a and Vélez-Ruiz and Barbosa-Cánovas 1998, 2000).

When  $\tau_y = 0$  and  $n = 1$  the HB model degenerates to the Newton model (Equation 2.6 Rao 1999):

$$\tau = \mu \dot{\gamma} \quad (2.6)$$

where  $\mu$  is the viscosity [Pa.s] which is constant.

Milk at low concentrations below 23%TS is Newtonian (Vélez-Ruiz and Barbosa-Cánovas 1998, 2000). Trinh *et al.* (2002a) found that the Newtonian behaviour persisted up to 34.4%TS, which is higher than the limits observed by Vélez-Ruiz and Barbosa-Cánovas (1998, 2000). Trinh *et al.* (2002a) argued that the difference lies in the high shear rates used during the reconstitution of his RCM samples.

An important parameter not measured by any of the authors quoted so far is the fluid elasticity during age thickening.

#### 2.4.4 Methods of Viscosity Measurement

The methods of viscosity measurement have often been controversial. Questions have been raised about their reliability and relevance. Kiesecker and Southby (1965) were concerned that “the type of viscometer and temperature used in the determination of the viscosity of SCM vary considerably. As viscosity varies with temperature and rate of shear it is important that the same temperature and, where practicable, the same rate of shear be utilised in all evaluation”.

Many authors did not mention the shear rate and or shear stress used to report the RSCM apparent viscosity (Table 2.3). In addition, the viscometer used and the

conditions of measurements (such as shear rate, shear stress and measured temperature) of RSCM viscosity varied greatly among authors (Table 2.3).

Table 2.3 Reviews of the methods of RSCM viscosity measurement

| Authors                                | Equipment  | Conditions   |               |
|--|--|--|---------------|
|  |  | Shear rates  | Temperatures  |
| Cheng <i>et al.</i><br>(2000)          | A Brookfield RVT viscometer<br>Note: Standards Association of Australia 1978 | Not mentioned  | Not mentioned |
| Kieseker and Southby (1965)            | A Haake viscometer   | 50 sec <sup>-1</sup>   | 25°C          |
| Kieseker <i>et al.</i><br>(1984)       | A Brookfield RVT viscometer  | Not mentioned  | 25°C          |
| Lawrence <i>et al.</i><br>(1963)       | A Haake and Ferranti co-axial viscometer                                     | 50 sec <sup>-1</sup>   | 25°C          |
| Lawrence <i>et al.</i><br>(2000, 2001) | A Brookfield RVT viscometer  | 20 rpm with spindle no. 4  | 25°C          |
| Muller and Kieseker (1965)             | Not mentioned  | Not mentioned  | Not mentioned |
| Newstead <i>et al.</i><br>(1978)       | A Brookfield RVT viscometer  | 10 rpm with spindle no. 2,3  | 30°C          |
| Rohm (1988)                            | A seale type, Contraves Rheomat 15, measuring system C                       | At rate setting 10 after recording the flow curve within 100 seconds | 25±0.02°C     |
| Sinha and De<br>(1972)                 | A Hoppler's viscometer   | Not mentioned  | Not mentioned |

A number of standard methods for measuring the apparent viscosity of RSCM have been proposed by different groups of users in an effort to make results from different workers easier to compare. The method of the Standards Association of Australia 1978 was adapted from the original work by Kiesecker and Southby (1965). It has been used by Cheng *et al.* (2000) and Lawrence *et al.* (2000, 2001). These authors noted that the method uses a Brookfield RVT viscometer with spindle no. 4 at 20 rpm.

Lawrence *et al.* (2001) compared the viscosity of RSCM made from different milk powders using the Australian (the standard association of Australia 1978) and Dutch (Weerstra *et al.* 1988) methods. The viscosity values obtained with the Australian method were higher than those obtained with the Dutch method. However, the Australian and Dutch viscosities of different powders showed a linear correlation. Thus either method can be used to compare the viscosities of RSCM made from different powders provided that the methods are followed consistently.

Since RCM and RSCM are thixotropic products, their shear thinning behaviour is an important characteristic and cannot be obtained from a single value of the apparent viscosity even when the temperatures and shear rates are specified. A full flow curve is needed. Full flow curves have been reported in the study of RCM (e.g. Trinh 2006; Trinh and Yoo 1997 and Trinh *et al.* 2002a), SCM (e.g. De Felipe *et al.* 1991 and Samel and Muers 1962a) and RSCM (e.g. Rohm 1988)

With thixotropic fluids, the actual details of measurement of the flow curves matter because the material breaks down differently depending on the duration of shear, even at one shear rate. Rohm (1992) showed that one can get different flow curves and different thixotropic hysteresis areas for yoghurt by varying the number of points measured in shear sweeps and the time intervals between points. Trinh (2006) also showed this effect. Thus a good protocol for the measurement of RSCM rheology should detail clearly the measuring time, shear range and shear steps covered, in addition to the parameters described in many of the papers published in the literature.

### **2.4.5 Factors Affecting Viscosity and Age Thickening of RSCM**

Viscosity is used as one of the key descriptors of RSCM quality. The viscosity of RSCM depends on many factors, which can be divided into four major groups: processing factors, ingredient factors, composition factors and handling factors of the RSCM product.

#### **(1) Processing factors**

Several unit operations used in the manufacture of RSCM, especially homogenisation and pasteurisation have been proven by several authors (Choat 1979; Kieseker 1982; Lawrence *et al.* 1963, 2000, 2001; Muller and Kieseker 1965; Newstead 1982 and Pont 1960) to have an effect on the viscosity and age thickening of RSCM.

#### ***Homogenisation***

Homogenisation has a significant effect on the viscosity of RSCM (Kieseker 1982; Lawrence *et al.* 1963, 2000, 2001 and Pont 1960). Researchers (e.g. Lawrence *et al.* 2000, 2001) have found that higher apparent viscosities were observed when higher homogenisation pressures were used in all cases of their experiments. High viscosity values also had an effect on age thickening (Choat 1979; Kieseker 1982; Lawrence *et al.* 1963, 2001; Muller and Kieseker 1965; Newstead 1982 and Pont 1960).

#### ***Pasteurisation***

Lawrence *et al.* (2000, 2001) have shown that the apparent viscosities increased when the pasteurisation temperature increased (88 and 92°C) for a fixed holding time and when the holding time (30 sec and 5min) increased when the temperature was kept constant. However, heating for 5 minutes was excessive. Samples were not heat stable and thickened then blocked the processing lines. Thus, pasteurisation may be used to adjust viscosity. However, this is seldom done because it affects other product qualities such as colour and microbiological performance (Kieseker 1982 and Newstead 1982).



## **(2) Ingredient factors**

The type of milk powder used has a large effect on the rheological behaviour of RSCM. Unfortunately, a full understanding of the relationship between powder type and rheological behaviour is still not available and many manufacturers still run pilot RSCM production trials with test milk powders to ensure their suitability before buying them.

### ***Milk powder effects***

#### **- Heat treatment during the manufacture of the milk powder**

The level of heat treatment on milk powder used in RSCM manufacture has a major effect on viscosity (Lawrence *et al.* 1963, 2000; Muller and Kiesecker 1965 and Newstead 1982) and also age thickening (Lawrence *et al.* 2001 and Newstead 1982). This level is measured by the whey protein nitrogen index (WPNI), which expresses the amount of undenatured whey proteins remaining in the powder. Low-heat milk powders are defined as those having a WPNI greater than 6 mg of whey protein per gram of powder; medium-heat WPNI 1.5-6 mg/g and high-heat powder the WPNI below 1.5 mg/g (Jensen 1990 and Sanderson 1970). Fresh concentrated solutions of skim milk and whole milk have viscosities that increase dramatically with the level of preheating (e.g. Vilder and Moermans 1983). But the effect of milk preheat on the viscosity of RSCM is different and more confusing. For example, Cheng *et al.* (2000) found that powders given a low-heat treatment (72°C for 30 seconds) generally produced RSCM with higher viscosity than those made from powder given a medium preheat treatment (75-80°C up to 2 minutes). On the other hand, Lawrence *et al.* (1963) investigated the behaviour of low-heat, medium-heat, high-heat and a 50:50 blend of low-and high-heat SMP on viscosity of RSCM. They found that low-heat and the 50:50 blend of powder tended to give lower viscosities both initially and after storage than high-heat powder.

However, the WPNI index is not the only factor affecting the viscosity of RSCM. The season and location of powder manufacturer also have an effect.



### - Seasonal and location effects

The seasonal variation of milk plays a significant role on the RSCM viscosity (Lawrence *et al.* 2000; Muller and Kieseker 1965 and Newstead *et al.* 1978). Newstead *et al.* (1978) found that the initial viscosity and rate of age thickening of RSCM were slightly higher in August and September at the beginning of the milk powder season which extends in New Zealand from August to March. Muller and Kieseker (1965) also found there was a seasonal effect on the viscosity of RSCM made from powder in Australia.

The RSCM made from powder manufactured at different locations have different viscosities even when the powders are made under the same process conditions (Kieseker 1982; Muller and Kieseker 1965 and Newstead *et al.* 1978).

The viscosity of the stored samples showed a more marked seasonal effect than the initial viscosities of the sample (Newstead *et al.* 1978). This illustrates the necessity for undertaking storage trials as well as measuring the initial viscosity when testing SMP for use in RSCM, especially when powder from early in the season is used. Most of the seasonal variation occurred in the first part of the season, up to the end of October, when it is known to be difficult to produce SMP suitable for use in RSCM.

A viscosity test for SMP to be used for RSCM production was introduced by Kieseker and Southby (1965) and Weerstra *et al.* (1988). The method is to produce RSCM with the tested milk powder, then measure the initial viscosity of the RSCM. If the initial viscosity is in the accepted range, the tested SMP is suitable for making RSCM. Lawrence and Muller (1963) reported that the target initial viscosity should be 30-45 poise. However, Lawrence *et al.* (2001) used the two Australian and Dutch tests to measure the viscosities of RSCM from the same SMP, and found that “neither method was sufficiently reliable for the predicting the viscosity of RSCM made under ... a variety of ... processing conditions”.

### ***Stabilisers***

Stabilisers have a major effect on age thickening. Some stabilisers are added to products to retard gelation, while some of them increase the risk of gelation. Citrate (Walstra *et al.* 1999) and orthophosphate (Heintzberger *et al.* 1972 and Walstra *et al.* 1999) are known to accelerate gelation in UHTST-sterilised products, presumably because of their binding of calcium. Polyphosphates retard gelation both in UHTST and canned evaporated milk (Heintzberger *et al.* 1972 and Walstra *et al.* 1999). Upadhyay (1998) reported that polyvalent anions could form bridges between calcium atoms of calcium caseinate micelles and facilitate primary aggregation. Furthermore, the more insoluble or undissociated relevant calcium salts present the stronger bond between calcium micelles. This could explain the varying effect of different polyvalent anions. In contrast, monovalent anions such as fluoride fail to form ionic bridges and retard age thickening even though they can combine with calcium atoms of calcium caseinate.

### **(3) Composition factors**

#### ***Total solids (%TS)***

The total solids have an influence on the viscosity of concentrated milk products (Carić 1994; Clarke 1999; Heintzberger *et al.* 1972; Lawrence *et al.* 1963; Muller and Kieseker 1965; Trinh *et al.* 2002a and Vélez-Ruiz and Barbosa-Cánovas 1998). Increasing the percentage of total solids causes an increase in RSCM viscosity shown in Figure 2.4. Both Lawrence *et al.* (1963) and Muller and Kieseker (1965) suggest that the most suitable % TS for RSCM in term of viscosity was 74-76. Walstra *et al.* (1999) reported that this explained why the SCM from EU standard (74.5%TS) thickened faster during storage than that of US standard (73.5%TS).

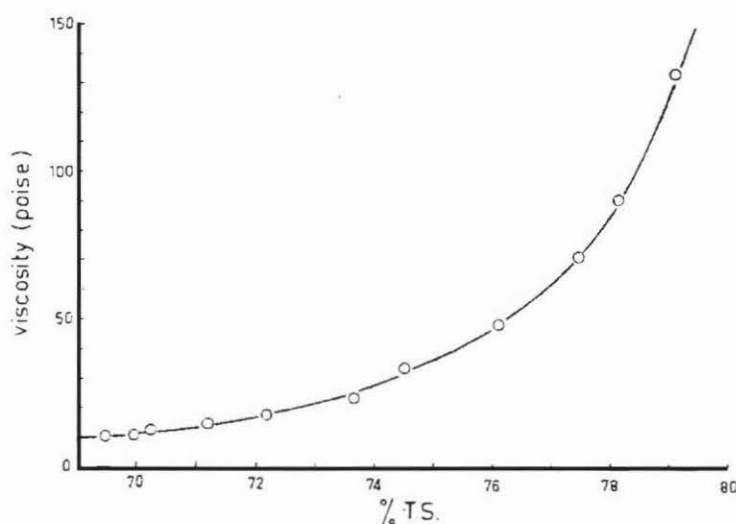


Figure 2.4 Relationship between total solids (% TS) and the viscosity of RSCM (Muller and Kieseker 1965).

### ***Protein content***

Among the dissolved solids, the proteins play the biggest role in age thickening (Carić 1994). An increase in protein content will increase the tendency for age thickening (Heintzberger *et al.* 1972 and Upadhyay 1998). The protein content of raw milk is influenced by many factors such as the feed, breed of cows, time of the season and lactation. However, most milk powders are now standardised for protein content.

### **(4) Product handling factors**

The finished RSCM product is usually stored for varying times at both the manufacturing company and at the retailer levels. This stage of product handling has a significant effect on viscosity of RSCM as well.

### ***Storage temperature***

Storage at elevated temperatures has a huge impact on the increasing viscosity of condensed milks (Carić 1994; Heintzberger *et al.* 1972; Kieseker 1982; Newstead 1982; Rohm 1988; Samel and Muers 1962b; Trinh *et al.* 2002a and Upadhyay 1998).

However, the influence of storage temperature is difficult to predict in practice because RSCM is rarely stored under strict temperature control. Thus the temperature of commercial RSCM fluctuates during storage and this temperature history is most of the time unknown.

### ***Storage time***

Since RSCM is a time-dependent product. Hence the viscosity of sweetened condensed milk (SCM and/or RSCM) increases with storage time even at a constant temperature (Carić 1994; Lawrence *et al.* 2001; Nieuwenhuijse 2003; Samel and Muers 1962b; Sinha and De 1972 and Upadhyay 1998) and a key issue is the determination of a maximum storage time available before the product thickens beyond acceptable limits.

## **2.5 DEFECTS**

This section reviews the defects that can occur in RSCM. They can be divided into two groups: common and unusual defects. The two most common defects of RSCM are a sandy texture (Blais *et al.* 1985; Carić 1993, 1994; Clarke 1999; Early 1998; Jensen and Nielsen 1982; Speer 1998 and Walstra *et al.* 1999) and excessive age thickening (Carić 1993, 1994; Clarke 1999; and Varnam and Sutherland 2001). Modern technology has eliminated spoilage by microorganisms such as buttons produced by mould and thickening produced by bacteria (Clarke 1999). The high sugar ratio in RSCM is designed to prevent bacteria-induced defects (Blais *et al.* 1985; Carić 1994; Clarke 1999; Jensen and Nielsen 1982 and Nieuwenhuijse 2003), which are caused by recontamination of the product during the canning processes.

### **2.5.1 Sandy Texture or Sandy Mouthfeel**

A sandy texture or a sandy mouthfeel is unacceptable to customers when the product is consumed.

A sandy texture appears during production or storage when lactose crystals grow too large, typically greater than 25  $\mu\text{m}$ , when they can create a gritty taste (sandiness) and tend to sediment (Blais *et al.* 1985 and Early 1998). However, other authors quoted different critical sizes of lactose crystals, such as  $>15\mu\text{m}$  (Carić 1994);  $>25\mu\text{m}$  (Early 1998);  $>30\mu\text{m}$  (Speer 1998) and 23-35 $\mu\text{m}$  (Blais *et al.* 1985).

Large lactose crystals are created by improper crystallisation. There are many causes such as a low rate of crystal growth, slow cooling, poor mixing (insufficiently intensive agitation), high concentration of total solids, a high concentration of added sucrose (more than 64.5%), low viscosity, very low storage temperature (less than 0°C) and temperature oscillations during storage (Carić 1994).

### 2.5.2 Sedimentation of Lactose

This sedimentation happens when SCM and/or RSCM has low viscosity and contains large lactose crystals (Blais *et al.* 1985). Large crystals become a coarse paste and precipitate to the bottom of the containers. Proper cooling and intensive agitation are necessary to avoid crystal aggregation (Carić 1994).

### 2.5.3 Buttons

Buttons are curd particles, which are formed by small aggregates of mycelium and coagulated casein. This defect appears on the surface of the product (Blais *et al.* 1985). They are usually reddish-brown, and are produced by fungi, particularly *Aspergillus*. These develop until the oxygen has been exhausted. Their enzymes are responsible for the formation of the curds.

Adequate pre-heating and effective protection against environmental contamination between the evaporation and canning stages can prevent this problem. The can should be sealed in a vacuum.

#### 2.5.4 Rancid Flavour

This flavour is due to the effect of lipase on the milk fat (Blais *et al.* 1985 and Carić 1994). This enzyme is present when the deactivation is not complete or lipolytic microorganisms are not destroyed due to inadequate heating treatments, and also because of increased heat-resistance at strong sugar concentrations. A rancid off-flavour in the product also occurs in the filled SCM containing coconut or palm kernel oil (Nieuwenhuijse 2003).

In the past, a rancid metallic flavour could be caused by an increased concentration of copper ions (Carić 1994). They also catalysed fat oxidation in the product. The rancid metallic flavour hardly occurs these days because all dairy plants use stainless steel piping.

#### 2.5.5 Thickening

Thickening may be caused by the presence of bacteria. In this case, there is an increase in viscosity and acidity, as well as the development of a stale and cheesy flavour (Blais *et al.* 1985). This defect is mainly due to micrococci and it can be prevented by using a sugar ratio of 64.5% in the aqueous phase. This concentration produces high osmotic pressure in which bacteria are unable to grow (Varnam and Sutherland 2001).

Other factors not related to microorganisms have already been discussed mentioned in *section 2.4.5*.

#### 2.5.6 Maillard Browning

The Maillard reaction, a non enzymatic browning reaction, is the interaction between a free amino group on the milk proteins, particularly lysine, and the aldehyde group of a reducing sugar. Maillard reactions are accelerated with high temperature (Jensen and Nielsen 1982), which may cause hydrolysis (inverting) of sucrose and form reducing sugar. Browning during storage is serious if temperatures exceed 25°C (Nieuwenhuijse 2003). Maillard browning reactions can also have a negative affect on

the flavour as well. As long as the flavour changes are not excessive, the slight changes that do occur are considered to be a normal property of stored RSCM.

### 2.5.7 Microorganisms

Defects of microbiological origin in RSCM are caused by bacteria, fungi and yeast due to inadequate heat treatment. Recontamination may also occur if the cleaning procedures prior to processing are inadequate or if the air in the canning area is improperly filtered (Nieuwenhuijse 2003). The growth of micrococci and fungi usually causes lumps and off-flavours in the product, while the growth of yeast causes bulging of cans (by gas formation) and off-flavours.

According to the microbiological quality standard, 1 ml RSCM must not contain any coagulase-positive staphylococci, sulfite-reducing *Clostridia*, *Proteus* species, or *Escherichia coli* (Carić 1994).

#### (1) Bacteria

Other bacteria such as *Micrococcus*, *Streptococcus*, *Staphylococcus*, *Bacillus* have been implicated in the spoilage of RSCM, particularly osmotolerant bacteria. Typical spoilage patterns involve thickening, acid production, proteolysis and lipolysis. This bacterial defect can be avoided through the proper sterilisation of equipment and high sugar concentration in the aqueous phase (about 64.5%) (Carić 1994).

Members of the *Enterobacteriaceae* have also been implicated in the spoilage of bulk, low sugar condensed milk and produce acid and gas (Varnam and Sutherland 2001).

#### (2) Fungi

Fungi such as *Aspergillus*, *Catenumaria* and *Penicillium* usually occur on the surface of products. Some fungi can produce enzymes and acids, which lead to agglomerates formation and undesired smell (Carić 1994). The fungi infection can be protected by aseptic practices, vacuum packaging in cans and a reduction of headspace containing sufficient oxygen for excessive growth (Carić 1994 and Varnam and Sutherland 2001).

### **(3) Yeast**

RSCM is subjected to spoilage by osmotolerant yeasts, especially *Torulopsis* and *Lactis condens*i (Carić 1994 and Varnam and Sutherland 2001). These yeasts mostly originate from sugars, and then cause the transformation of sucrose to alcohol and gas (such as carbon dioxide), which can swell the cans. Growth of this organism is slow, particularly at lower ambient temperatures. The incidence of spoilage has been much reduced by improved hygiene and control of the sugar entering the process.



## CHAPTER 3 MATERIALS AND METHODS

This chapter describes the materials, equipment, manufacturing procedures and analytical methods used for the study of reconstituted concentrated milk (RCM) and recombined sweetened concentrated milk (RSCM). *Section 3.1* provides the specifications of materials used; *section 3.2* lists the equipment; *sections 3.3* describes the protocols of operation for the manufacture of RCM and RSCM and *section 3.4* presents the analytical methods employed.

### 3.1 MATERIALS

The material used for the preparation of RCM and RSCM are listed separately below.

#### 3.1.1 RCM

RCM was manufactured by reconstituting milk powder with RO water.

##### (1) Medium Heat Skim Milk Powder (MH-SMP)

Reconstituted MH-SMP concentrate was used to study the rheology of RCM. The MH-SMP was obtained from the Fonterra Cooperative Groups Ltd. (New Zealand).

##### (2) Whole Milk Powder (WMP)

Reconstituted WMP concentrate was used in a preliminary study to follow the development of permanent changes during age thickening of RCM. It was made from WMP obtained from the Fonterra Cooperative Group Ltd. (New Zealand) with a specified composition of protein 26.6%, fat 25%, lactose 40.76%, ash 5.44% and moisture 3.93%.

### **3.1.2 RSCM**

Recombined Sweetened Condensed Milk (RSCM) was manufactured from the following ingredients (1-4) to meet New Zealand standards which state that the RSCM should contain at least 28% milk solids and 8 fat %. The calculation used to formulate the RSCM is shown in Appendix 1. RSCM samples were kept in containers (5-6) for the storage trials.

#### **(1) WMP**

Trial 1: WMP was obtained from Fonterra Cooperative Group Ltd. (New Zealand) with a specified composition of protein 25%, fat 26.8%, lactose 39.1%, ash 5.8% and moisture 3.3%.

Trial 2: WMP was obtained from Fonterra Cooperative Group Ltd. (Pahiatua plant, New Zealand) with a specified composition of protein 26.6% and fat 25%. Moisture content as determined by a vacuum drying method was 3.17%.

#### **(2) Fresh Frozen Milk fat for Recombining (FFMR)**

Because the amount of fat present in the WMP supplied did not match the specifications for RSCM, extra milk fat was added according to the calculations shown in Appendix 1. FFMR was also obtained from the Fonterra Cooperative Group Ltd. (New Zealand) with a specified composition of 99.95% milkfat and 0.05% moisture.

#### **(3) Sugar**

White sugar, standard A was purchased from Chelsea Sugar (Auckland, New Zealand).

#### **(4) Lactose powder**

RSCM manufacturing grade very fine seeding lactose powder was donated by Fonterra Cooperative Group Ltd. (New Zealand).

### **(5) Cans and lids**

The RSCM samples were contained in lacquered cans with the following dimensions: 6.51 cm in diameter and 4.7 cm in height and capacity 150 ml. The cans and lids for the RSCM storage trial were provided by Prepared Foods Palmerston North (New Zealand). The cans were made of tin-plate with the general purpose (GP) 2 coating. The RSCM storage trial 1 samples were stored in cans.

### **(6) Plastic containers**

Plastic containers, size 70ml, from Biolab Limited (Auckland, New Zealand) were used to store the RSCM storage trial 2 samples.

## **3.2 EQUIPMENT**

This section presents equipment used for the manufacture of the RCM and RSCM samples and for the analysis of properties of the milk samples.

### **3.2.1 Production equipment**

The RSCM manufacturing equipment consisted of a recombination rig, a homogeniser, a high shear mixer, a plate heat exchanger (PHE) and a can seamer. The equipment for the manufacture of the RCM only used the recombination rig and the PHE.

#### **(1) Recombination rig**

A custom designed recombination rig was built by a former postgraduate student, Dr Binh Trinh, as shown in Figure 3.1 (Trinh *et al.* 2002b). It was the main piece of equipment used to produce both the RCM and RSCM samples for this thesis. The recombination rig consisted of a 4L mixing tank with a water jacket (also called a jacketed stainless steel vessel) which was fitted with an agitator (model RW20.n gear I, IKA Labortechnik, Malaysia). The desired temperature of the mixing tank was controlled by a water heating system which circulated water through the jacket that surrounded the mixing tank. A circular disc (baffle) was installed above the four-blade

propeller to prevent vortex formation when mixing at high speed. The sample was recirculated through the rig and back by a mono pump model S4F202 (Mono Pumps NZ Ltd., New Zealand). The sample could be diverted to flow through a removable capillary tube. The diameter of the capillary tube could be varied and its function was to impose different applied shear rates to the mixture being re-circulated through the tube. The recirculation in the rig was carried out at a flow rate of 80 L/hr for RCM and 60 L/hr for RSCM. The outlet pipe from the rig could be linked to a PHE to heat the sample to a target storage temperature which was independent from the mixing and recirculation temperatures.

This recombination rig was chosen for this work because it allowed the shear rate to be manipulated during the production of the RCM and RSCM samples to see what effect varying shear rate would have on the rheological properties of ageing RCM and RSCM.

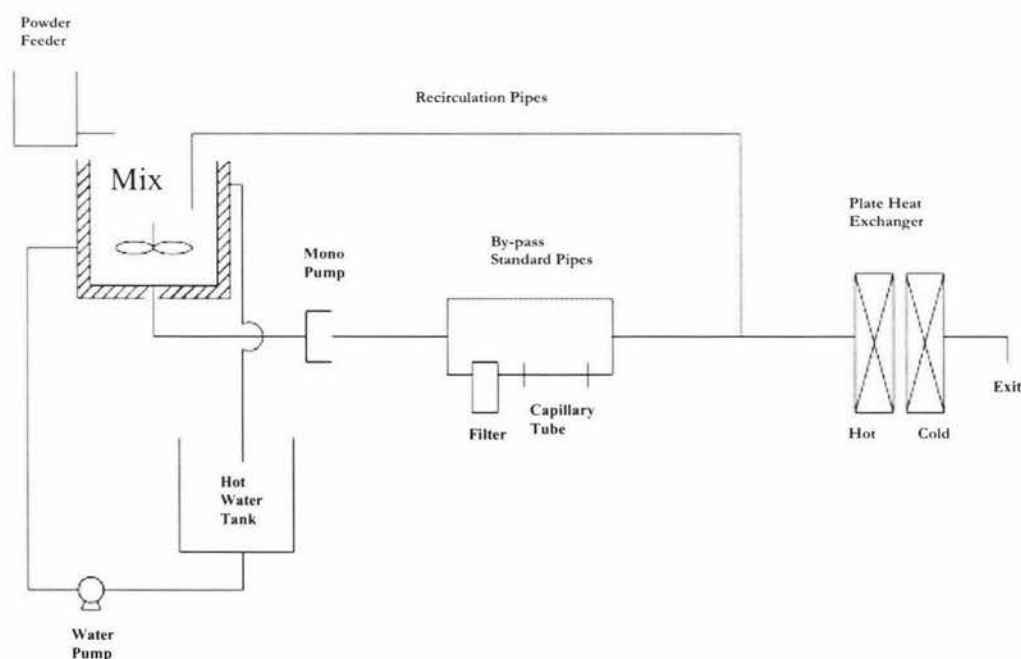


Figure 3.1 Diagram of the recombination rig (Trinh *et al.* 2002b).

## (2) Homogeniser

A two-stage homogeniser model Lab, Type 12.50H (Rennie, Denmark) was used to homogenously combine the sugar-milk solution with the added milk fat and also to

prevent fat separation when the product was stored. It could be operated with a first-stage pressure in the range 0-1000 bar and a second-stage in the range 0-400 bar. For this work, only the second stage was performed.

### (3) High shear mixer

A high shear mixer, Silverson model L4R (Silverson Machines Ltd, England) was used to pre-mix the added milk fat and the mixture of WMP, water and sugar before homogenisation.

### (4) Plate Heat Exchanger (PHE)

A plate heat exchanger (PHE) model M3-FG (Alfa-Laval New Zealand Ltd, New Zealand) operating in the range 0-150°C was used to heat up or cool down the sample to the desired temperature in different experiments. A diagram of the PHE used in the study is shown in Figure 3.2.

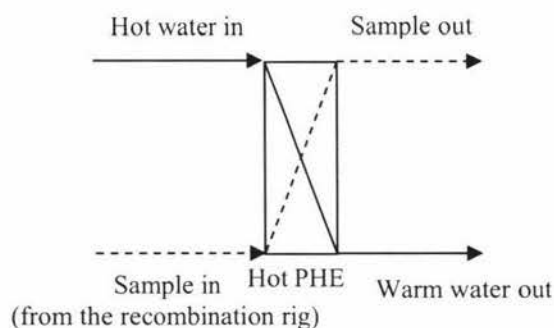


Figure 3.2 Schematic of the PHE system used to heat/cool the sample.

### (5) Can seamer

A can seamer Model 710 series 2 (John Heine & Son Pty Ltd., Australia) was used to seam the lids onto the cans after filling with RSCM.

3.2.2 Analytical equipment

The following equipment was used to determine the rheology, particle size and colour of the samples.

(1) Viscosity

Viscosity changes during storage were analysed with a rheometer model Parr-Physica Rheolab MC1 (Anton Paar, Germany). This equipment was equipped with a Julabo F25 water heater (Julabo, Germany) to control the temperature of the measuring chamber. This rheometer is a rotational type assembled with the coaxial cylinder (a cup and a bob) as a measuring system. For RCM samples, the spindle Z2.1 was used while spindle Z3 was used for RSCM samples (Table 3.1).

Table 3.1 Specifications of spindle design Z2.1 and Z3

|                             | Design |        |
|-----------------------------|--------|--------|
|                             | Z2.1   | Z3     |
| Cup radius [m]              | 0.0244 | 0.0136 |
| Bob radius [m]              | 0.0239 | 0.0125 |
| Gap between cup and bob [m] | 0.0005 | 0.0011 |

(2) Particle size

Particle Size Distribution (PSD) was measured by a Mastersizer E (Malvern Instruments Ltd., UK).

(3) Colour

Colour changes to the RSCM during storage were measured by a Chroma Meter CR-200 (Minolta Ltd., Japan). This equipment was calibrated with a standard white plate (CR-A43, Minolta Ltd., Japan).

### 3.3 EXPERIMENTAL METHODS

The two experimental series in this thesis involving RCM and RSCM have been summarized in Appendix 2. The main equipment in RCM and RSCM production was the recombination rig. The generic description of the operation of the recombination rig is presented first in *section 3.3.1*. Details of parameter settings such as the shear rate applied and the temperature are reported in the description of specific RCM and RSCM experiments in *section 3.3.2* and *section 3.3.3* respectively.

#### 3.3.1 Recombination rig operation

At the beginning of each experiment, the capillary tube suitable for the desired recirculation shear rate was installed in the recombination rig (Figure 3.1). The recombination rig was cleaned with a clean-in-place (CIP) cycle consisting of a hot water rinse, a sodium hydroxide solution (60ml of 50% sodium hydroxide in 5L of water) wash, another hot water rinse, a nitric acid solution (60ml of 68% nitric acid in 5L of water) wash and a final hot water rinse respectively. The agitator in the tank was set at its fastest speed (no. 10, 500rpm) and was operated at this speed throughout the CIP cycle to ensure that the solution was homogenised and the concentration of cleaning agents were uniform. The recirculation through the recombination rig and heat exchanger by the mono pump too was set at a maximum (Table 3.2). The heat exchanger was used to maintain the recirculating fluid at the desired temperature for cleaning. Each acid and/or alkaline solution was recirculated in the combination rig for 20 minutes. At the end of the CIP run the agitator and mono pump were turned off and the piping system was drained before the recombination operation was commenced. This CIP cleansing method dramatically reduced the mesophilic and thermophilic bacteria numbers in the system and subsequent recombined product (Trinh *et al.* 2002b).

After CIP, a predetermined amount of water was poured into the 5L vessel. Then the mono pump and the agitator were set at their fastest speed and the powdered ingredients were slowly added to the mixing tank from a hopper fitted with a screw feeder that was situated above the mixing tank. The speed of the feeder was adjusted

to avoid the production of solid lumps. The recombination continued until the solid ingredients were completely dissolved, after which time the feed screw was turned off. Then the agitator was turned down to the medium speed (no.4, 200rpm) during the rehydration and/or recirculation step.

At the end of a run, the recombination rig was cleaned with a sodium hydroxide wash and a hot water rinse.

Recirculation in the recombination rig could be operated at 6 shear levels by suitable selection of the flow rate and the diameter of the removable capillary tube. Only three nominal shear rates were used in this work for RCM and RSCM as shown in Table 3.2.

After recombination and rehydration were completed, the product could be further heated to any desired temperatures by pumping the solution through the PHE or collected straightaway for storage test or transferred to the next step of the RSCM process.

Table 3.2 Shear rate applied in the recombination rig.

| Recirculation flow rate | Shear level | Capillary internal diameter | Shear rate applied     |
|-------------------------|-------------|-----------------------------|------------------------|
| RCM at 80 L/hr          | High        | 1.76 mm                     | $40,000\text{s}^{-1}$  |
| RSCM at 60L/hr          | Low         | 5.7 mm                      | $900\text{s}^{-1}$     |
|                         | High        | 1.76 mm                     | $31,000\text{ s}^{-1}$ |

### 3.3.2 Procedure for RCM experiment

The procedure and conditions used to prepare the RCM were identical to those used by Binh Trinh (Trinh 2006) so that the results of this study could be compared with his. The RCM was manufactured by mixing the MH-SMP with RO water at  $35^{\circ}\text{C}$  to achieve the desired % total solids content (TS). This mixture was sheared at  $40,000\text{s}^{-1}$



(Table 3.2) as described above. During powder reconstitution, 0.05g sodium azide per 100 ml of solution was added as a preservative. Complete dissolution of the powder normally required 2 hours. Then the reconstituted milk was recirculated for another hour to ensure complete hydration. The RCM experiments consisted of two trials which investigated the age thickening and the reshearing behaviour of the RCM concentrates (Figure 3.3).

In all RCM storage trials, the beaker holding the sample was immersed in a water bath set at the desired storage temperature and covered with aluminium foil to minimise water evaporation. A sample was taken from the finished RCM solution to confirm the %TS. Rheological measurements were performed at regular time interval until the sample gelled. Simultaneously part of the sub-samples were diluted for particle size measurements.

In the first trial, the MH-SMP was reconstituted to  $45 \pm 0.5\%$  TS and then heated to two storage temperatures to obtain data for the two types of age thickening identified by Trinh (2006): type 1 for temperatures below  $65^{\circ}\text{C}$  and type 2 for temperatures above  $65^{\circ}\text{C}$ .

- $50^{\circ}\text{C}$  (*run A1*) to compare with the literature data for type 1 age thickening (Bievenue *et al.* 2003a and Snoeren *et al.* 1982)
- $75^{\circ}\text{C}$  (*run A2*) to study the type 2 age thickening phenomenon, involving the denaturation of whey protein especially  $\beta$ -lactoglobulin.

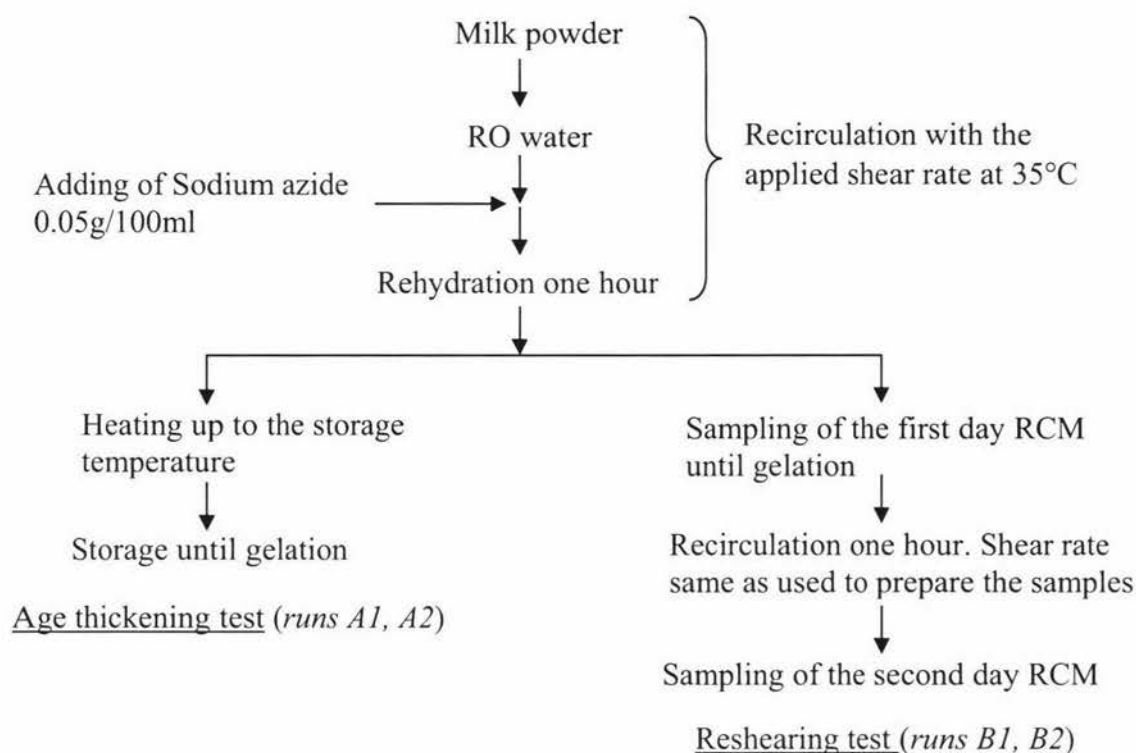


Figure 3.3 Flowchart of RCM experiments

In the second trial, the WMP was reconstituted to  $50 \pm 0.5\%$  TS, then stored at this temperature for 23 hours in a water bath. The samples were stored at 35°C to study the changes in structure in type 1 age thickening which is more common in RSCM storage than in type 2. On the second day, the rig was again cleaned according the CIP specifications before reloading the aged sample from day 1 and reshearing by recirculation at  $40,000\text{s}^{-1}$ , 35°C for 1 hour. The agitator was operated at medium speed (no.4, 200 rpm). Then the resheared sample was stored in the water bath at 35°C for another 23 hours. Because of hold-up rinse water in the mono pump of the recombination rig the resheared sample had a slightly lower %TS than the original WMP concentrated sample. One percent drop of TS ( $49 \pm 0.5\%$ ) was considered acceptable for the second day sample. This study was carried out in duplicated runs (runs B1 and B2).

### 3.3.3 Procedure for RSCM experiment

The first RSCM experiment was carried out with the aim of gaining familiarity with the process used to manufacture RSCM and to test the different protocols for RSCM manufacture. Once a final protocol was identified, the RSCM for the storage trials was manufactured with two shear levels (Table 3.2).

#### (1) Familiarisation with RSCM manufacture

A process for making RSCM in New Zealand was reported by Choat (1979) as described in *section 2.3*. However, this process had to be adapted for use in the recombination rig. The familiarisation runs for RSCM manufacture and process modifications were numbered *C1 to C4*. The most suitable process was identified from these experiments and then used to manufacture the RSCM for the storage trials.

#### *First modification of RSCM process (run C1)*

In the first RSCM experiment (*run C1*) the recombination temperature was changed from 45-50°C as recommended by Choat (1979) to 35°C and a recirculation shear rate of 31,000s<sup>-1</sup> was applied. The temperature of 35°C was chosen because it was easier to control the age thickening of concentrated milk products during recombination at lower temperatures (Trinh 2006 and results described in *section 4.1.1*). The plan of *run C1* is shown in Figure 3.4.

The WMP and the RO water were weighed in proportions stipulated by calculations in Appendix 1. After the WMP had been completely dissolved in the RO water (about 1 hour), the reconstituted milk was hydrated without agitation for 15 minutes. The sugar was then added over a period of about 45 minutes with the agitator going. The FFMR was melted and added to the mixture in the vessel.

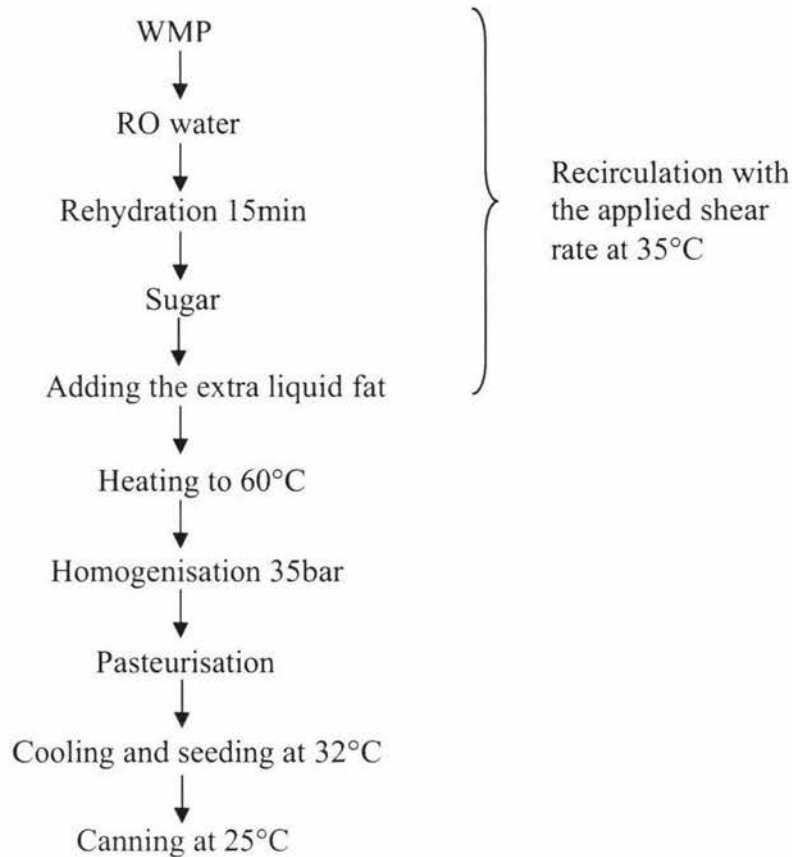


Figure 3.4 Plan of RSCM process *run C1* adapted from Choat (1979).

*Run C1* was stopped at this step. This was because the undissolved sugar clogged and burnt out the stator of the mono pump. Several problems were learned from *run C1*.

Problem 1: At the recombination temperature of 35°C, the sugar could not dissolve completely. The undissolved sugar crystals collected inside the mono pump and damaged the stator. *Runs C2 and C3* were designed to overcome this problem.

Problem 2: From the Choat (1979) method, the extra fat was melted and added to milk solution which was then heated up to 60°C and homogenised at 3.5 MPa (35 bar). In *run C1* when the RSCM solution was withdrawn from the recombination rig, the liquid fat was seen to be floating on the surface of the milk solution in the mixing tank. Clearly the liquid fat was not mixing throughout the milk mixture. To solve this

problem, the extra amount of melted fat was added after the milk solution was withdrawn from the rig and heated to up 60°C before homogenisation.

Problem 3: Another problem was the vague specification of the pasteurisation process described in the literature (Choat 1979 and Newstead 1982) with a range of temperatures between 80 - 90°C and holding times between 30 seconds - 2 minutes being suggested by the two researchers. Different pasteurisation temperatures and time combinations were tested in *runs C2 and C3*.

### ***Process modification for optimum sugar dissolution (runs C2, C3)***

In *runs C2 and C3* (Figure 3.5) the dissolution temperature was maintained at 35°C. In *run C2* the sugar was first dissolved in 90°C water for 30 minutes. The sugar solution was then transferred to the mixing tank of the recombination rig which was controlled at 35°C, then the milk powder added. The agitator was set at the highest speed (no.10, 500 rpm). After the WMP was fully dissolved, the solution was recirculated at  $31,000\text{s}^{-1}$  for another hour to allow any entrained air to escape and for the milk powder to be fully hydrated. A new sequence of mixing was introduced to solve the problem of oil floating on the surface (Problem 2). The fat was melted and added to the milk solution after it had been hydrated and removed from the rig. The two-phase system was pre-mixed with the high shear mixer before homogenisation at 35 bar.

In *run C3*, a new step was added: a further 30-minute recirculation of the homogenised sample. The agitator was set at the medium speed (no.4, 200 rpm). The purpose of this step was to breakdown any structure that might have built up during the short period between the time the solution was taken out of the homogeniser and put into the rig for heat treatment.

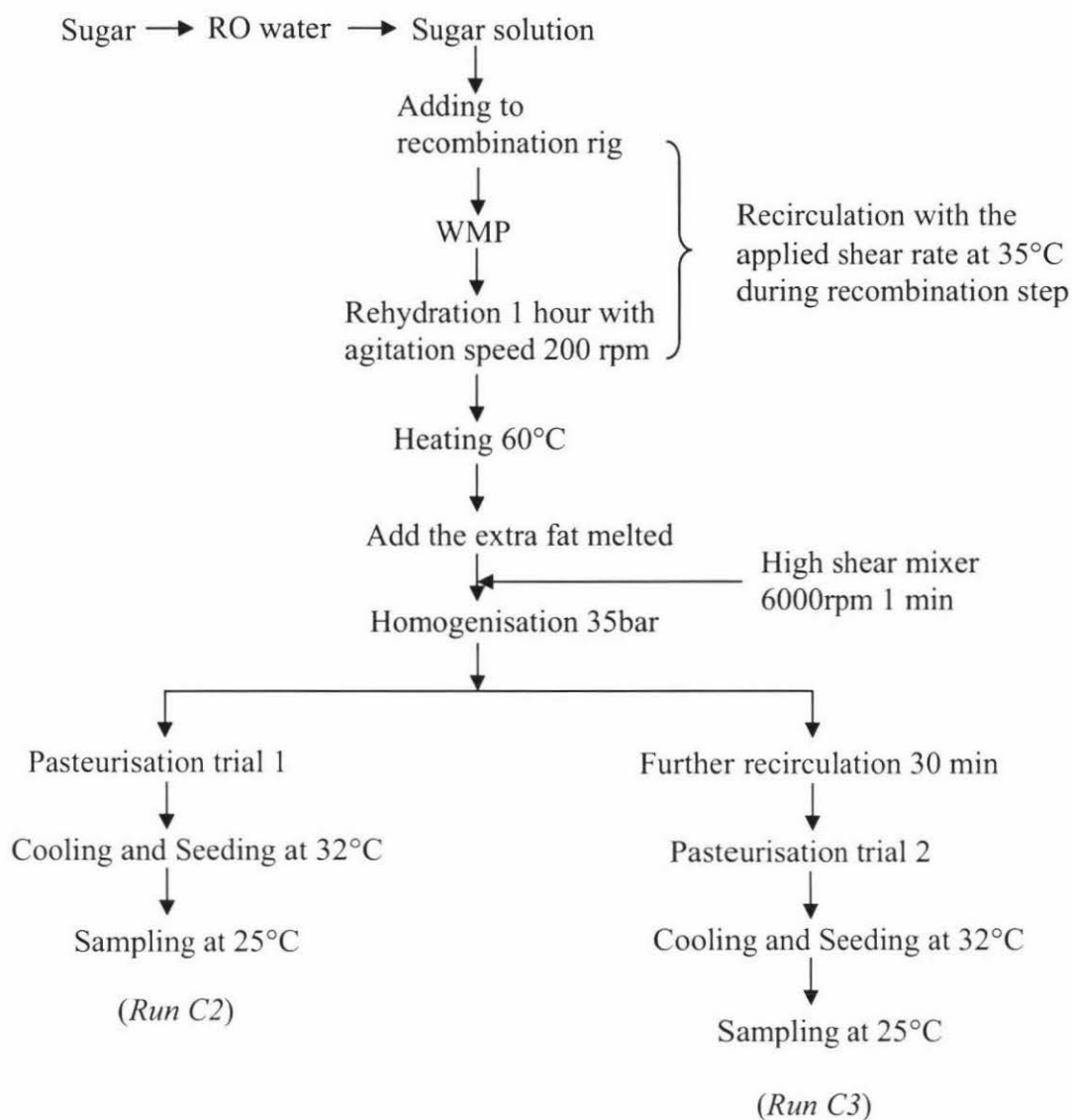


Figure 3.5 Plans for runs C2 and C3.

Pasteurisation trials were conducted after homogenisation in runs C2 and C3. Choat (1979) quoted that the highest pasteurisation temperature and the shortest time was 90°C for 30 seconds. Unfortunately, due to the fact that the capacity of the hot water supply was only designed for 85°C it was impossible to meet Choat's (1979) recommended pasteurisation temperature. Consequently, in the first pasteurisation trial performed in run C2 the pasteurisation was conducted at 85°C for 1 minute. Small lumps were observed as the mixture exited the PHE. To avoid this problem, the temperature had to be reduced.

In the second trial performed in *run C3* pasteurisation was conducted at 75°C for 15 seconds as suggested by Rod Bennett (personal communication, 29th August 2005). Lumps were no longer observed and these pasteurisation settings were kept in *run C4*.

After pasteurisation, the mixture was cooled down in an ice bath to 32°C, transferred to a water bath controlled at 32 °C. Seeding lactose was added and stirred slowly for 15 min for lactose crystallisation. The RSCM was cooled further to 25°C to take a sample for measurement of initial viscosity.

***Development of final protocol for RSCM preparation (run C4)***

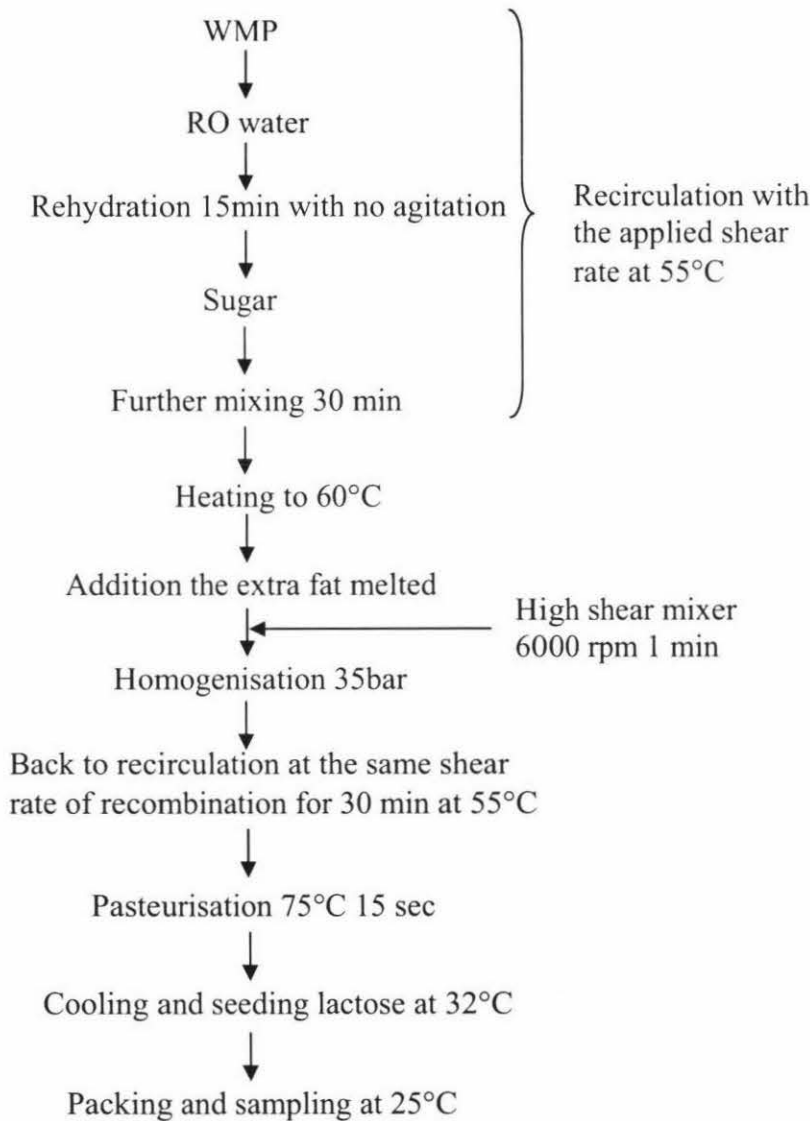


Figure 3.6 Final protocol for RSCM preparation (*run C4*).

In run C3, the viscosity of the RSCM produced was much higher than normally quoted in the literature (e.g. Kiesecker and Southby 1965) as reported in details in *section 4.2.1*. The reason for the high viscosity might be due to the early addition of sugar before the addition of milk powder and it was decided to revert to a traditional method in which milk powder was added first. This could only be done by using a mixing temperature of 55°C (Kiesecker *et al.* 1984). The agitator was set at the highest speed (no.10, 500 rpm). After the WMP was completely dissolved in the RO water (about 1 hour), the reconstituted milk was hydrated without agitation for 15 minutes. Sugar was then added (about 45 minutes) with agitation at the highest speed. After all the sugar was added to the mixture, it was allowed a further 30-minute of mixing to assure that all the sugar was completely dissolved. After that the process was the same as *run C3*. The experimental runs for the manufacture of the RSCM are summarised in Figure 3.6.

The initial viscosity of the RSCM produced by *run C4* came back to the normal range as shown in the results (*section 4.2.2*). Thus, it was decided to produce RSCM for the storage trials from the process used in *run C4*.

## **(2) RSCM storage trials**

Two different shear levels, high ( $31,000\text{s}^{-1}$ ) and low ( $900\text{s}^{-1}$ ), were chosen after studying the work of Trinh *et al.* (2003) on the effect of shear on the age thickening rate of RCM. The %TS and fat content of the RSCM that were produced were determined to ensure that they complied with the targeted standard values. The RSCM samples were stored at the following controlled temperatures 30, 40 and 50°C. These different storage temperatures were selected because an intention of the experiments was to develop an accelerated test for age thickening of RSCM. The principle of the accelerated age thickening test was to store the samples at elevated temperatures to induce faster chemical reactions and from the accelerated kinetics infer the age thickening behaviour at low temperatures which usually take longer to reach the same level. Two trials were conducted.



***RSCM storage trial 1 (ST1)***

Due to the limited amount of milk powder left over from the RCM study only four high-shear runs (*runs D1 - D4*) and one low-shear run (*run D5*) of RSCM manufacture could be conducted at the same high shear level in ST1. The RSCM samples were packed in 150ml cans and randomly stored at 30 or 40 or 50°C. According to Lawrence *et al.* (1963), age thickening of RSCM samples stored at 40°C for 7-14 days was equal to that of samples stored at 30°C for 2-3 months and at 20°C for 4-6 months. It was therefore decided to conduct ST1 with RSCM storage at 30°C for 3 months; 40°C for 14 days and 50°C for 7 days. In each run, cans stored at 30°C were taken to analyse every three weeks, at 40°C every 2 days and at 50°C every day. Each can taken was analysed for rheology behaviour, particle size distribution (PSD) and colour. Each measurement was carried out in triplicate.

***RSCM storage trial 2 (ST2)***

The lesson from ST1 was that more samples and therefore more RSCM needed to be produced in each run to give an adequate number of points against time. In ST2 a storage time up to 12 weeks was targeted. Measurement could be stopped earlier if the sample had visually gelled. Three runs of high shear level (*runs E1-E3*) and three runs of low shear level (*runs E4-E6*) were produced again by the final modified process (*run C4*). Each run of the three runs produced enough RSM for one storage temperature (Table 3.3). In this trial, RSCM was packed in a smaller plastic container of 70 ml. The same analytical tools as were used for ST1 were used for the ST2 samples. Each measurement was carried out in triplicate. RSCM measurements were performed once a week for samples stored at 30 and 40°C. But the RSCM samples stored at 50°C were analysed twice a week due to the fast rate of age thickening at the high temperature that were observed in ST1.

Table 3.3 Summary of runs in ST2 trial

| Run number | Shear level | Storage temperature | Duration of Storage |
|------------|-------------|---------------------|---------------------|
| <i>E1</i>  | High        | 30°C                | 12 weeks            |
| <i>E2</i>  | High        | 40°C                | 12 weeks            |
| <i>E3</i>  | High        | 50°C                | 12 weeks            |
| <i>E4</i>  | Low         | 30°C                | 12 weeks            |
| <i>E5</i>  | Low         | 40°C                | 12 weeks            |
| <i>E6</i>  | Low         | 50°C                | 12 weeks            |

3.4 ANALYTICAL METHODS

This section discusses two issues: The measurement of the physical properties of the RCM (viscosity and particle size) and RSCM samples (viscosity, colour and particle size) and the chemical analyses carried out to determine the composition of the RCM (total solid) and RSCM (total solid, fat content and sugar content)

3.4.1 Measurement of physical Properties

(1) Viscosity

The rheology of RCM and RSCM was measured using a rotational Physica Rheolab MC1 rheometer (Anton Par, Germany) in control shear stress mode (CSS). In the CSS mode, a torque was set and the shear rate was measured. The control software was Rheosolve version 3.08. This equipment was supplied with a Julabo F25 water heater (Julabo, Germany), which connected to the water jacket of the chamber where the cup and the bob, a coaxial geometry, were inserted. The spindle designs used were Z2.1 for RCM and Z3 for RSCM (Table 3.1). The Z3 spindle was chosen for the RSCM samples because of the high viscosity of the RSCM samples and the Z2.1 for the RCM samples.

All samples were subjected to a shear sweep test which consisted of three phases. In the first phase, the torque was increased from 0.5 mNm to 50 mNm and 200 data points collected at 1second intervals. In the second phase, the torque was held at 50 mNm for 15 measurement points and in the last phase, the shear stress was decreased from 50 mNm to 0.5 mNm and a further 200 data points were collected. Each replicate measurement used a fresh sample (not previously sheared).

The shear rate and viscosity of each measurement point were reported by Rheosolve software (Anton Par, Germany). In this thesis, however, they were modified with a non-Newtonian correction which was not available in this software (Appendix 3).

Trinh *et al.* (2005) calibrated the Paar Physica MC1 rheometer using standard oil solutions. They found that the data were unreliable at the combination of low torque and spindle speed. They recommended that data at less than 1.5 mNm and 20 rpm were unreliable and should be truncated. This truncation applied in this work.

## **(2) Particle size**

The particle size distribution (PSD) of the RSCM was determined by a Mastersizer E (Malvern Instruments Ltd., UK) using the NAD presentation for emulsions. A sample was prepared by pre-dilution of the RSCM with RO water 1:1 (v/v) to make sub-sampling easier. A small amount of a pre-diluted sample of RSCM was loaded into the equipment mixer then more RO water was added until the obscuration ranged between 19 to 21 and then a particle size distribution was obtained.

## **(3) Colour**

A tristimulus colorimeter (Minolta Ltd, Japan) was first standardised against a standard white plate (CR-A43, Minolta Ltd., Japan) before a colour measurement of the RSCM in a plastic petri dish was determined. The RSCM colour was measured by the reflection off the surface using the light source Illuminant D<sub>65</sub>. The results were presented as L, a and b values where the L value represented the lightness or the brightness of the sample, the a value was a measurement of the red (+a) to the green (-a) tints and the b value was a measurement of the yellow (+b) to the blue (-b) tints.

### 3.4.2 Compositional analysis

The composition of the various recombined products was determined to confirm that they complied with the target values used to determine weights of the ingredients to be used in the production of RSCM.

#### (1) Total solids content (TS)

The total solids measurement of RSCM was adapted from the AOAC official method 920.115 D for total solids (AOAC 2000a). The sample was prepared by dilution of RSCM with RO water (1:1 w/w). An aluminium foil was accurately weighted. Ten grams of acid washed sand was added to the aluminium foil. Then it was placed into a hot air oven at  $100\pm2^{\circ}\text{C}$  for one hour. It was removed from the oven and placed to a dessicator at room temperature for 30 min before its weight (A) was recorded. Approximately three grams of diluted RSCM sample was added to the dry sand and aluminium foil then accurately weighted (B) before it was replaced in the oven for 18 hours. After 18 hours, it was removed and again put in a dessicator for 30 min. Finally, it (dry sample + dry sand + dry aluminium foil) was reweighed and the weight recorded (C). The total solids content was calculated by subtracting the dry weight of milk sample from the original weight of sample. Triplicate samples were analysed.

Calculation of total solids: 
$$\text{TS (\%)} = \frac{C - A}{B - A} \times 100$$

Then the dilution factor was used to obtain the correct total solids.

The total solids measurement content of the RCM was obtained by using the AOAC official method 990.20 (AOAC 2000b). Triplicate samples were analysed. There were three different steps of total solids measurement between RSCM and RCM. However, the basic principle was still the same. The RCM samples were not diluted; there was no sand added into the aluminium foil and they were kept in the hot air oven at  $100\pm2^{\circ}\text{C}$  for only 4 hours. For the RSCM sample, four hours in the hot air oven was not enough time to ensure constant weight.

## (2) Fat content

Mojonnier fat extraction followed the AACC method 30-16 (AACC 1995). Triplicate samples were analysed. RSCM was added into the Mojonnier apparatus. The weights of the Mojonnier apparatus and Mojonnier apparatus with RSCM were recorded to obtain the accurate weight of RSCM for calculation. About 4 grams of RSCM were dissolved in 10 ml of RO water in the Mojonnier apparatus then 2 ml of ammonium hydroxide were added. Ten ml ethanol was added to prevent foaming. The mixture was mixed by rocking the tube to ensure the liquid contents flowed to each end of the Mojonnier tube. The stopper was released occasionally to prevent pressure build-up in the tubes. The mixture was put in a water bath at 60°C for 5 minutes. Five drops of phenolphthalein were added, the solution cooled to room temperature, to create a pink colour. Twenty-five ml of diethyl ether were added first to the solution then 25 ml of petroleum ether. After the addition of each ether the tube was rocked for 1 minute to ensure complete extraction of the lipid content. The tubes were placed in the Mojonnier centrifuge and centrifuged at 600 rpm for 2 minutes to ensure that the two phases were completely separated. The bottom layer (aqueous) was a pink colour because of the binding of phenolphthalein. The above clear layer was transferred to a pre-weighed beaker which was placed on a steam bath in a fume cupboard to evaporate the ethers.

The remaining pink solution was again loaded with 5 ml of ethanol and re-extracted with only 15ml of diethyl ether together with 15ml of petroleum ether for 30 seconds. The mixture was centrifuged at 600 rpm for 2 minutes. The clear layer was added to the first extract.

After the ethers were evaporated, the beaker containing the extracted fat was dried further in a hot air oven at 100±2°C for 90 minutes and cooled down in a desiccator for 30 minutes before weighing.

Calculation of fat content: 
$$\% \text{ Fat} = \frac{\text{weight of dry extracted fat}}{\text{weight of RSCM}} \times 100$$

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An RSCM sample starting with 4 grams gave approximately 0.3 grams of final extracted fat.

## CHAPTER 4 RESULTS AND DISCUSSIONS

This chapter reports the results of experiments on reconstituted concentrated milk (RCM) in *section 4.1* and recombined sweetened condensed milk (RSCM) in *section 4.2*. The rheology and particle size distribution (PSD) of RCM during storage is presented in *section 4.1.1* and the reshearing investigation is examined in *section 4.1.2*. The study of RSCM is divided into 2 sub-sections; *4.2.1* Development of the RSCM process and *4.2.2* Storage trials.

### 4.1 RECONSTITUTED CONCENTRATED MILK (RCM)

#### 4.1.1 Behaviour of RCM during storage

The behaviour of RCM during storage was characterised with a series of flow curves and PSDs taken at different intervals of storage time. From the flow curve, a number of complimentary curves were generated including changes of apparent viscosities, normalized hysteresis loop area (HLA), the yield stress ( $\tau_y$ ), the consistency index ( $K$ ) and the flow index ( $n$ ) with time.

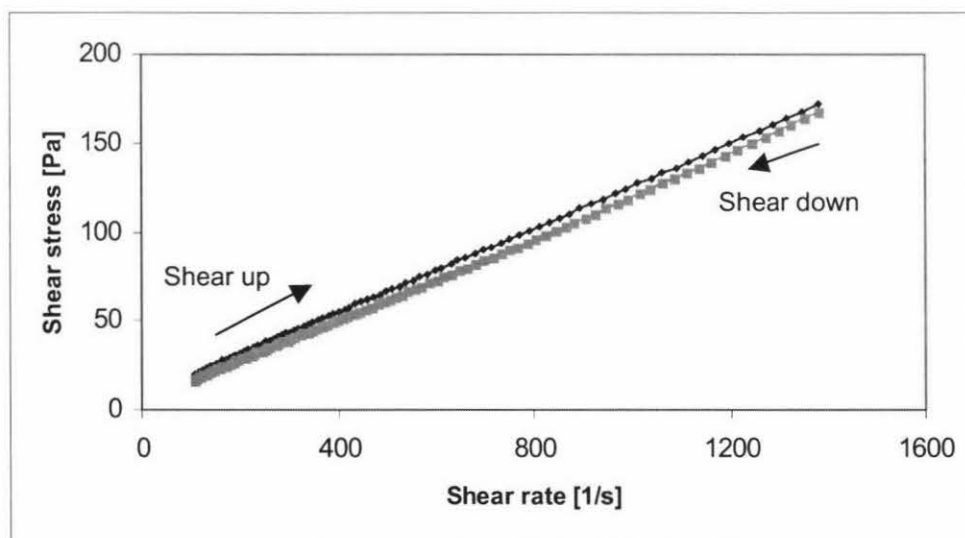


Figure 4.1 Flow curve at the onset measurement of RCWM sample made and stored at 35°C.

Figure 4.1 presents the time zero flow curve of reconstituted concentrated whole milk (RCWM) made and stored at 35°C while Figure 4.2 shows the time zero flow curve of reconstituted concentrated skim milk (RCSM) made at 35°C but stored at 50 and 75°C. All the RCM flow curves exhibited the same pattern but differed with respect to the magnitude of the area between the up and down curves called the hysteresis loop area, HLA (Figures 4.1, 4.2 and 4.3). As seen in Figures 4.1, 4.2 and 4.3, the up and down legs do not coincide and show time dependency (Steffe 1996). The flow curves were all convex, which was an indication of shear thinning (Steffe 1996). Therefore, this fluid exhibited thixotropic non-Newtonian behaviour.

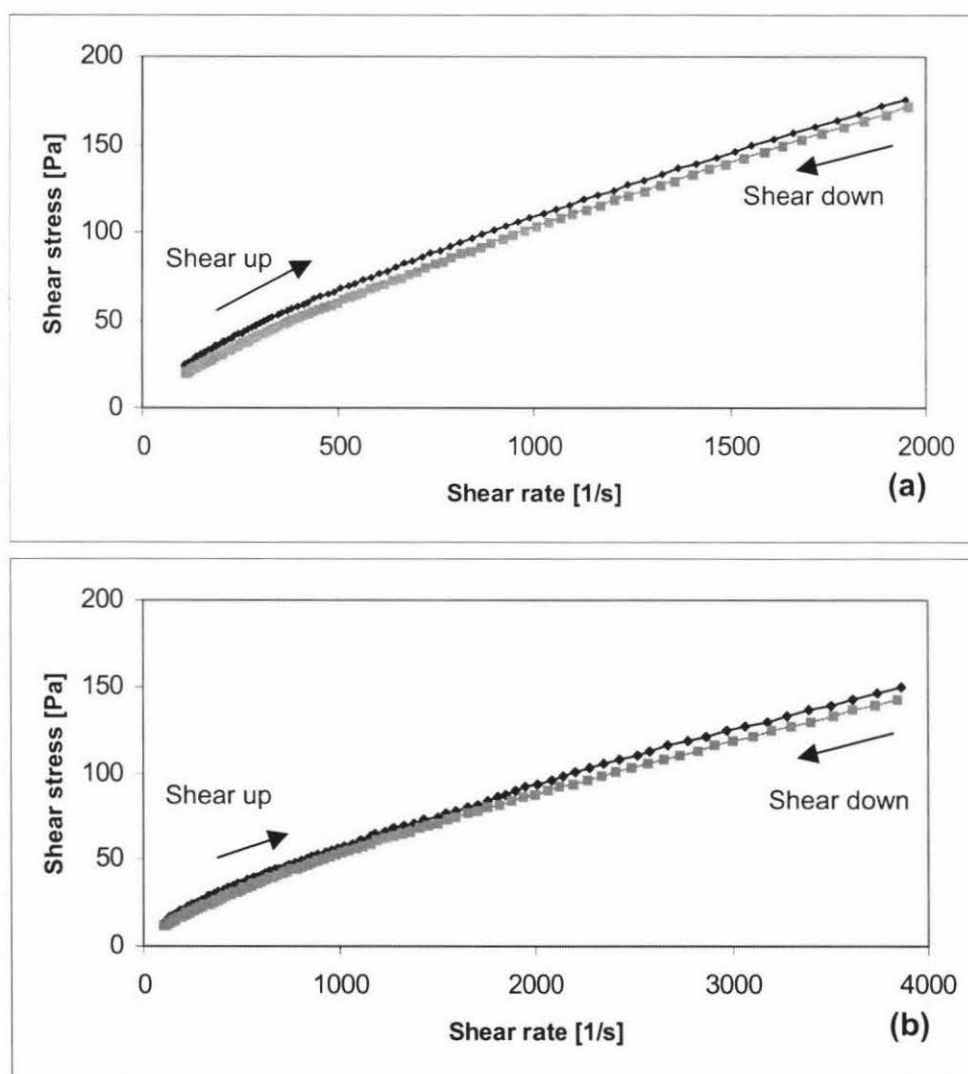


Figure 4.2 Flow curves at the onset measurement of RCSM sample made at 35°C and stored at (a) 50°C and (b) 75°C.



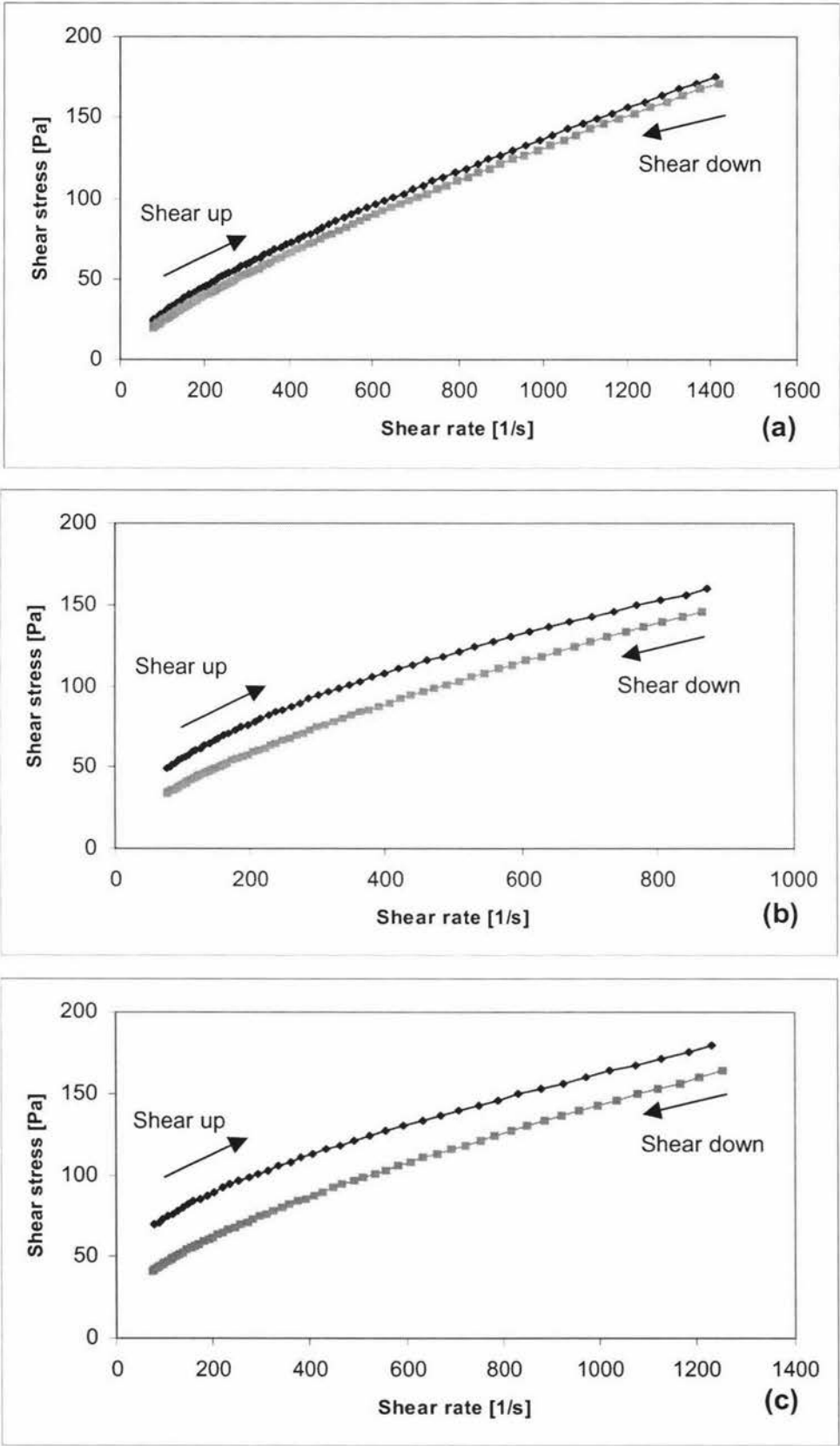


Figure 4.3 Effect of storage time at 50°C on the flow curves of 45%TS RCSM for (a) 0 hour (b) 2 hours and (c) 5.25 hours.

The storage time plays an important role in the development of the rheological characteristics of RCM (Trinh 2006, Trinh and Schraakenrad 2002; Trinh and Yoo 1997 and Trinh *et al.* 2002a). The effect of age thickening can be illustrated with the viscosity-time curve of RCSM at 50°C in Figure 4.4. The apparent viscosity was calculated from the flow curve measured from the up leg at the fixed shear stress of 100.7 Pa and applied with a non-Newtonian correction (Appendix 3). The RCM viscosity increased with storage time as reported by previous workers (Trinh 2006, Trinh and Schraakenrad 2002 and Trinh *et al.* 2002a).

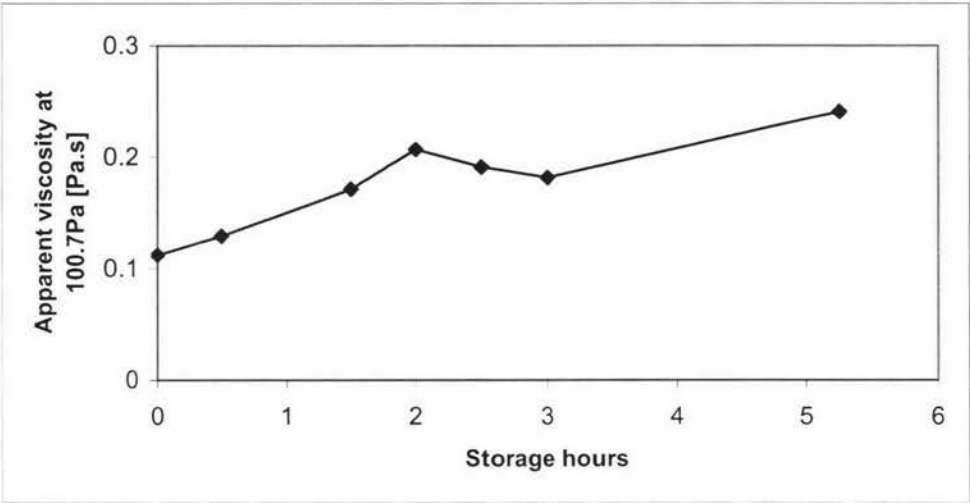


Figure 4.4 Effect of storage time at 50°C on apparent viscosity of 45%TS RCSM selected from the up leg and a shear stress of 100.7Pa.

The viscosity-time curve in Figure 4.4 presents a handy and simplified picture of age thickening and is especially useful when comparing different samples (Bienvenue 2003b; Rohm 1988; Samel and Muers 1962a,b; Sinha and De 1972; Snoeren *et al.* 1982, 1984; Trinh 2006, Trinh and Schraakenrad 2002; Trinh and Yoo 1997 and Trinh *et al.* 2002a) but it leaves out many characteristics that also change with time such as the development of thixotropy and shear thinning.

The experimental flow curves were summarised by fitting them with the Herschel-Bulkley (HB) model (see Equation 2.3 in *section 2.4.3*).

The HB model fitted most of the experimental data very well as shown in Figure 4.5.

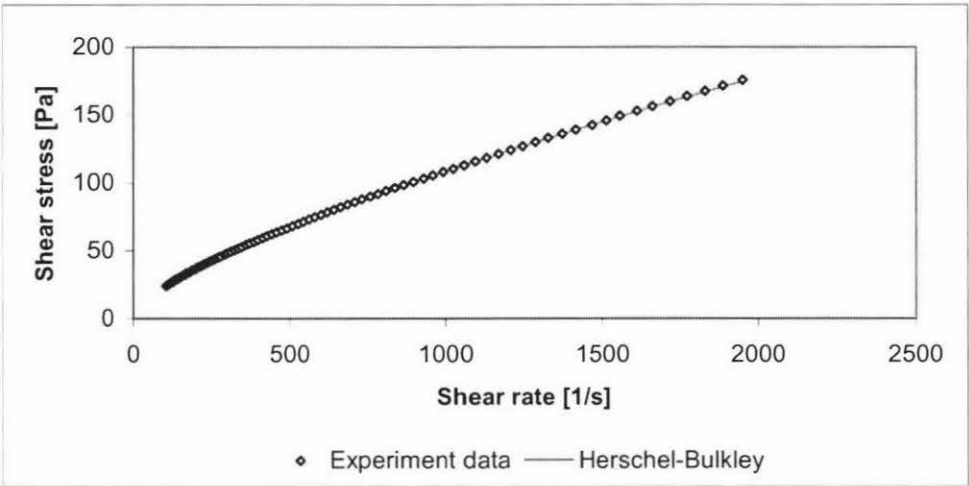


Figure 4.5 Comparison of experimental data of 45%TS RCSM at 50°C, time zero and shear up leg with the predicted curve generated using the Herschel-Bulkley calculation.

After the flow curves were summarised by the HB model, the HB parameter values of each flow curve are shown in Figures 4.6 and 4.7. Figure 4.6 shows the changes in the yield stress ( $\tau_y$ ) and the consistency index ( $K$ ) whilst Figure 4.7 shows the flow behaviour index ( $n$ ) of a 45%TS RCSM at 50°C calculated from the shear up leg with time.

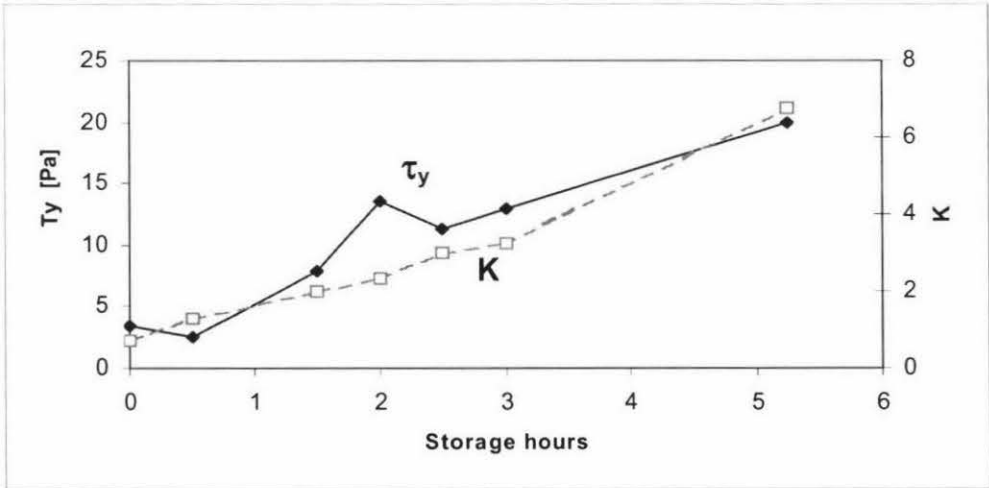


Figure 4.6 Yield stress ( $\tau_y$ ) and the consistency index ( $K$ ) of a 45%TS RCSM stored at 50°C with time calculated from the shear up leg.

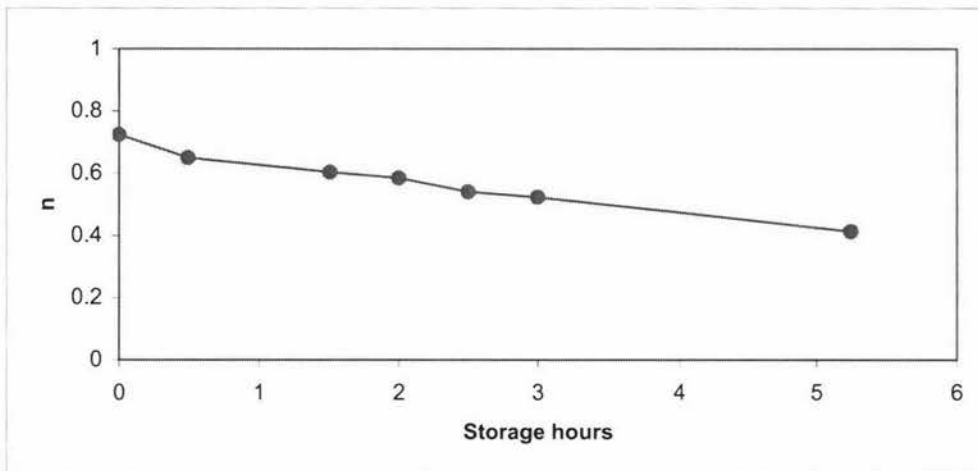


Figure 4.7 Flow behaviour index ( $n$ ) of 45%TS RSCM stored at 50°C with time calculated from the shear up leg.

$\tau_y$  and  $K$  increased with time at a similar rate which was roughly similar to the trend observed for the apparent viscosity (Figure 4.4). An increasing value of  $K$  with short term storage time indicates that the solution became thicker with time and an increasing value of  $\tau_y$  indicates that the material developed more solid-like characteristics with time.  $n$  dropped from a value of 0.72 at zero time to 0.42 after 5.25 hours of storage. This showed that the viscosity was becoming more shear dependent with time. This modelling of the flow curve, which has been adopted by most previous workers (Bienvenue *et al.* 2003a,b; De Felipe *et al.* 1991; Rohm 1988; Snoeren *et al.* 1984; Trinh and Schraekenrad 2002; Trinh and Yoo 1997 and Vélez-Ruiz and Barbosa-Cánovas 1998), did show one important factor, namely an increasing level of thixotropy with time.

The area between the shear up and shear down legs is called the Hysteresis Loop Area (HLA) and is normally interpreted as an indication of thixotropic behaviour (Steffe 1996). This has been applied previously by other research workers to SCM e.g. Samel and Muers (1962b) and RCM e.g. Trinh (2006). However, very few previous workers have calculated the changes in the HLA. Dolz *et al.* (2000) and Tárrega *et al.* (2004) calculated the HLA for pharmaceutical and food products, but they did not examine

the development of HLA with time. The approach taken in this work is modelled after Trinh (2006).

The normalised HLA was calculated using Equation 4.1. The normalised HLA is a measure of the ease that the structure can be broken down by shear. The higher the HLA value, the more easily the structure breaks down with shear.

$$\text{Normalised HLA} = \left[ \frac{\sum_{n=0}^n (\text{Area under up leg})_n}{\dot{\gamma}_n - \dot{\gamma}_0} \right] - \left[ \frac{\sum_{m=0}^m (\text{Area under down curve})_m}{\dot{\gamma}_0 - \dot{\gamma}_m} \right] \quad (4.1)$$

Figure 4.8 shows the normalised HLA of an RCM sample stored at 50°C from time equal zero up to 5.25 hours. As shown in Figure 4.8, the normalised HLA increases very fast during the first two hours and more slowly afterwards.

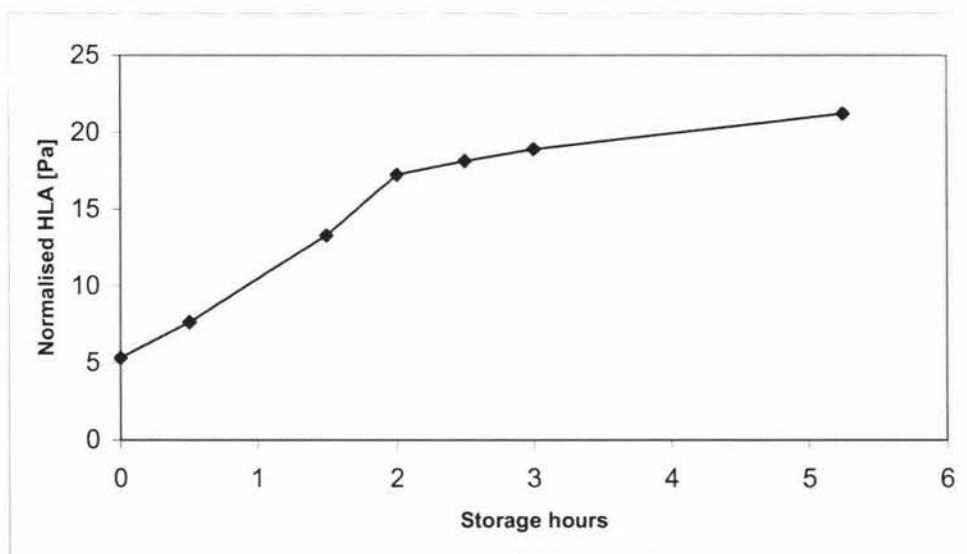


Figure 4.8 Normalised Hysteresis Loop Area (HLA) of 45%TS RCSM stored at 50°C.

The storage temperature also has an important influence on the rheology of RCM (Trinh *et al.* 2002a). Figure 4.9 shows the apparent viscosity of 50% TS RCWM stored at 35°C and 45% TS RCSM stored at 50 and 75°C. All the viscosities were measured at the storage temperature then converted to viscosity at 35°C. This was

done using Equation 4.2 to make a correction based on the log-linear relationship between viscosity and temperature (Rao 1999) as indicated by the equation is shown below (Appendix 4);

$$\ln \mu = \frac{B}{T} + C \quad (4.2)$$

where  $\mu$  is viscosity [Pa.s],  $T$  is temperature [Kelvin],  $B$  and  $C$  are parameters. The parameters,  $B$  and  $C$ , are derived from the sample measured at zero time. These parameters were assumed to apply to samples that have been stored for sometime.

The rates of age thickening of RCWM and RCSM were shown to be very similar when stored at 35 and 50°C, but much higher at 75°C. This suggests that the mechanism of age thickening at 35 and 50°C was different from the mechanism at 75°C. Trinh (2006) suggested that there are two distinct types of age thickening and that these were defined by a critical storage temperature. One likely explanation for the different rates was related to the behaviour of the whey protein as these denatured and aggregated above 65°C, particularly  $\beta$ -lactoglobulin that reacted with the casein micelle at temperatures above 72°C (Dannenberg and Kessler 1988).

The viscosity measurements for the three curves shown in Figure 4.9 were stopped when the samples were visibly gelled. Clearly the gel network was formed more quickly at high temperature (19 hours for 35°C, 5.25 hours for 50°C and 1.75 hours for 75°C)

The HLA also increases with storage temperature (Figure 4.10). Note that the apparent viscosities and therefore the shear stresses of the flow curve used to calculate the normalised HLA in Figure 4.10 have not been reduced to the same basic temperature of 35°C but reflect the storage temperature. Because of that the HLA at 50°C is substantially higher than 35°C.

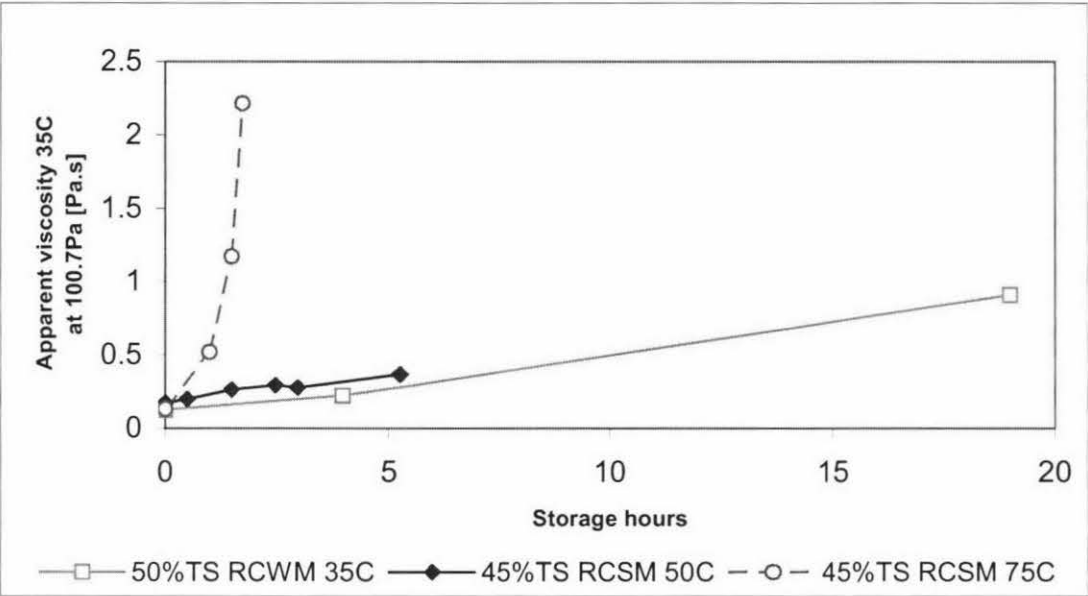


Figure 4.9 Effect of storage temperature on the apparent viscosity at 100.7Pa of RCM converted to the same basis of 35°C.

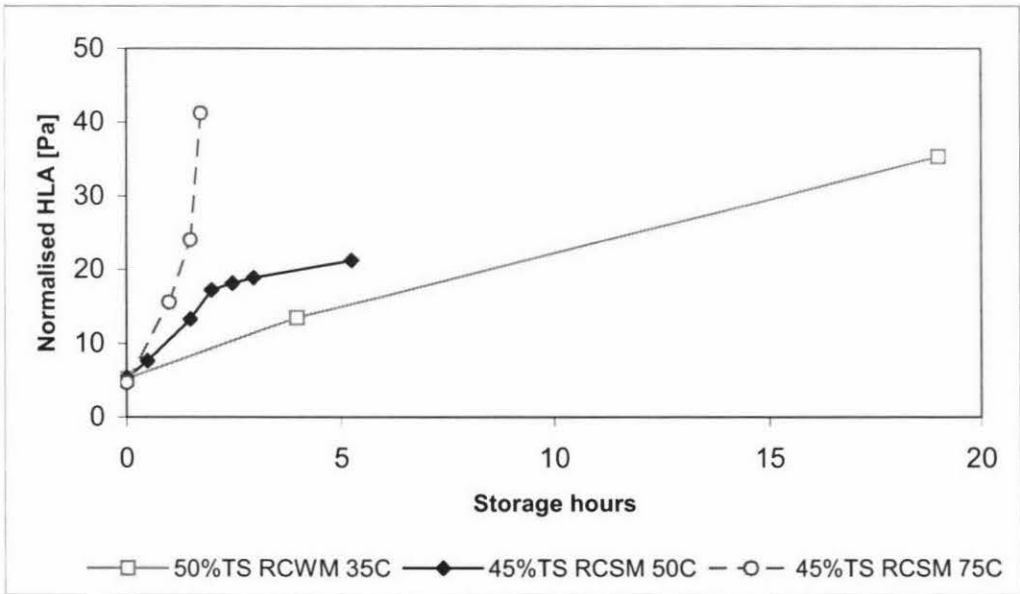


Figure 4.10 Effect of storage temperature of 35, 50 and 75°C on normalised HLA of RCM.

The particle size distribution (PSD) was measured to provide complementary data to the rheological measurement in Figure 4.4. Figure 4.11 is an example of the PSD of 45%TS RSCM stored at 50°C up to 11.5 hours.

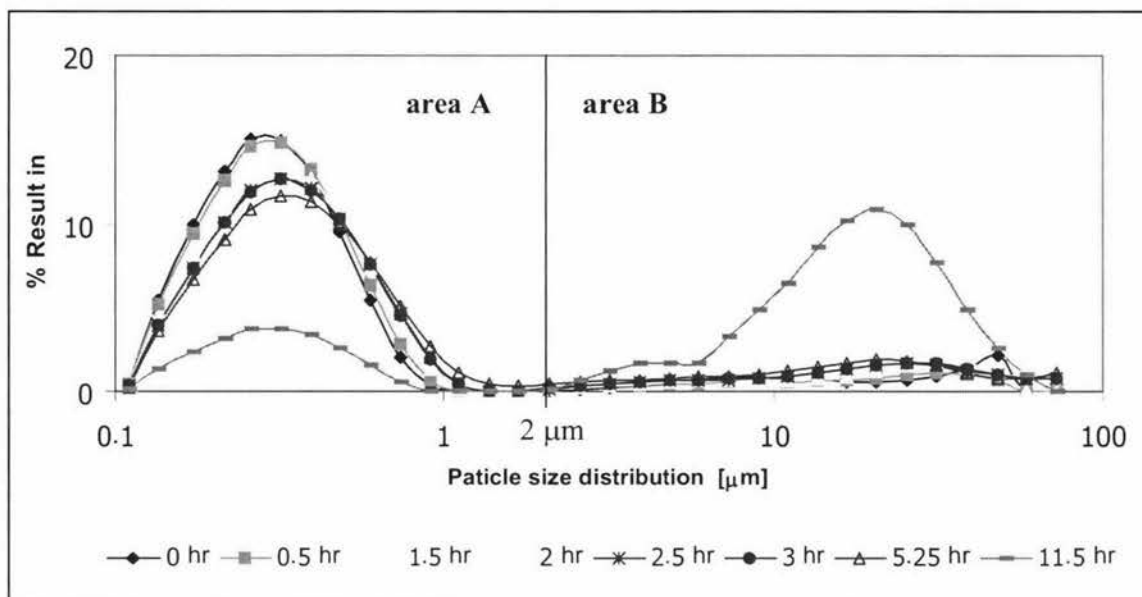


Figure 4.11 Particle size distribution of 45%TS RSCM stored at 50°C up to 11.5 hours.

In Figure 4.11, the PSD is divided into two zones: one below a diameter of 2  $\mu\text{m}$  (area A) and one above (area B). In milk, the unaggregated protein and the fat particle are smaller than 1  $\mu\text{m}$ . Thus, an increase in area B indicates an increase in the number of large aggregates as shown in Figure 4.11. Obviously area A will decrease when area B increases because two add up to 100% so the two graphs in Figure 4.12 are different ways of presenting the same information. The PSD curve at 11.5 hours shows a much more significant peak in area B than all other curves. As noticed before that the RSCM sample gelled after 5.25 hours stored at 50°C. The unusual peak at 11.5 hours indicates that the bonds present in the gel were much stronger than the bonds in the flocs present in the milk before gelation. They were not broken easily when the samples were diluted for particle size measurement in the Mastersizer E.



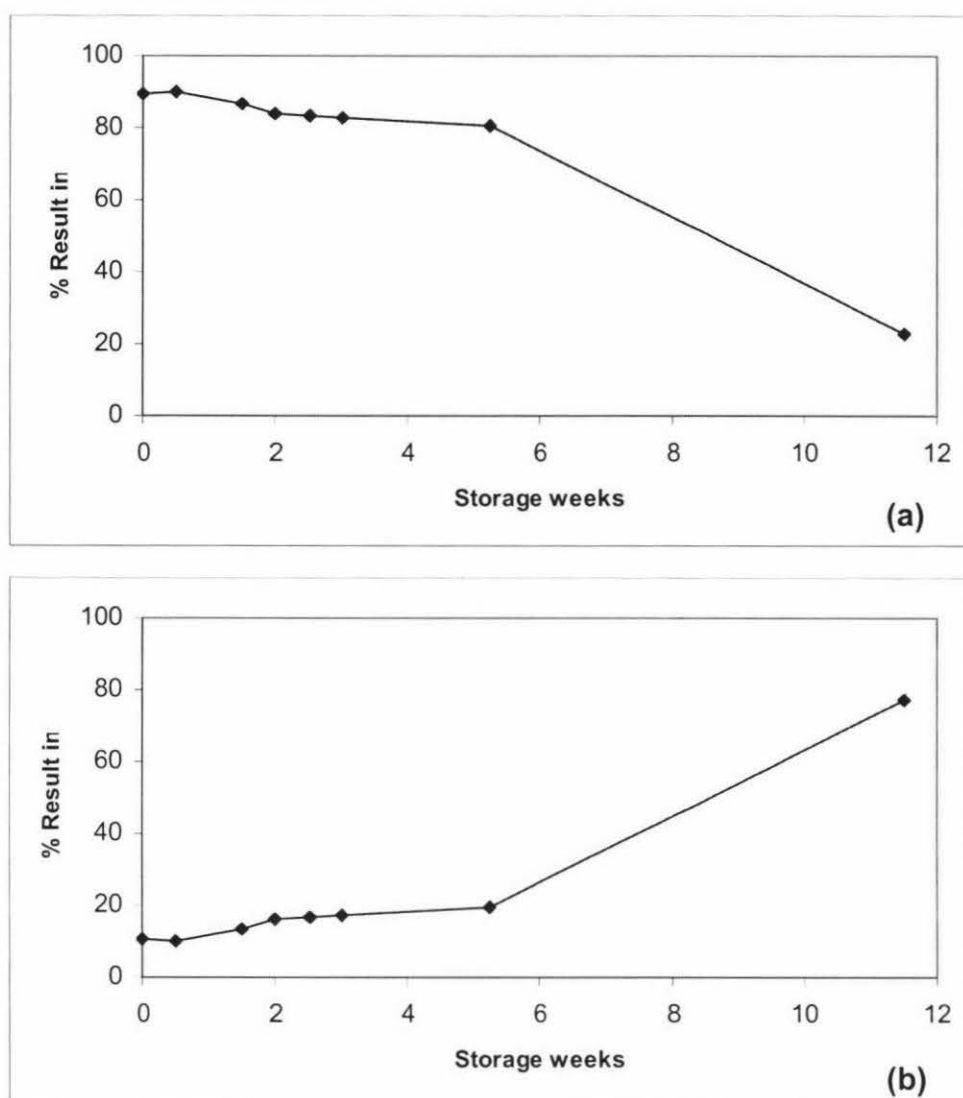


Figure 4.12 Schematic of (a) area A (size < 2  $\mu\text{m}$ ) and (b) area B (size  $\geq 2 \mu\text{m}$ ) of a 45%TS RCSM stored at 50°C for 11.5 hours.

Figure 4.13 shows that the peak in the B area is much more pronounced when the RCSM was stored at 75°C even for short (up to 1.75 hours) and before the milk has gelled. Clearly the bonds created in the flocs at 75°C were more difficult to break by dilution for PSD measurement. Since whey proteins participate in aggregation above 65°C (Dannenberg and Kessler 1988), the types of bonds involved with storage below and above 65°C are quite different. Thus, the particle size measurement supports the

hypothesis of two types of age thickening suggested by the viscosity measurement in Figure 4.9. Trinh (2006) discussed the issue more fully.

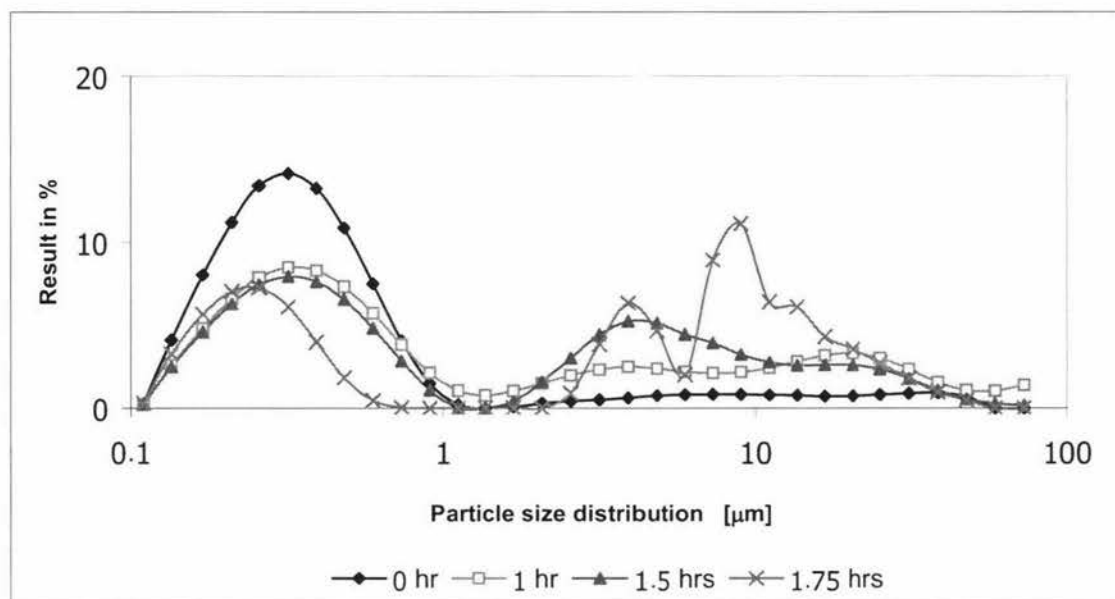


Figure 4.13 Particle size distribution of 45%TS RSCM stored at 75°C up to 1.75 hours.

#### 4.1.2 Reshearing investigation

The presence of aggregates that could not be destroyed by dilution as evidenced in Figures 4.11 and 4.13 have led some authors like Bienvenue *et al.* (2003a) to argue that these aggregates are a proof of the formation of irreversible bonds in the flocs formed during age thickening. We tested this hypothesis that irreversible bonds were formed during age thickening by reshearing a sample of age thickened RCWM. The RCWM was reconstituted to 50%TS at 35°C and stored at the same temperature for 23 hours. Then the sample was resheared again at  $40,000 \text{ s}^{-1}$  for 1 hour in the recombination rig and stored for another 23 hours at 35°C. This experiment was performed twice (set A and set B). The total solids of set A and B were 50.98% and 51.56% respectively.

Figure 4.14 shows the viscosity at 0, 4, 19 and 23 hours on the first and the second day experiment at the reference shear stress of 100.7Pa. The viscosity increased by

approximately a factor of 5 over the first day, but reshearing reduced the viscosity of the age thickened sample to a viscosity of approximately 0.15 Pa.s which was practically identical to the zero time first day viscosity of 0.12 Pa.s. The major difference between the first day and second day samples was the lack of age thickening over the second day after shearing. The slight increase in viscosity over the first 4 hours on the second day was probably due to the presence of the small number of air bubble entrained into the sample during the reshearing operation. The same trend was observed in both set A and set B. Thus the aggregates formed during storage on the first day could be almost completely disturbed by high shear, but not by dilution. Once resheared, the sample lost its ability to reform large new flocs.

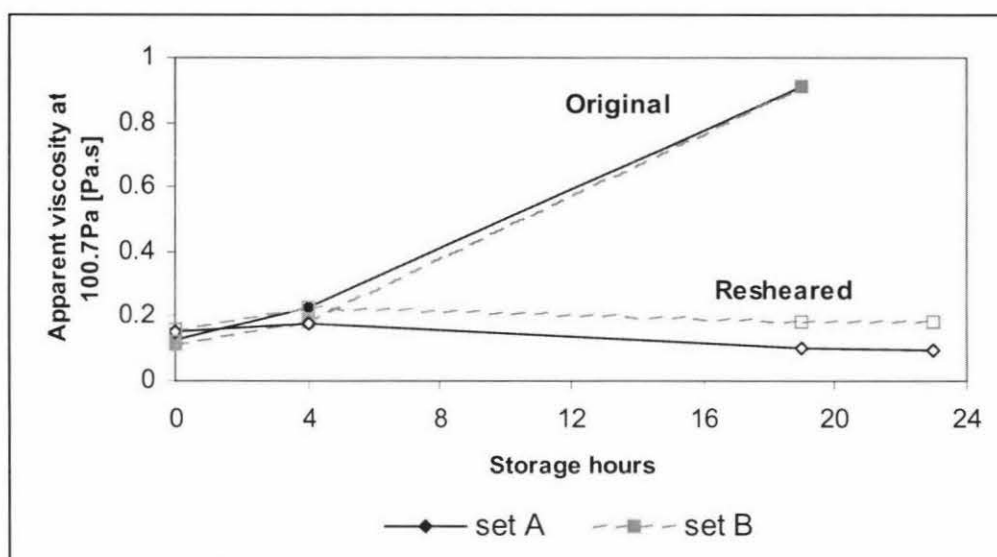


Figure 4.14 Double shearing of 50%TS RCWM sample produced and stored at 35°C with two replicated runs.

The PSD of a 50%TS sample of RCWM stored at 35°C showed no change with time either over the first day or after reshearing on the second (Figure 4.15) indicating that the type of bond formed at this solids concentration (50%TS) and storage temperature (35°C) were very weak and easily overcome by dilution. Trinh (2006) observed the same effect.

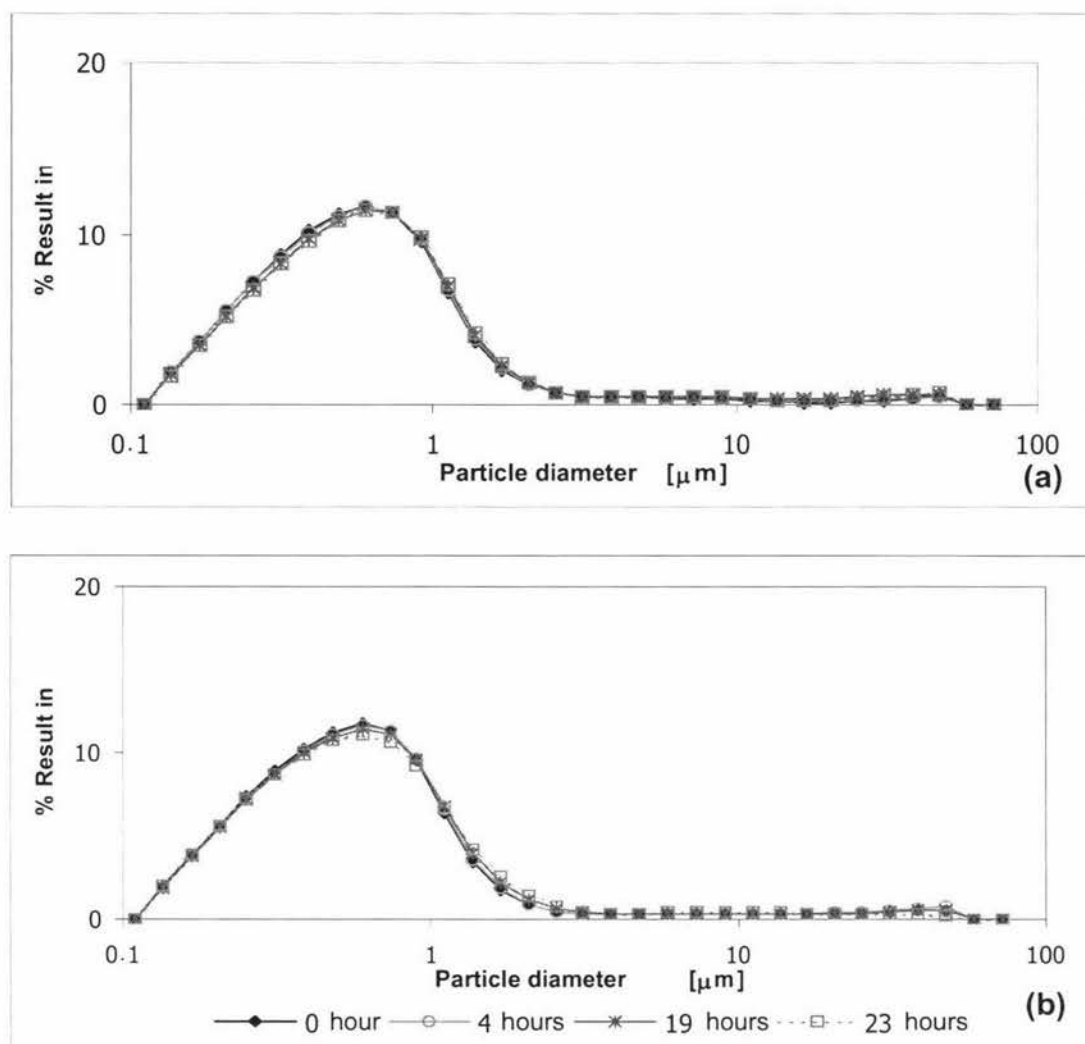


Figure 4.15 Particle size distribution of the double shearing experiment of 50%TS RCWM processed and stored at 35°C (a) the first day experiment (b) the second experiment (with reshearing).

## 4.2 RECOMBINED SWEETENED CONDENSED MILK (RSCM)

This section firstly discusses the results of trying different processes (*runs C1-C4*) to manufacture RSCM with the equipment available (*section 4.2.1*) and the results of two storage trials (*runs D1-D5* and *runs E1-E6*) using a novel method of RSCM manufacture (*section 4.2.2*).

#### 4.2.1 Development of an RSCM manufacturing process

RSCM was manufactured according to the most common process discussed in the literature review *section 2.3*, except that a recombination temperature of 35°C was used instead of 55°C (*run C1*). Because our recombination rig could only produce 2 litres per batch, this was insufficient for the storage trials. Instead two batches were mixed consecutively then combined before homogenisation. The recombination temperature of 35°C was chosen so as to avoid significant age thickening of the first batch while the second batch was being mixed. However, it was found that the sugar did not dissolve completely at a recombination temperature of 35°C. Lee (1959) also found, when recombining a mixture of protein, fat and sugar at 100°F (37.8°C), the sugar did not dissolve properly. So he had to reheat the solution to 180°F (82.22°C) to ensure the complete solubilisation of lactose and sucrose.

Interesting observations were made in *run C2* when we tried to deal the problem of sugar dissolution without raising the temperature of mixing. The sugar was dissolved first in a steam bath then the sugar solution was cooled down to 35°C and the milk powder added. The viscosity of the final RSCM measured at 201.29Pa and 25°C was quite high at 5.81 Pa.s compared with the average value (3.87 Pa.s) for *runs D1-D4* when the protein was added first. Figure 4.16 gives the full flow curve for *run C3* (sugar added first) and *run D1* (milk powder added first). Clearly the order in which the ingredients, particularly protein and sugar, are added has a strong effect on the viscosity of the final product. Other researchers like Lee (1959) have also noticed that “there are doubtless several ways in which the various ingredients can be added” but to the author’s knowledge no one has reported this observation before. There have been times when the dairy industry has found it difficult to make RSCM to the right viscosity. Usually the viscosity is too low. In New Zealand, this problem, when it happens, occurs round about March and is likely due to a seasonal effect on the quality of milk (Tuoc Trinh, personal communication, 4th August 2006). Adding sugar, or some of the sugar first as in *runs C2 and C3* may help to reduce this problem.

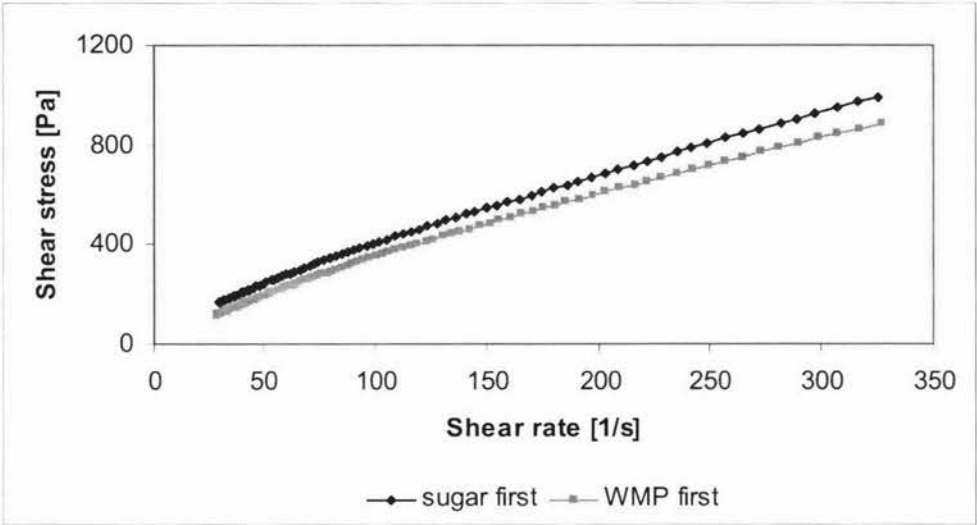


Figure 4.16 Flow curve at time zero of (a) sugar added first (b) WMP added first

Another problem was observed in *run C2* when pasteurisation of the homogenised RSCM product was conducted at 85°C for 60 seconds as suggested by Choat (1979). The RSCM product was badly destabilized because lumps of protein aggregates were observed after the pasteurisation step. A gentler regime of pasteurisation 75°C for 15 seconds (Rod Bennett, personal communication, 29th August 2005) was used instead and an observation of the RSCM sample produced by this process indicated no lumping of proteins in *run C3*. This pasteurisation regime was also very effective for the control of yeast and mould as no growth was observed on the surface of the RSCM samples when stored at 30, 40 and 50°C for 3 months.

4.2.2 Storage trials

RSCM samples for the various long-term storage trials were manufactured with recirculation at 2 nominal shear rates: high shear at 31,000s<sup>-1</sup> (*runs D1-D4* and *E1-E3*) and low shear rate at 900s<sup>-1</sup> (*runs D5* and *E4-E6*).

Two trials were conducted. The first storage trial (ST 1) was designed to store RSCM at 30°C for 3 months, 40°C for 14 days and 50°C for 7 days. Four batches (*runs D1-D4*) were produced and each recirculated at 31,000s<sup>-1</sup>. RSCM cans were randomly selected and stored at the three temperatures: 30, 40 and 50°C. Only one batch (*run*

D5) was manufactured at  $900\text{s}^{-1}$  and stored at  $50^{\circ}\text{C}$  for 7 days. The results of this run were not shown in this thesis because the storage time was too short and conducted at only one temperature. There was insufficient milk powder from the existing batch to produce any more samples for the low-shear experiment, and a new experimental trial was conducted with an extended storage time.

In the second storage trial (ST 2), the RSCM samples for each storage temperature and shear rate was produced in a single batch to ensure homogeneity between samples. This was made possible by reducing the size of the sample containers from 250 ml to 70 ml. Again, RSCM was produced at two shear rates of 31,000 and  $900\text{ s}^{-1}$  and stored at 30, 40 and  $50^{\circ}\text{C}$  for up to 12 weeks or until it gelled.

In this section, the main results are concentrated on the results of ST 2. The results of ST 1 are used to support the phenomenon that was observed at the beginning of the storage period in ST2.

(1) Rheology of RSCM

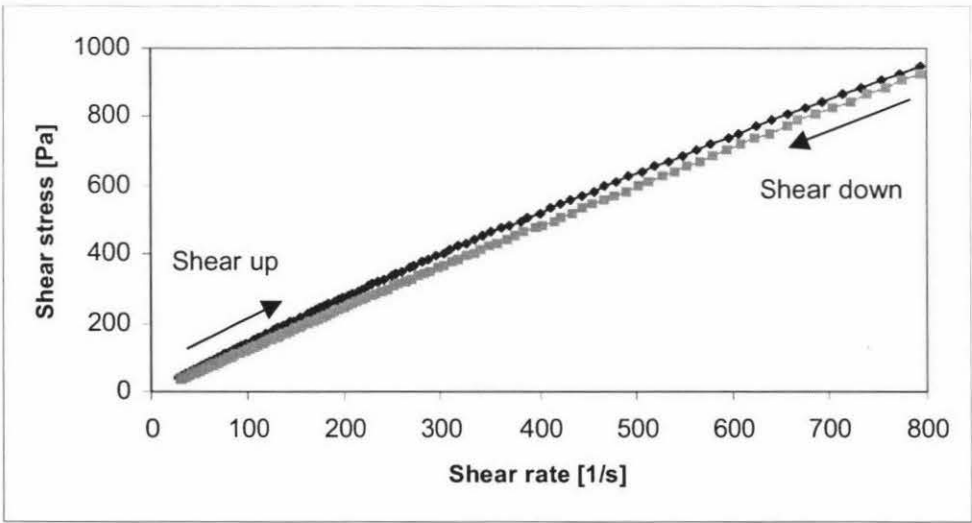


Figure 4.17 Flow curves of RSCM manufactured at high shear rate at  $30^{\circ}\text{C}$  and time zero.

All RSCM flow curves exhibited thixotropic non-Newtonian behaviour. For example Figure 4.17 presents the time zero flow curves of RSCM made at high shear rate at 30°C.

The apparent viscosity was obtained for the fixed shear stress of 201.29Pa from the up leg of the flow curves measured at the storage temperature. It is plotted against storage time in Figure 4.18 (a) for high-shear and (b) for low-shear manufacture.

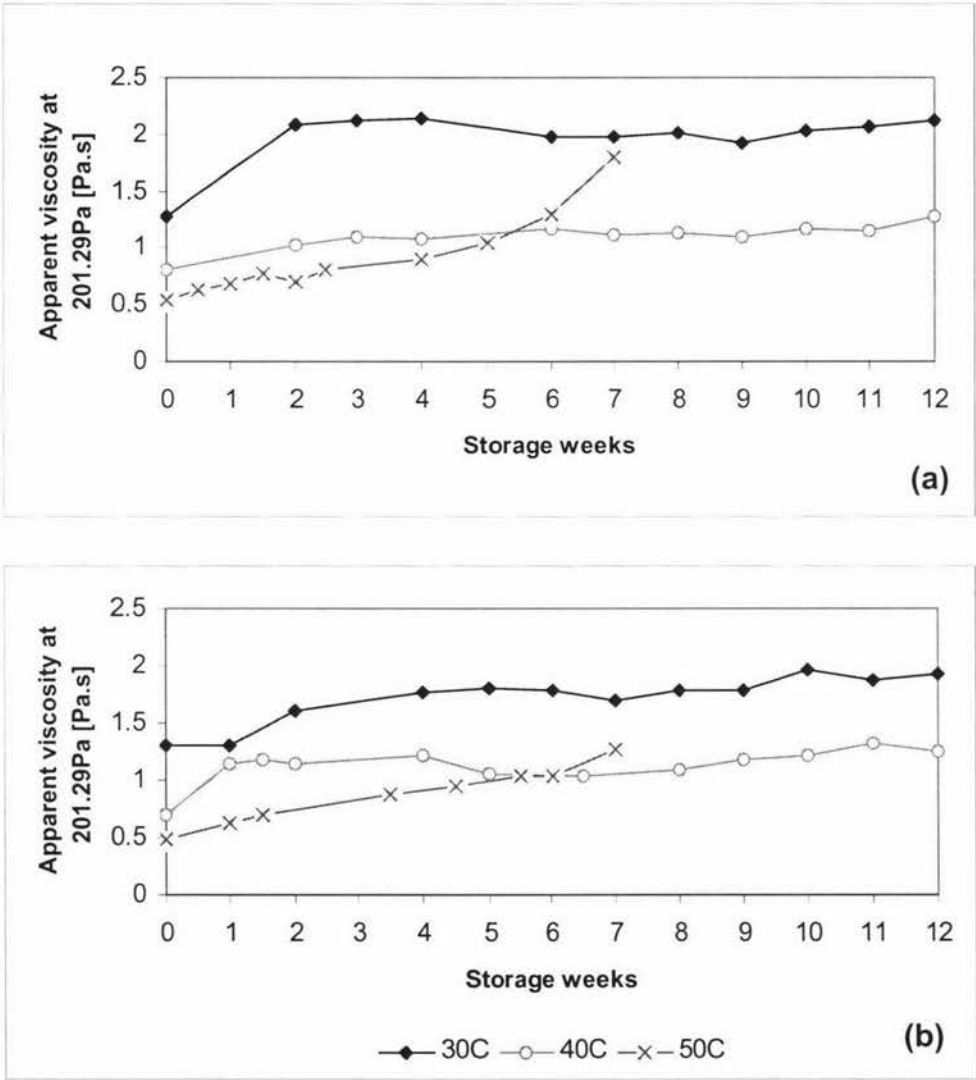


Figure 4.18 Changes of apparent viscosity of RSCM at 201.29Pa measured at storage temperature (30, 40 and 50°C) against storage time (a) high-shear and (b) low-shear manufacture. SD of these points are shown in Appendix 5.



As seen in Figure 4.18, there is a significant increase in apparent viscosity in the first 1 or 2 weeks then a much slower increase for storage temperatures of 30 and 40°C. The apparent viscosities of samples stored at 50°C increases continuously until they gelled at week 7. The results of high-shear and low-shear RSCM show the same trend. The samples of low-shear RSCM stored at 40°C week 7, and at 50°C week 0.5, were mishandled and therefore they were omitted from Figure 4.18.

It is much easier to compare these curves by quoting the apparent viscosity at the same reference temperature. The non-Newtonian corrections were performed in the same manner as for the RCM results in *section 4.1.1*. The details of the correction method are found in Appendix 3. The reference temperature at 20°C was chosen to facilitate comparison with literature data (Samel and Muers 1962b). The apparent viscosities recalculated for the temperature of 20°C are shown in Figure 4.19.

Beyond week 4, there is little difference between the curves for the samples stored at 30 and 40°C and little evidence of age thickening within the uncertainty of the experimental data (Figure 4.19). On the other hand, the curves for samples stored at 50°C show a fair amount of age thickening. This holds true for both high- and low-shear RSCM. The increase in viscosity between time zero and week 3 is very similar for all three temperatures for both high-shear and low-shear RSCM. This suggests that the changes in apparent viscosity in the first portion of the curves, i.e., the first 2 - 3 weeks of storage, follow a mechanism which is relatively independent of the storage temperature and different from the mechanism in the latter portion of the curves (beyond 4 weeks approximately). The most obvious change in the stored samples was a slow rise of the air bubbles that were minimised but not completely eliminated during the manufacture. This happened during the first 2-4 weeks of storage depending on the sample viscosity and the size of the original bubbles in the particular batch. The traditional age thickening effects of RSCM were only clearly observed once the air escaped from the samples and no longer interfered with the rheological measurements.

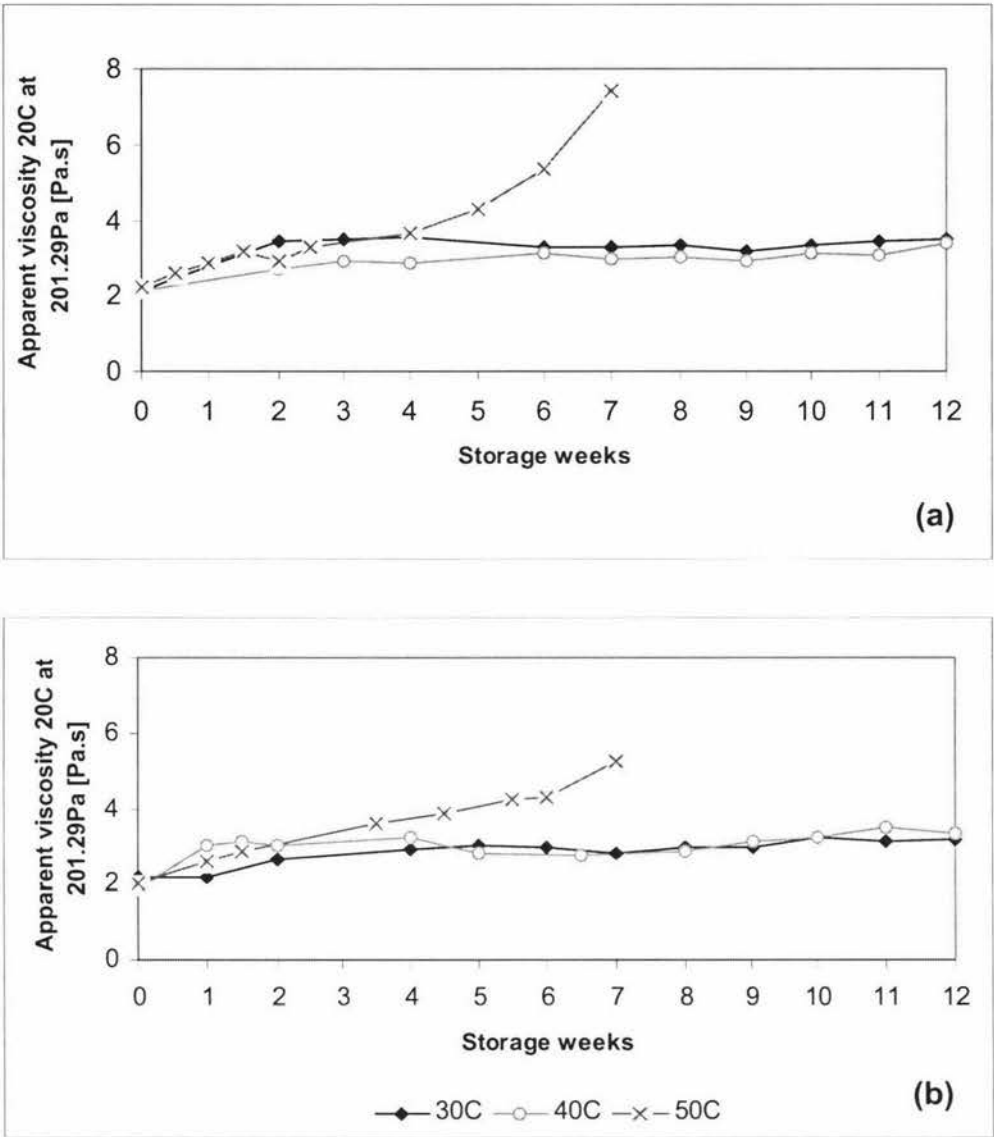


Figure 4.19 Changes of apparent viscosity of RSCM at 201.29Pa measured at storage temperature (30, 40 and 50°C) then converted to 20°C over storage time (a) high-shear and (b) low-shear manufacture.

In fact, the RSCM barely aged at all over the 12-week storage period when stored at 30 and 40°C. It would appear that the application of shear ( $900$  and  $31,000\text{s}^{-1}$ ) during recombination of the WMP for the production of the RSCM samples had succeeded in removing the propensity of the RSCM to age thickening. It was surprising that the change in shear rate from  $900$  to  $31,000\text{s}^{-1}$  did not make a big difference. The breakdown of the structure of a time dependent fluid is a function of both shear rate

and duration of shear. In this case, shear was applied for approximately 3 hours whilst the WMP was reconstituted. Because of the long duration of shear, it is possible that even  $900\text{s}^{-1}$  was sufficient shear rate to completely destroy the age thickening tendency of RSCM. Samel and Muers (1962a) made a similar observation when they took a sample of SCM and sheared it in a Hobart mixer for two hours. Unfortunately, they did not report the shear rate of the mixer. It is possible that their sample was given the same shear as the sample sheared at  $900\text{s}^{-1}$  in this experiment. However, the fact that shearing regime of Samel and Muers (1962a) did not completely destroy the tendency of the SCM to age thicken only slowed it down suggests that the amount of shear imparted by a Hobart mixer over 2-hour mixing period was less than was used in this study. Its interesting that these two researchers did not incorporate their observations into the development of a new process to reconstitute SCM.

The RSCM flow curves were summarised by the Herschel-Bulkley (HB) model in the same way as for the RCM samples. An example of the experimental data and the HB model fitted curve is shown in Figure 4.20 using the up leg data of high-shear RSCM at  $50^\circ\text{C}$  and week 5.

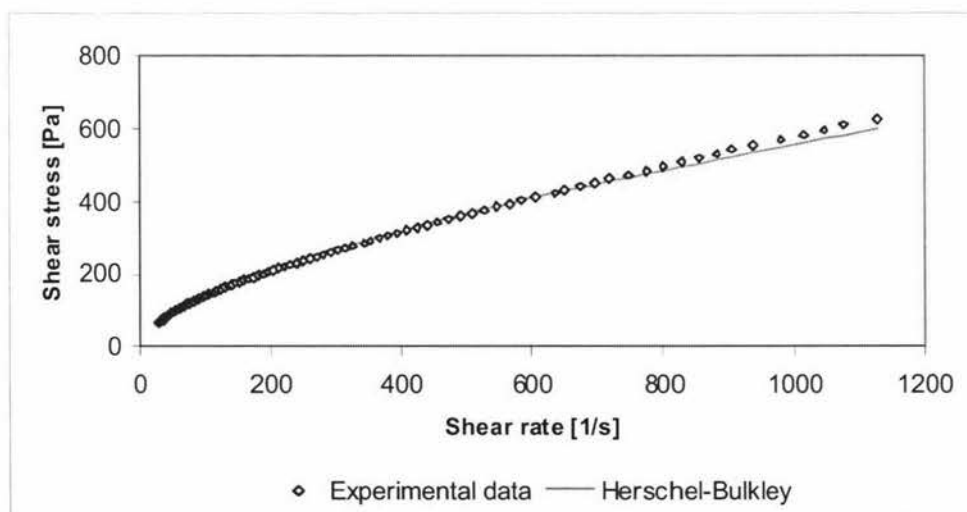


Figure 4.20 Comparison of experiment data of high-shear RSCM stored at  $50^\circ\text{C}$  week 5 and shear up leg with Herschel-Bulkley calculation.

The HB parameters of high-shear and low-shear RSCM stored at 30 and 40°C are shown in Figure 4.21 and at 50°C in Figure 4.22. Results show that the high-shear and low-shear RSCM have the same trend at every storage temperatures.

Figures 4.21 and 4.22 show that the trends of consistency coefficient ( $K$ ) values are very similar to the viscosity trends in Figure 4.19. The flow behaviour index ( $n$ ) values decrease and the  $K$  values increase with storage time (Figures 4.21 and 4.22) especially at 50°C storage. Storage at 30 and 40°C, the  $n$  values decrease very fast at first with storage time then stayed fairly constant at a value of approximately 0.8 which is an indicator of weak shear dependence while the  $K$  values increase rapidly in the first 2 weeks and more slowly from week 3 onwards. De Felipe *et al.* (1991) also observed a decrease in  $n$  and an increase in  $K$  values during their RSCM stored at 37°C for 45 days.

As it turned out, the curves at 30 and 40°C do not have a yield stress ( $\tau_y$ ) value of any significance along 12 weeks storage (Figure 4.21) and as a consequence the HB model degenerates to the power law model. This indicates that the bonds involved in the flocs are very weak. In contrast, a clear development of  $\tau_y$  values has been observed after 4 to 5 weeks of storage at 50°C (Figure 4.22).  $\tau_y$  is the stress that must be applied to a material to make it begin to flow. It implies that the material's structure at rest was strong and solid-like. Awadhwal and Singh (1985) and Higg and Norrington (1971) also found that the  $\tau_y$  value of SCM was negligible at time zero. Sone (1972) reported a  $\tau_y$  range between 125 and 1000 dynes/cm<sup>2</sup> (12.5 and 100 Pa) from original data published by Samel and Muers (1962a). In fact, Samel and Muers (1962a) did not report the values of  $\tau_y$  in their work. They only plotted flow curves from three shear rates of 4.61, 19.7 and 49s<sup>-1</sup>. Therefore, the  $\tau_y$  values reported from Sone (1972) came from extrapolation. De Felipe *et al.* (1991) also found that the yield stress was negligible even after their RSCM storage at 37°C for 45 days.

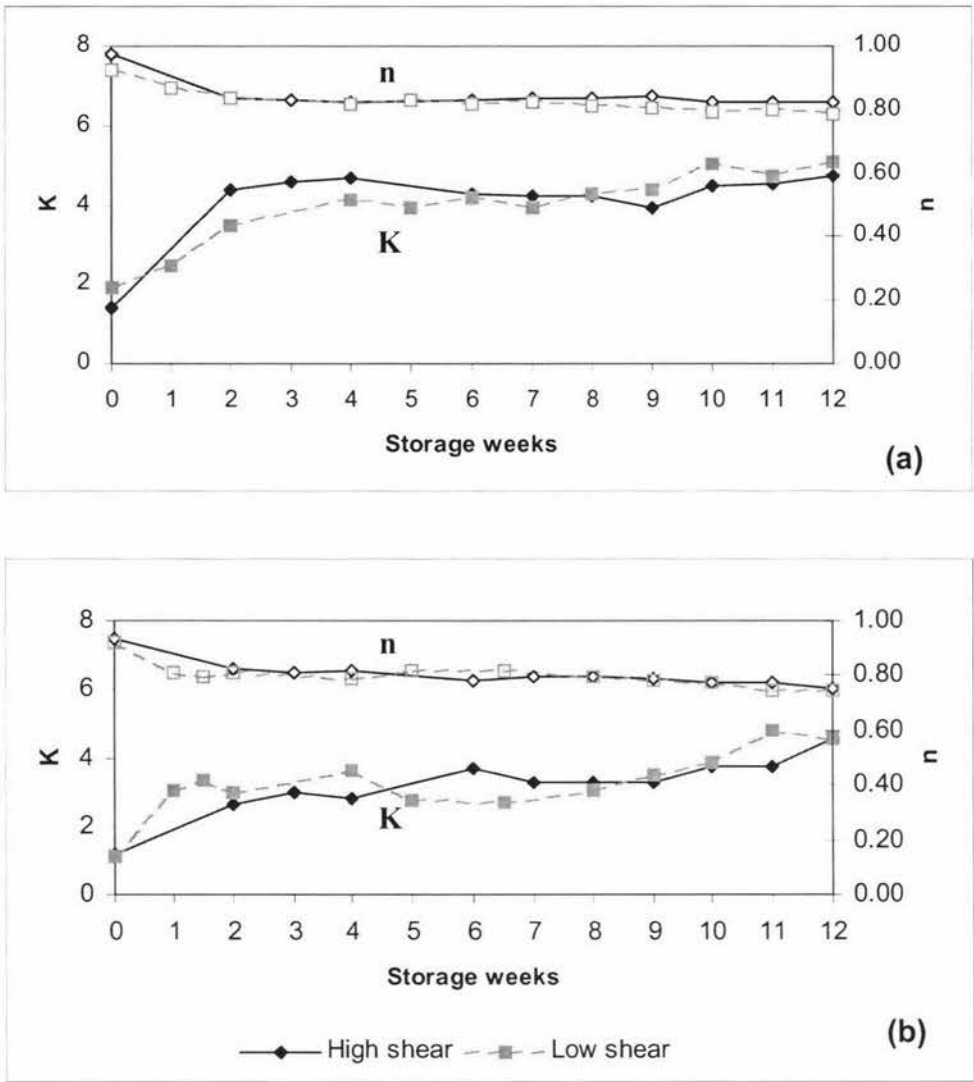


Figure 4.21 Herschel-Bulkley parameters of high-shear and low-shear RSCM stored at (a) 30°C and (b) 40°C where  $K$  is the consistency index and  $n$  is the flow behaviour index. SD of these points are shown in Appendix 5.

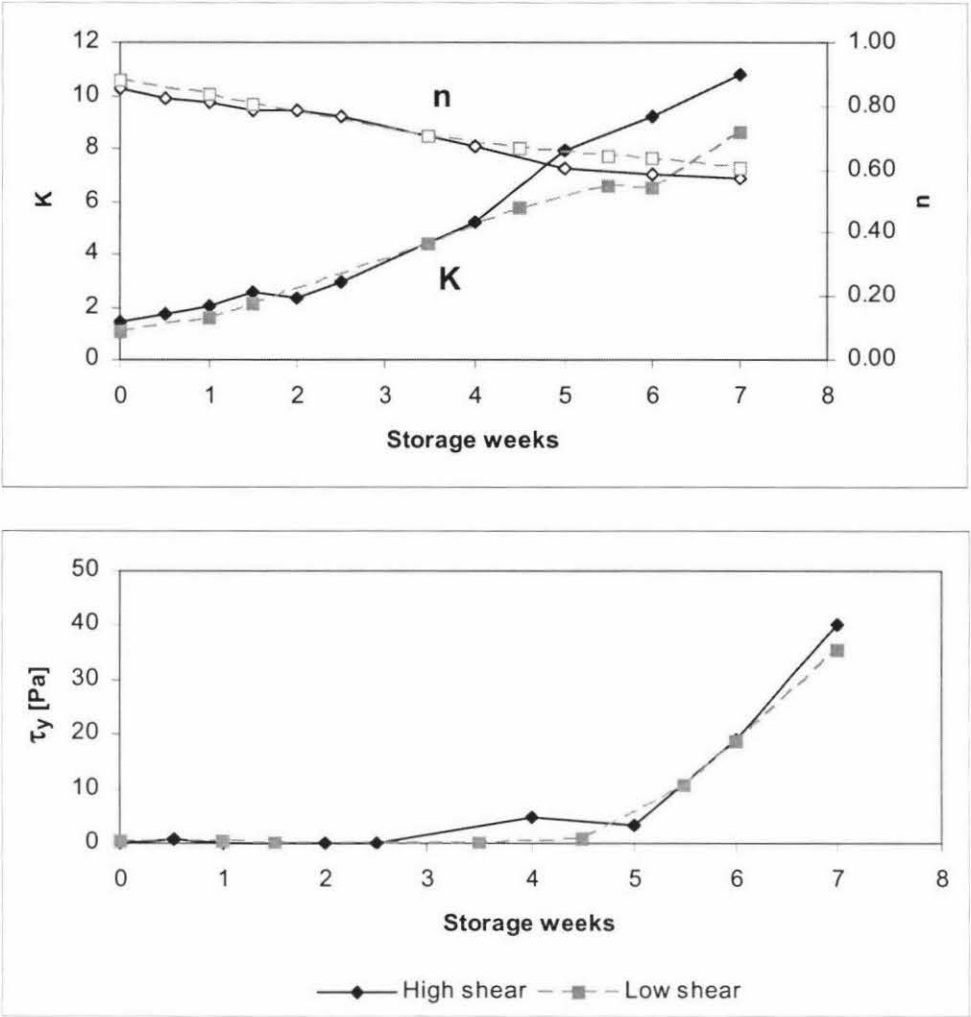


Figure 4.22 Herschel-Bulkley parameters of high-shear and low-shear RSCM stored at 50°C where  $K$  is the consistency index,  $n$  is the flow behaviour index and  $\tau_y$  is the yield stress. SD of these points are shown in Appendix 5.

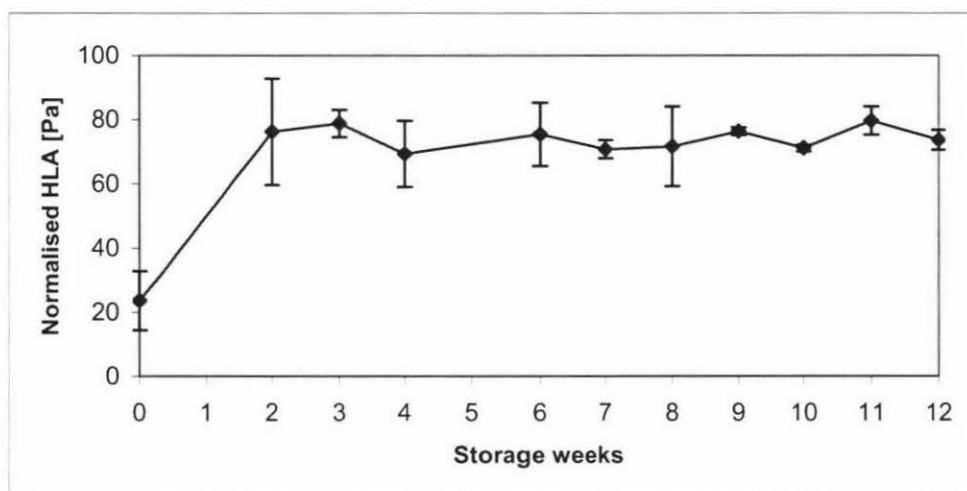


Figure 4.23 Example of the noise (SD) at the measurement points for the normalised HLA of high-shear RSCM stored at 30°C.

During the storage trial, the areas between the up and down curves, called the HLA, increased. Trinh (2006) introduced the use of HLA as a quantitative parameter for studying age thickening of time dependent food products whereas the HLA was only used qualitatively in previous work. This technique is applied here to RSCM for the first time. Figure 4.23 gives an example of the changes in normalised HLA during storage time with an error bar (standard deviation: SD). The error bar indicating the uncertainty in the data was relatively large at the beginning of storage, about 20-40%. This is possibly related to the varying amount of air in samples. As seen in Figure 4.23, in later weeks the noise decreases. This is probably because most of the air has come out from the samples. The plot between the normalised HLA at storage temperatures against storage times is shown in Figure 4.24 (a) for high-shear and (b) for low-shear RSCM. The data points omitted in Figure 4.24 are the high-shear RSCM sample at 40°C week 8 and the low-shear RSCM sample at 30°C week 5 and 50°C week 6 because of the measured flow curves were not smooth. The normalised HLA of RSCM changes in the same pattern as the apparent viscosity changes in Figure 4.19 at all three storage temperatures: 30, 40 and 50°C.

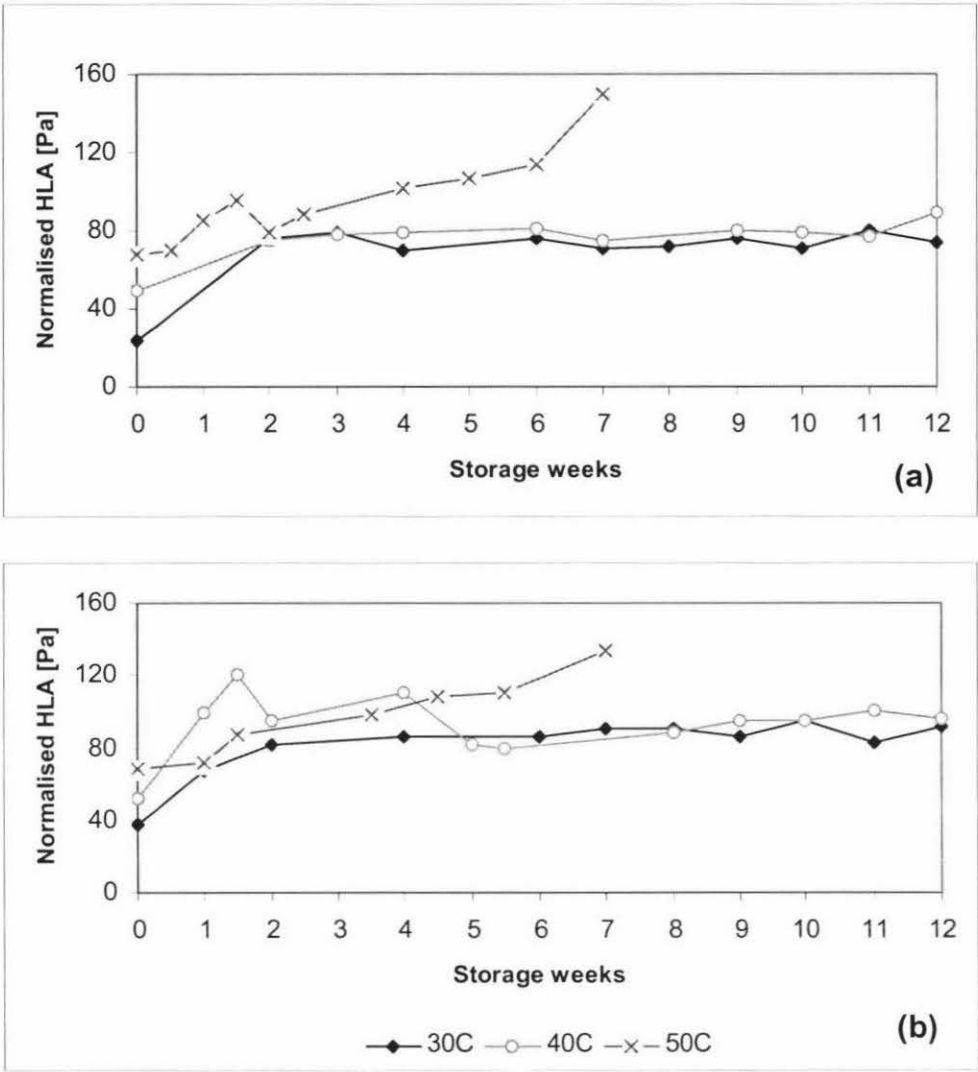


Figure 4.24 Normalised HLA of (a) high-shear and (b) low-shear samples of RSCM stored at 30, 40 and 50°C up to 12 weeks or until it gelled. SD of these points are shown in Appendix 5.

The apparent viscosities at storage temperatures of 30, 40 and 50°C in ST 1 are shown in Figure 4.25. These results, most of which only cover the early period of RSCM rheological behaviour, show the same trend as ST 2 in Figure 4.18. All three curves in ST 1 have higher absolute values than in ST 2, which may be due to the different batches of milk powders used.



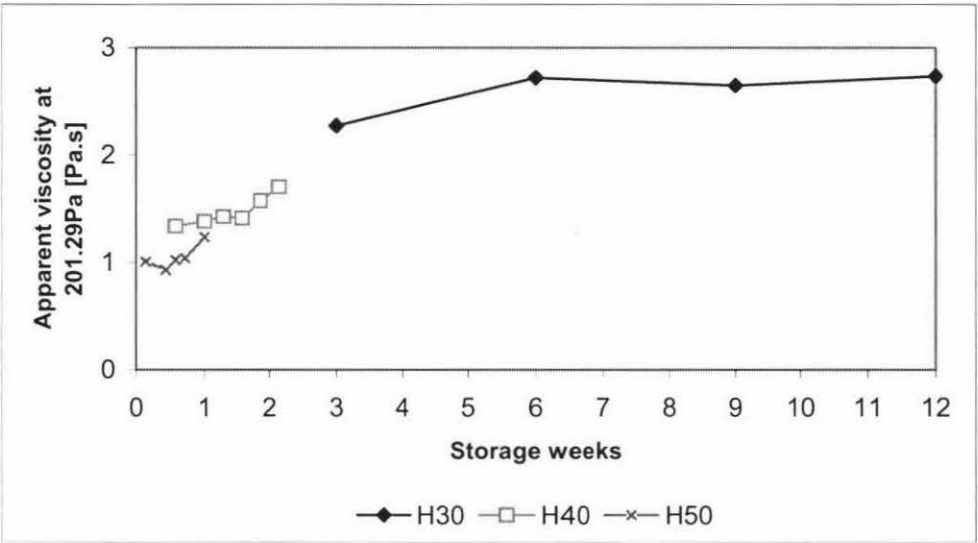


Figure 4.25 Apparent viscosities at 201.29Pa of high-shear RSCM trial 1 at storage temperatures 30, 40 and 50°C.

**(2) Particle Size Distribution (PSD) of RSCM**

The particle size distribution (PSD) of samples of RSCM stored at 30 and 40°C show little changes over time for both high-shear and low-shear RSCM which is compatible with the relative lack of age thickening. An example of a full curve PSD of high-shear RSCM stored at 30°C is shown in Figure 4.26.

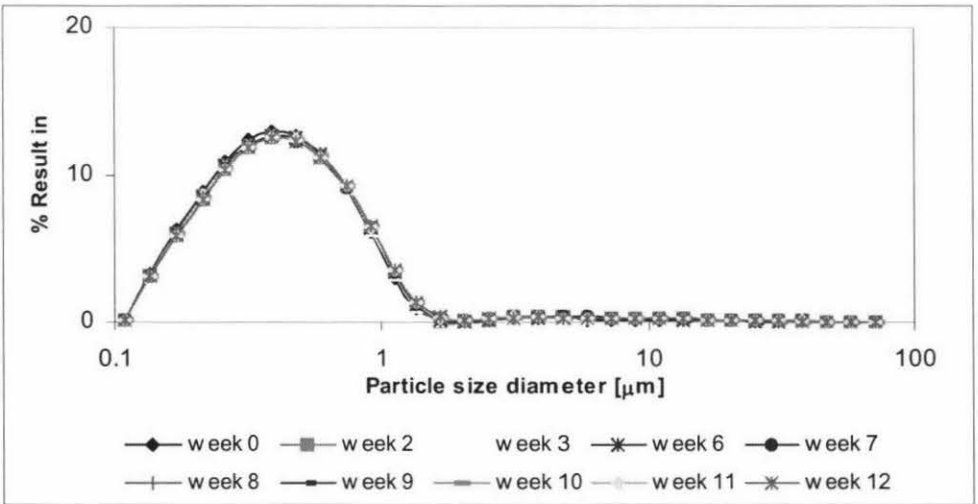


Figure 4.26 Particle size distribution of high-shear RSCM stored at 30°C for 12 weeks.

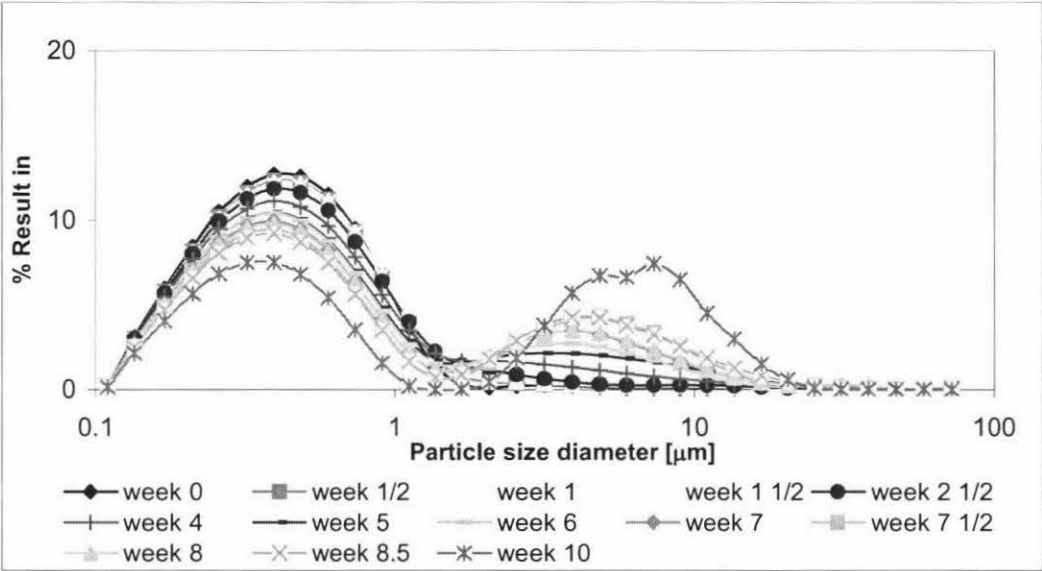


Figure 4.27 Changes of the particle size distribution of high-shear RSCM stored at 50°C for 10 weeks.

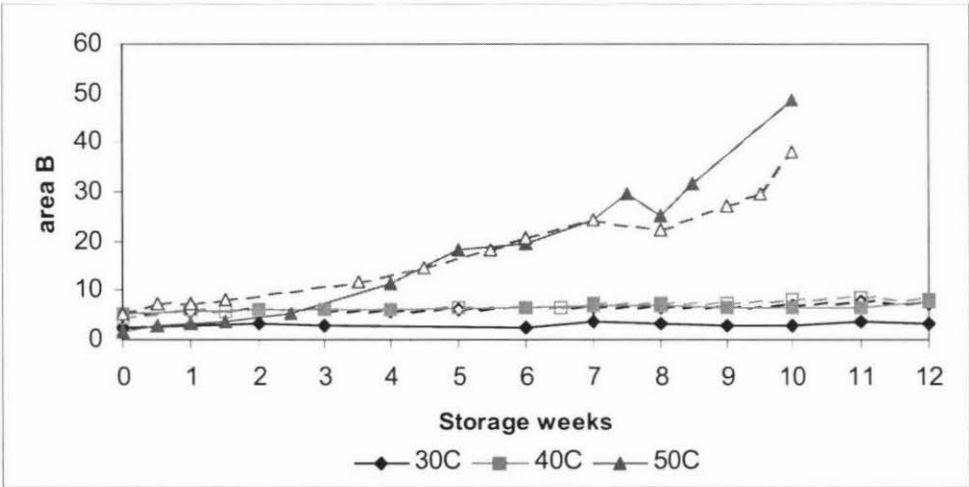


Figure 4.28 Area B (particle sizes larger than 2 μm) of high-shear and low-shear RSCM stored at three temperatures: 30, 40 and 50°C. The full line represents high-shear RSCM and the dashed line represents low-shear RSCM.

On the other hand, the PSD for RSCM stored at 50°C show a steady and then dramatic growth after 4 weeks of particles larger than 2 μm as shown for example in Figure 4.27. We again divided the PSD in to two zones: area A and area B. Figure 4.28 summarises the changes in the B areas of high-shear and low-shear RSCM stored at the three storage temperatures. At 30 and 40°C, there is little change compared to time

zero. But at 50°C, the high-shear and low-shear RSCM, both show a significant and comparable increase in area B, which is reflected in the decrease in area A. Area A is equal to 100 - area B.

This is to be expected since the apparent viscosities at storage temperature 50°C show a continued increase until the sample gelled (Figure 4.18). While the difference in apparent viscosity of the high-shear and low-shear RSCM cannot be distinguished within experimental error, the PSD at zero time of the sample stored at 30°C shows that the peak for low-shear RSCM is further to the right indicating a higher level of aggregation than for the high-shear RSCM. This effect of shearing during recombination is in line with previous work in the research team at Massey University (Trinh *et al.* 2003).

The area B for both high-shear and low-shear samples of RSCM stored at 30 and 40°C for approximately two weeks and at least for 1 week for 50°C. An example is shown for ST 1 in Figure 4.29 but the same holds true for ST 2. This aggregation cannot be used as an explanation for the significant changes in viscosity in the early stage of storage (Figures 4.18 and 4.25) and the rise of air bubbles that were observed visually in the sample is a much more plausible explanation.

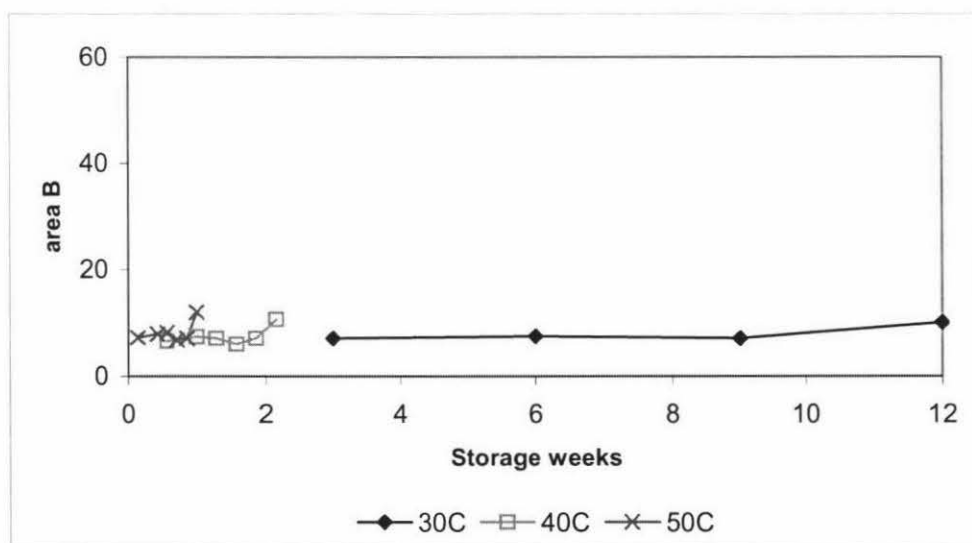


Figure 4.29 Area B (particles larger than 2  $\mu\text{m}$ ) of high-shear RSCM trial 1 stored at three temperatures: 30, 40 and 50°C.

(3) Colour Development

The colour of all the RSCM samples was originally whitish but developed a yellow-brown tint with storage time. This effect was weak at 30°C and became stronger at 40°C. At 50°C a pronounced brown colour developed from week 2 onwards (Figure 4.30). This development was captured in the evolution of brightness (L), red chroma (a) and yellow chroma (b) values shown in Figures 4.31, 4.32 and 4.33 respectively.

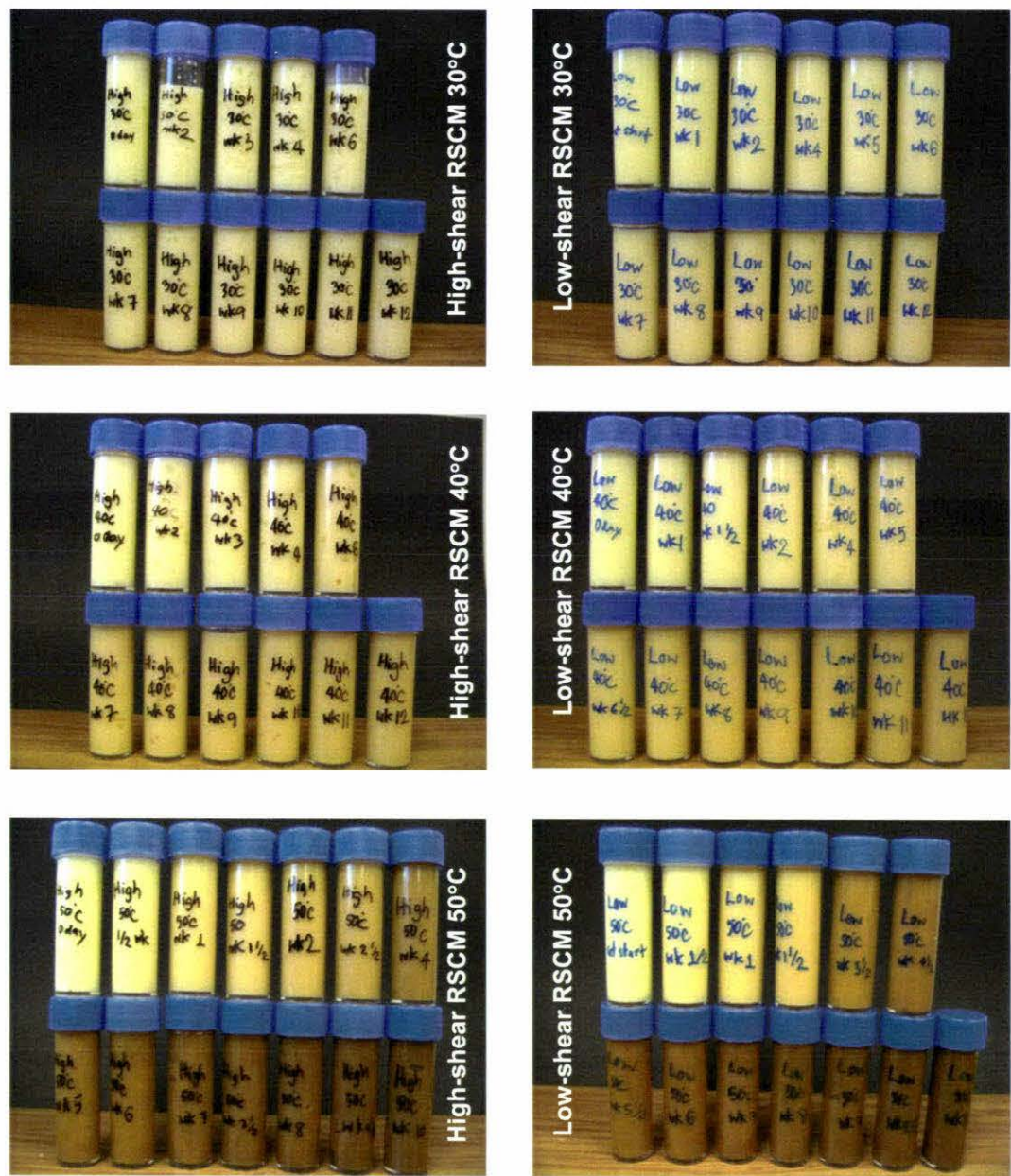


Figure 4.30 Visual appearances of high-shear and low-shear RSCM stored at three temperatures of 30, 40 and 50°C.

The L values of samples stored at 30 and 40°C are very close together but decrease dramatically with storage time at 50°C (Figure 4.31). This corresponds with the trend observed in Figure 4.19 where the changes in apparent viscosity over time are much more dramatic at 50°C. The difference in trends between storage temperatures of 30 and 40°C on the one hand and 50°C on the other hand is also seen in the trends of the a values (Figure 4.32). But the changes in the b values are more complex (Figure 4.33). In particular the b values at 50°C goes to a maximum after 2 weeks before decreasing with time, indicating that the sample goes from a white to a creamy colour in the first 2 or 3 weeks then becomes brown as the red tint increases and the yellow tint decreases. These results are in complete agreement with the photographic evidence in Figure 4.30.

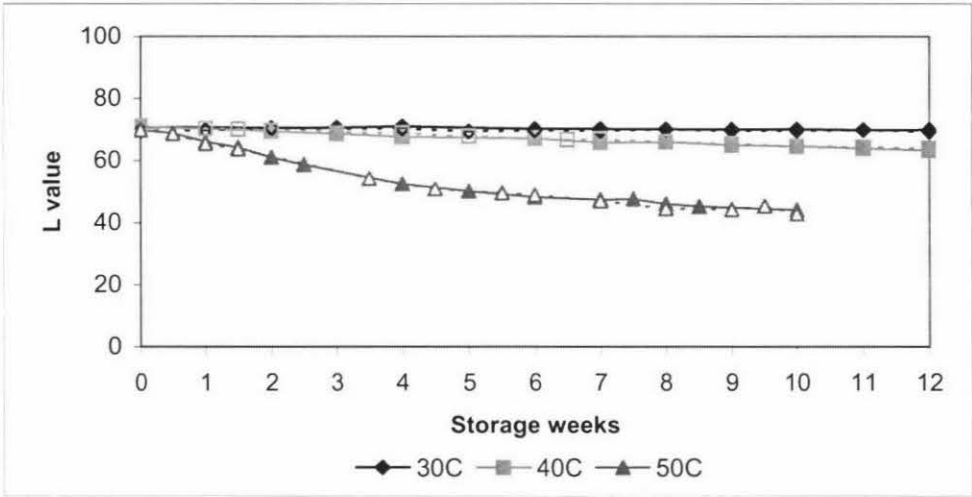


Figure 4.31 Changes of L value (brightness) of high-shear and low-shear RSCM stored at three temperatures: 30, 40 and 50°C. The full line represents high-shear RSCM and the dashed line represents low-shear RSCM. SD of these points are shown in Appendix 5.

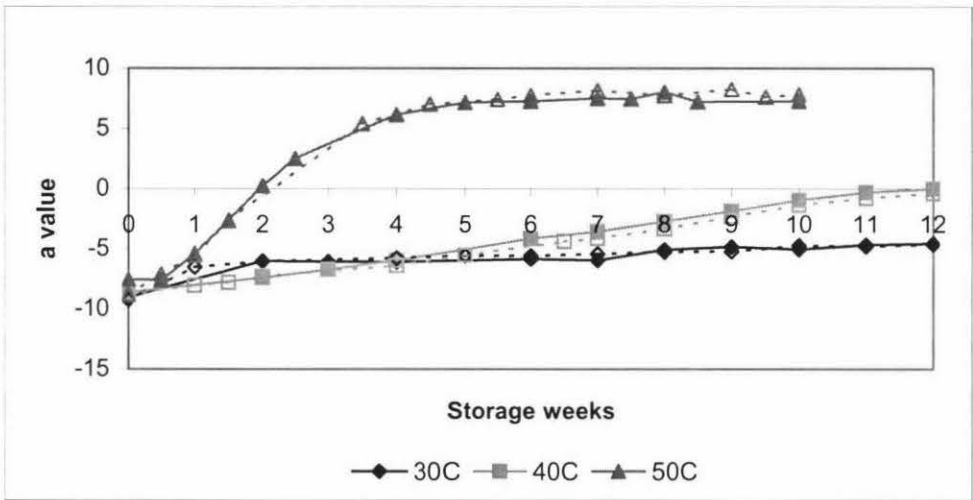


Figure 4.32 Changes of a value (red chroma) of high-shear and low-shear RSCM stored at three temperatures: 30, 40 and 50°C. The full line represents high-shear RSCM and the dashed line represents low-shear RSCM. SD of these points are shown in Appendix 5.

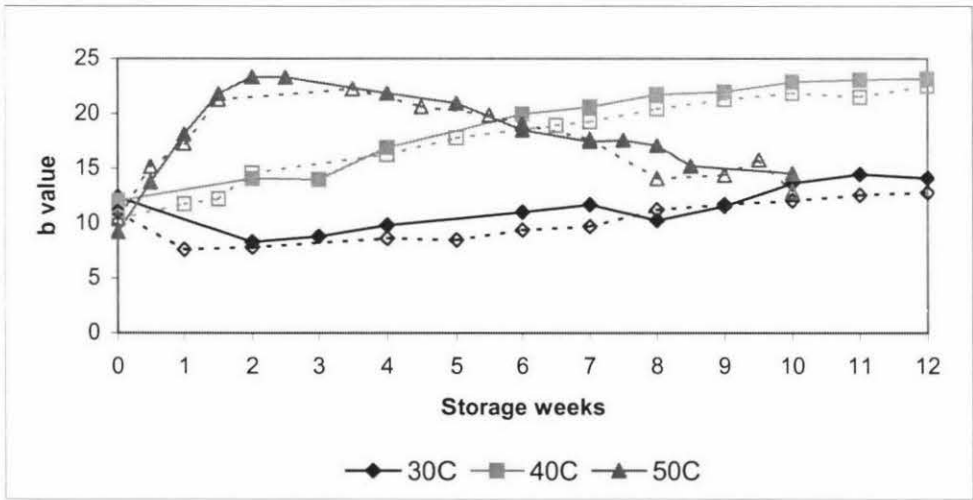


Figure 4.33 Changes of b value (yellow chroma) of high-shear and low-shear RSCM stored at three temperatures: 30, 40 and 50°C. The full line represents high-shear RSCM and the dashed line represents low-shear RSCM. SD of these points are shown in Appendix 5.



The browning of concentrated milk enriched with sugar during storage has been reported by many previous workers (Patel *et al.* 1996; Samel and Muers 1962b and Venkatachalam *et al.* 1993). All authors agreed that it increased with storage temperature. But there were some disagreements about the specific storage temperature where it became unacceptable. Samel and Muers (1962b) tested the rate of age thickening of RSCM at 20, 30, 39, 44 and 55°C because “higher temperatures could not usefully be used because of the excessive caramelisation which occurs”. They recommended storage at 39°C only. Patel *et al.* (1996) measured the level of browning of SCM made with buffalo milk by monitoring absorbance with a reflectometer. They argued that browning followed a zero kinetic model and found that the Arrhenius plot for absorbance could be described by two straight lines with different slopes (activation energies,  $E_a$ ) meeting at the temperature of about 30°C. In this work, the rates of change of both colour and viscosity are dramatically different at 50°C compared to 30 and 40°C.

Samel and Muers (1962b) attributed browning to excessive “caramelisation”. This is not well supported by particle size measurements (Figures 4.26 and 4.27). One would expect that caramelised sucrose would dissolve well in water and therefore the very dilute samples fed to the Mastersizer E would not show the dramatic increase in particle size evidenced in Figure 4.27 if the changes in colour were created by caramelisation of the sucrose. Browning is more likely to involve the Maillard reaction. This is also the view of Patel *et al.* (1996) who followed the Maillard reaction with the production of the HMF or 5-hydroxy-methyl-furfural moiety. Venkatachalam *et al.* (1993) argued that sucrose, being a non-reducing sugar, did not participate in the Maillard reaction. Only samples of concentrated skim milk enriched with lactose showed evidence of browning.

Maillard reactions create relatively strong bonds that cannot be disrupted by the dilution process used in Mastersizer measurements, which explains the particle size increase at 50°C shown in Figure 4.27. Einstein showed that the viscosity of a suspension is a function of the volume fraction of the dispersed phase (e.g Cheng and Schachman 1955). In complex colloidal solutions the apparent volume fraction of the

dispersed phase increases as the particle flocculates (Mills *et al.* 1991) and the viscosity therefore also increases. Thus the increase in viscosity, level of permanent flocculation and browning at 50°C in Figures 4.19, 4.27 and 4.31 may be related to the same reaction.

One of the original aims of the thesis was to define the accelerated storage conditions under which RSCM should be conducted. This study would suggest that samples should not be stored at 50°C because of the deleterious and unrepresentative reactions that occurred at this and higher temperatures. Instead the maximum storage temperature for accelerated storage trials for RSCM should probably be 45°C and possibly lower.

Figures 4.34 and 4.35 show a comparison between the apparent viscosities of SCM produced by Samel and Muers (1962b) with the values for the high-shear (Figure 4.34) and low-shear RSCM (Figure 4.35) produced in this work. Samel and Muers (1962b) labelled these values as “initial viscosity” measured after production and sample stored immediately. They quoted the viscosity at the nominal shear rate of  $4.61\text{ s}^{-1}$ . The MC1 Paar Physica rheometer used in this work has a lower limit of the reliability of approximately 20 rpm and 1.5mNm (Trinh *et al.* 2005). And therefore the viscosities for this work presented in Figures 4.34 and 4.35 were calculated from the parameters of the Herschel-Bulkley model presented in Figures 4.21 and 4.22. In addition, they were all corrected to a reference of 20°C.

Figures 4.34 and 4.35 show clearly that

1. At any particular temperature and time the viscosity of the sample in this work is significantly lower than that of Samel and Muers (1962b).
2. At any particular temperature the rate of age thickening of the sample in this work is much slower than that observed by Samel and Muers (1962b).
3. Age thickening is almost negligible for the sample in this work stored at 30 and 40 °C.
4. Increasing the recirculation shear rate from 900 to  $31,000\text{ s}^{-1}$  does not make a great difference in age thickening of the RSCM in this work.



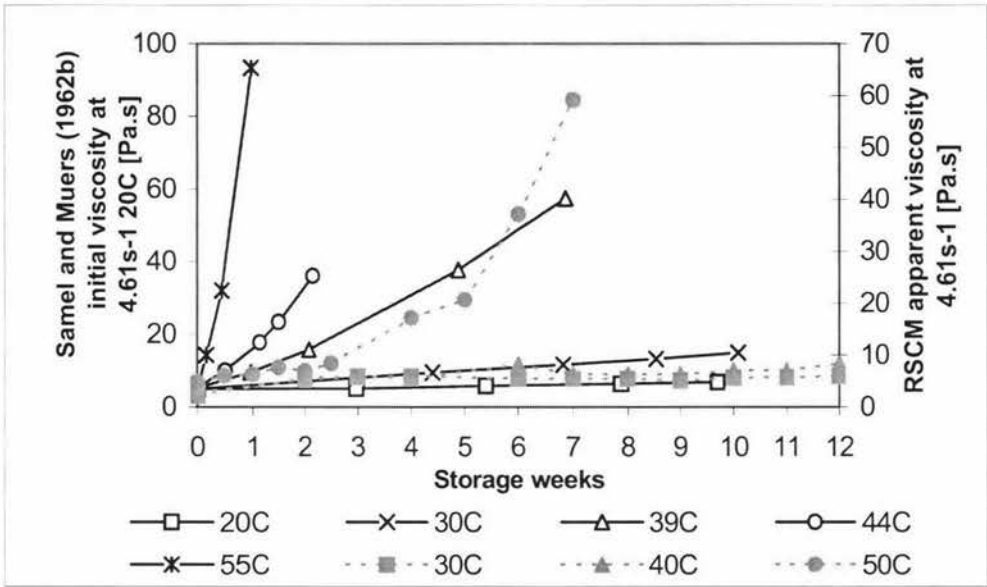


Figure 4.34 Comparison of our high-shear RSCM data converted to 4.61s<sup>-1</sup> at 20°C presented in dashed lines with the initial viscosity of Samel and Muers (1962b) presented in full lines.

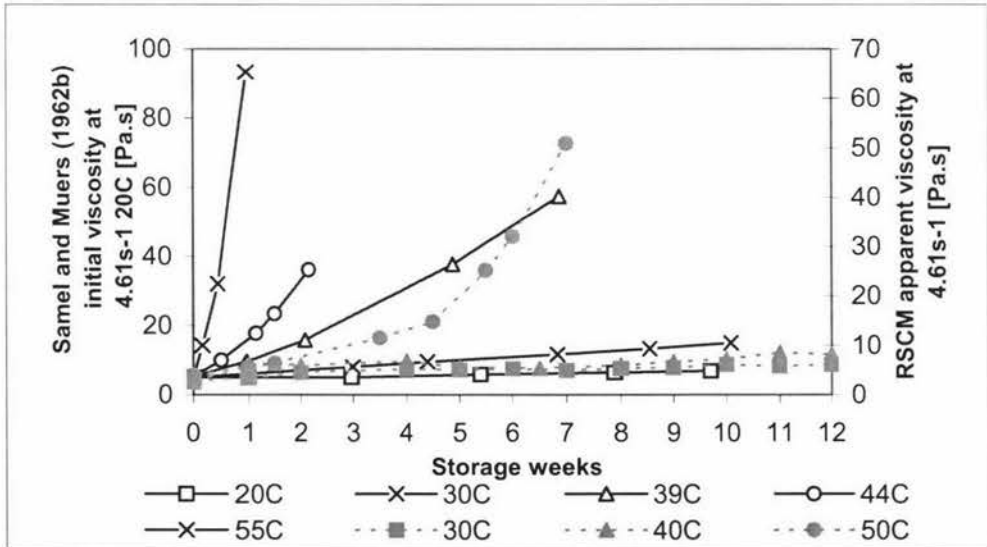


Figure 4.35 Comparison of our low-shear RSCM data converted to 4.61s<sup>-1</sup> at 20°C presented in dashed lines with the initial viscosity of Samel and Muers (1962b) presented in full lines.

## CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

This study of Reconstituted Concentrated Milk (RCM) showed that both the viscosity and the HLA increased with storage time and the trend of the two rheological properties were similar. When the Herschel Bulkley model was fitted to the flow curves, its parameters ( $\tau_y \uparrow$ ,  $K \uparrow$ ,  $n \downarrow$ ) varied also with time. Age thickening was accelerated by increasing storage temperature between 35 and 75°C.

Two things were discovered during this study of RCM age thickening; the particle size, as measured by the Malvern Mastersizer, only increased during storage at high temperature for example 75°C. There was a small, almost negligible change of particle size with storage time at 35°C. One may conclude that the flocs that were formed at 35°C could be completely disrupted by the dilution process necessary for measurement in the Malvern Mastersizer and only the bonds formed at high temperature (75°C) were strong enough to withstand dilution.

It was found that reshearing completely destroyed the bonds in the flocs. This was shown by the fact that the apparent viscosities of the resheared samples came back to the level of the freshly made RCM and the particle size distributions did not change throughout the storage and reshearing process. Moreover, the resheared samples no longer exhibited age thickening upon further storage. This interesting phenomenon can be used to advantage in the manufacture of Recombined Sweetened Condensed Milk (RSCM).

An interesting observation was made during the development of the RSCM process. RSCM made by preparing the sugar solution first and then adding milk powder gave a much higher viscosity than the traditional process of adding sugar to the milk concentrate. This observation appeared to be new, the writer has found no reference in the literature discussing the effect of order of addition of sugar and milk protein on the viscosity of RSCM produced.

Recombined Sweetened Condensed Milk (RSCM) was produced with the reshearing process at two shear rates of  $900\text{s}^{-1}$  (low level) and  $31,000\text{s}^{-1}$  (high level) then stored at three storage temperatures at 30, 40 and  $50^{\circ}\text{C}$ . At all three temperatures the rate of age thickening of RSCM produced at both shear rates was found to be much lower than those reported in the classic paper of Samel and Muers (1962b). In fact, the RSCM barely aged at all over the 12-week storage period when stored at 30 and  $40^{\circ}\text{C}$  while RSCM samples stored at  $50^{\circ}\text{C}$  gelled by the 7th week. It would appear that the application of shear ( $900$  and  $31,000\text{s}^{-1}$ ) during recombination of the WMP for the production of the RSCM samples had succeeded in removing the propensity of the RSCM to age thickening. It was surprising that the change in shear rate from  $900$  to  $31,000\text{s}^{-1}$  did not make a big difference. One explanation may be the duration of shear because the breakdown of the structure of a time dependent fluid is a function of both shear rate and duration of shear. In this case, shear was applied for approximately 3 hours whilst the WMP was reconstituted.

Similarly, the particle sizes of RSCM samples stored at 30 and  $40^{\circ}\text{C}$  showed virtually no change with storage time but the particle size of samples stored at  $50^{\circ}\text{C}$  increased with storage time until they gelled.

Browning was observed to increase with storage temperature and time and was particularly severe in the  $50^{\circ}\text{C}$  samples.

### Recommendations

- The process modification of adding milk powder to a sugar solution should be applied during the period of the milk season when RSCM cannot be produced because the resulting viscosity is too low. This experiment may yield a simple method for dealing with seasonal variation of RSCM viscosity.

- This study should be repeated with the production of a control sample from the same batch of milk powder to show that the loss of age-thickening is due to the process design, not the powder properties.
- Obviously the accelerated storage trial is only valid if the reactions occur during storage reflecting the real commercial conditions. Since brown RSCM is obviously unacceptable to consumers, the temperature for accelerated storage trials should not exceed 40°C. It also suggests that RSCM should be shipped in chilled containers (<25°C) especially if it is destined for the tropics.

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**ABBREVIATIONS**

|           |                                       |
|-----------|---------------------------------------|
| ADPB      | Australia Dairy Produce Board         |
| AMF       | Anhydrous Milk Fat                    |
| CIP       | Clean In Place                        |
| CM        | Concentrated Milk                     |
| EM        | Evaporated Milk                       |
| EU        | European Union                        |
| FAO       | Food and Agriculture Organisation     |
| FFMR      | Fresh Frozen Milkfat for Recombining  |
| GMS       | Glycerol Monostearate                 |
| GMP       | Good Manufacturing Practice           |
| GP        | General Purpose                       |
| HLA       | Hysteresis Loop Area                  |
| MH-SMP    | Medium Heat – Skim Milk Powder        |
| MSNF      | Milk Solids Non Fat                   |
| PHE       | Plate Heat Exchanger                  |
| PSD       | Particle Size Distribution            |
| PV        | Peroxide Value                        |
| RCM       | Reconstituted Concentrated Milk       |
| RCSM      | Reconstituted Concentrated Skim Milk  |
| RCWM      | Reconstituted Concentrated Whole Milk |
| RO water  | Reversed Osmosis water                |
| RSCM      | Recombined Sweetened Condensed Milk   |
| SCM       | Sweetened Condensed Milk              |
| SMP       | Skim Milk Powder                      |
| ST        | Storage Trial                         |
| TS        | Total Solids                          |
| UHT       | Ultra Heat Treatment                  |
| UHTST     | Ultra High Temperature Short Time     |
| US or USA | United States of America              |



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|      |                             |
|------|-----------------------------|
| WHO  | World Health Organisation   |
| WMP  | Whole Milk Powder           |
| WPNI | Whey Protein Nitrogen Index |

## NOMENCLATURE

|                       |  |
|-----------------------|--|
| $a_w$                 | Water Activity   |
| $C_{s/w}$             | Sugar index or Sugar/water Concentration or Sugar Ration |
| $K$                   | Consistency index [Pa.s <sup>n</sup> ]                   |
| $n$                   | Flow behaviour index [Dimensionless]                     |
| $n$                   | Spindle speed [rpm]                                      |
| $R_c$                 | Cup radius [m]   |
| $R_b$                 | Bob radius [m]   |
| $S$                   | Percentage of sucrose content in product                 |
| $T$                   | Absolute temperature [Kelvin]                            |
| $W$                   | Percentage of moisture content                           |
| $\mu$                 | Viscosity [Pa.s]   |
| $\mu_B$               | Plastic viscosity [Pa.s]                                 |
| $\dot{\gamma}$        | Shear rate [s <sup>-1</sup> ]                            |
| $\dot{\gamma}_{corr}$ | Corrected shear rate [s <sup>-1</sup> ]                  |
| $\tau$                | Shear stress [Pa]  |
| $\tau_y$              | Yield stress [Pa]  |
| $\Omega$              | Angular velocity [rad/s]                                 |

## APPENDIX 1

### Calculation of ingredient used for RSCM formulation

#### Nomenclature

Milk powder composition (basis 100g WMP)

- A Protein weight in WMP, g
- B Fat weight in WMP, g
- C Moisture weight in WMP, g
- D MSNF weight in WMP, g =  $100 - B - C$

- W Weight FFMR needed per 100g RSCM
- X Weight WMP needed per 100g RSCM
- Y Weight water needed per 100g RSCM
- Z Weight RO sugar needed per 100g RSCM

#### RSCM composition adapted from US standards (Early 1998)

RSCM 100g consists of

|          |        |                            |
|----------|--------|----------------------------|
| MSNF     | 20 g   |                            |
| Fat      | 8 g    |                            |
| Sugar    | 45.4 g | (based on 63% sugar ratio) |
| Moisture | 26.6 g |                            |
| %TS      | 73.4   |                            |

Overall balance (basis 100g RSCM)

$$100 = X + Y + Z + W$$

Sugar balance

$$Z = 45.4 \text{ g}$$

MSNF balance

$$20 = \frac{XD}{100} \quad \text{then } X \text{ is known by this step}$$

Fat balance

$$8 = \frac{XB}{100} + W$$

Water balance (Sugar and FFMR are assumed to contain no water.)

$$26.6 = \frac{XC}{100} + Y$$

APPENDIX 2

Summary of the RCM and RSCM experimental runs

Table A2.1 Summary of RCM experimental runs

| Products | Purposes            | Runs | Details |                           |                      |
|----------|---------------------|------|---------|---------------------------|----------------------|
|          |                     |      | % TS    | Recirculation shear rates | Storage temperatures |
| RCSM     | Age thickening test | A1   | 45      | 40,000s <sup>-1</sup>     | 50°C                 |
|          |                     | A2   | 45      | 40,000s <sup>-1</sup>     | 75°C                 |
| RCWM     | Reshearing test     | B1   | 50      | 40,000s <sup>-1</sup>     | 35°C                 |
|          |                     | B2*  | 50      | 40,000s <sup>-1</sup>     | 35°C                 |

\*Run B2 is a replicate of run B1

Table A2.2 Summary of RSCM experimental runs

| Products | Purposes                              | Runs                       | Details                       |                             |                      |                          |                |
|----------|---------------------------------------|----------------------------|-------------------------------|-----------------------------|----------------------|--------------------------|----------------|
|          |                                       |                            | Recombination<br>temperatures | Recirculation<br>shear rate | Homoge-<br>nisation  | Further<br>recirculation | Pasteurisation |
| RSCM     | Familiarisation<br>of RSCM<br>process | C1*                        | 35°C                          | 31,000s <sup>-1</sup>       | 35bar                | -                        | -              |
|          |                                       | C2**                       | 35°C                          | 31,000s <sup>-1</sup>       | 35bar                | -                        | 85°C/ 1min     |
|          |                                       | C3**                       | 35°C                          | 31,000s <sup>-1</sup>       | 35bar                | 30min                    | 75°C/ 15sec    |
|          |                                       | C4*                        | 55°C                          | 31,000s <sup>-1</sup>       | 35bar                | 30min                    | 75°C/ 15sec    |
|          | Storage trial 1                       | D1<br>D2<br>D3<br>D4<br>D5 | Recirculation shear rates     |                             | Storage temperatures |                          | Storage times  |
|          |                                       |                            | 31,000s <sup>-1</sup>         |                             | }                    | 30°C                     | 12 weeks       |
|          |                                       |                            | 31,000s <sup>-1</sup>         |                             |                      | 40°C                     | 14 days        |
|          |                                       |                            | 31,000s <sup>-1</sup>         |                             |                      | 50°C                     | 7 days         |
|          |                                       |                            | 31,000s <sup>-1</sup>         |                             |                      |                          |                |
|          |                                       |                            | 900s <sup>-1</sup>            |                             | 50°C                 | 7 days                   |                |
|          | Storage trial 2                       | E1                         | 31,000s <sup>-1</sup>         |                             | 30°C                 |                          | 12 weeks       |
|          |                                       | E2                         | 31,000s <sup>-1</sup>         |                             | 40°C                 |                          | 12 weeks       |
|          |                                       | E3                         | 31,000s <sup>-1</sup>         |                             | 50°C                 |                          | 12 weeks       |
|          |                                       | E4                         | 900s <sup>-1</sup>            |                             | 30°C                 |                          | 12 weeks       |
|          |                                       | E5                         | 900s <sup>-1</sup>            |                             | 40°C                 |                          | 12 weeks       |
|          |                                       | E6                         | 900s <sup>-1</sup>            |                             | 50°C                 |                          | 12 weeks       |

\* Milk powder then sugar added.  
\*\* Sugar solution then milk powder added.

## APPENDIX 3

### Calculation of non-Newtonian correction

The shear stress reported by Rheosolve is exact and does not need modifications.

The shear rate,  $\dot{\gamma}$  is calculated in Rheosolve by multiplying the rotational speed by a shear rate factor unique to each spindle. This method is in fact only accurate for Newtonian fluids. An extra multiplier, called here the non-Newtonian correction must be incorporated to give the true shear rate at the bob surface (Trinh 2006). The simplified method for calculation of the shear rate at the surface of a cylindrical spindle (Steffe 1996) is given by Equation A3.1

$$\dot{\gamma}_{\text{corr}} = \frac{\Omega}{\ln \varepsilon} \left( 1 + \ln \varepsilon \times \frac{d(\ln \Omega)}{d(\ln \tau)} \right) \quad (\text{A3.1})$$

or

$$\dot{\gamma}_{\text{corr}} = \frac{\Omega}{\ln \varepsilon} (1 + m \ln \varepsilon) \quad (\text{A3.2})$$

under the condition  $m \ln \varepsilon < 0.2$

where  $\dot{\gamma}_{\text{corr}}$  is the corrected shear rate [ $\text{s}^{-1}$ ],

$\Omega$  is the angular velocity [ $\text{rad/s}$ ],

$\varepsilon = \frac{R_c}{R_b}$  with  $R_c$  is the cup radius and  $R_b$  is the bob radius [m],

and  $m = \frac{d(\ln \Omega)}{d(\ln \tau)} = \frac{d(\log \Omega)}{d(\log \tau)}$

The angular velocity ( $\Omega$ ) is calculated from the spindle speed (n) [rpm]

$$\begin{aligned} 1 \text{ rpm} &= \text{revolution per minute} \\ &= 2\pi \text{ rad per minute} \\ &= \frac{2\pi}{60} \text{ rad per second} \end{aligned}$$

Sample calculation: data from the third replicate of the high shear RSCM ST2 sample stored at 50°C for 6 weeks measured viscosities using spindle Z3. The radius of this cup is 0.0136m and bob is 0.0125m. Then  $\epsilon$  is equal 1.0848 and  $\ln \epsilon$  is equal 0.0814.

Table A3.1 Data from the rheometer

| Data point | n [rpm] | $\tau$ [Pa] | $\dot{\gamma}$ [ $\text{s}^{-1}$ ] | $\mu$ [Pa.s] |
|------------|---------|-------------|------------------------------------|--------------|
| 125        | 107.54  | 201.29      | 138.83                             | 1.45         |
| 126        | 112.53  | 206         | 145.28                             | 1.42         |

Data from Table A3.1 are manipulated to calculate the m value by calculating  $\Omega$  and taking natural logarithm of  $\Omega$  and  $\tau$  shown in Table A3.2.

Table A3.2 Manipulated data

| Data point | $\Omega = n \times \frac{2\pi}{60}$ | $\ln \Omega$ | $\ln \tau$ | m    |
|------------|-------------------------------------|--------------|------------|------|
| 125        | 11.26                               | 2.42         | 5.30       | 1.96 |
| 126        | 11.78                               | 2.47         | 5.33       |      |

For the data point 125,  $m \ln \epsilon = 1.96 \times 0.0814 = 0.16$

$$\dot{\gamma}_{\text{corr}} = \frac{11.26}{0.0814} (1 + 0.16) = 160.40 \text{ s}^{-1}$$

The true apparent viscosity is the ratio of the shear stress and the corrected shear rate.

$$\text{The true apparent viscosity} = \frac{201.29}{160.40} = 1.25 \text{ Pa.s}$$

## APPENDIX 4

### Calculation of apparent viscosity with temperature correction along storage time

During storage trials, apparent viscosities of samples stored at different temperatures can be compared only when they are converted to the same temperature basis. Equation A4.1 (Rao 1999) is used for this purpose.

$$\ln \mu = \frac{B}{T} + C \quad (\text{A4.1})$$

Where  $\mu$  is the apparent viscosity at a reference shear stress indicated in chapter 3 [Pa s];  $T$  is the absolute temperature [Kelvin = 273+°C];  $B$  and  $C$  are parameters determined from experimental data.

### Sample calculation

This calculation is based on samples of high shear RSCM ST 2 stored at different temperatures of 30, 40 and 50°C straight after the production (time zero).

#### Calculation of B and C parameters

$B$  and  $C$  parameters come from the curve between  $\ln \mu$  at time zero and  $\frac{1}{T}$  where  $B$  is a slope and  $C$  is the intercept point of Y axis.

Table A4.1 shows data of the high shear RSCM ST2 sample stored at 30, 40 and 50°C at time zero. These values are plotted in Figure A4.1 where the  $B$  parameter is found to be 4156.8 and the  $C$  parameter -13.482.



Table A4.1. Data of the high shear RSCM ST2 sample stored at 30, 40 and 50°C at time zero.

| Storage temperature [°C] | T [Kelvin] | $\frac{1}{T}$ | Apparent viscosity at time zero [μ, Pa.s] | ln μ    |
|--------------------------|------------|---------------|---|---------|
| 30                       | 303        | 0.0033        | 1.2748                                    | 0.2428  |
| 40                       | 313        | 0.0032        | 0.8081                                    | -0.2131 |
| 50                       | 323        | 0.0031        | 0.5454                                    | -0.6063 |

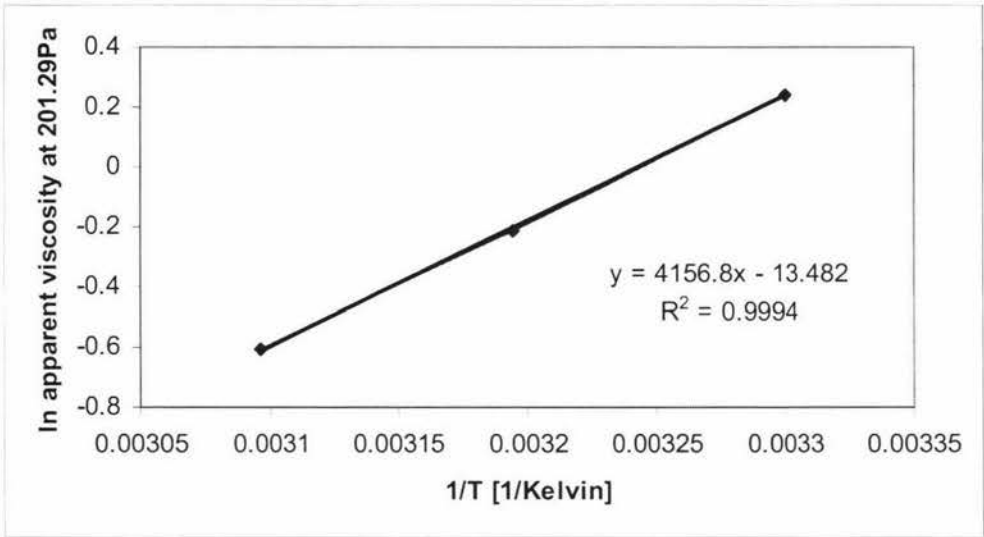


Figure A4.1 Plot of ln μ at time zero and  $\frac{1}{T}$  to obtain B and C value

Calculation of apparent viscosity at reference temperature along storage time

For time dependent materials, the parameters B and C may actually vary with storage time. We assume that B is constant for a given product but that C changes with storage time. In other words, it is assumed that the reaction kinetics encapsulated in the factor B are uniquely a function of the product make up but that the actual value of viscosity will vary with time. The parameter C for each storage trial temperature and time is calculated with Equation A4.2 from the measured apparent viscosity and the B value calculated from data at time zero.

$$C = \ln \mu - \left( B \times \frac{1}{T} \right) \quad (\text{A4.2})$$

For example: C parameter value calculates from the first replicate sample of high shear RSCM ST2 stored at 30°C for 6 weeks which has the apparent viscosity of 2 Pa.s:

$$C = \ln(2) - \left( 4156.8 \times \frac{1}{273 + 30} \right) = -13.03$$

Then the apparent viscosity of this sample at 20°C is calculated using Equation A4.3.

$$\mu = e^{\left( \frac{B}{T} + C \right)} \quad (\text{A4.3})$$

$$\begin{aligned} \mu &= e^{\left( \frac{4156.8}{273 + 20} - 13.03 \right)} \\ &= 3.18 \text{ Pa.s} \end{aligned}$$

APPENDIX 5

Standard Deviation (SD) of measured parameters in RSCM storage trial 2 (ST2)

*SD of apparent viscosities over 12 weeks storage*

The RSCM apparent viscosities were measured at a shear stress of 201.29 Pa. Each SD was calculated on the basis of triplicate measurement.

Table A5.1 SD of apparent viscosities of RSCM ST 2 stored at 30°C

| High shear   |      | Low shear    |      |
|--------------|------|--------------|------|
| Storage week | SD   | Storage week | SD   |
| 0            | 0.18 | 0            | 0.08 |
| 2            | 0.30 | 1            | 0.06 |
| 3            | 0.11 | 2            | 0.14 |
| 4            | 0.08 | 4            | 0.04 |
| 6            | 0.06 | 5            | 0.10 |
| 7            | 0.01 | 6            | 0.04 |
| 8            | 0.09 | 7            | 0.09 |
| 9            | 0.03 | 8            | 0.01 |
| 10           | 0.03 | 9            | 0.01 |
| 11           | 0.03 | 10           | 0.04 |
| 12           | 0.10 | 11           | 0.09 |
|              |      | 12           | 0.07 |

Table A5.2 SD of apparent viscosities of RSCM ST 2 stored at 40°C

| High shear   |      | Low shear    |      |
|--------------|------|--------------|------|
| Storage week | SD   | Storage week | SD   |
| 0            | 0.08 | 0            | 0.08 |
| 2            | 0.11 | 1            | 0.06 |
| 3            | 0.01 | 1.5          | 0.12 |
| 4            | 0.04 | 2            | 0.06 |
| 6            | 0.12 | 4            | 0.08 |
| 7            | 0.02 | 5            | 0.01 |
| 8            | 0.06 | 6.5          | 0.03 |
| 9            | 0.05 | 7*           | -    |
| 10           | 0.01 | 8            | 0.02 |
| 11           | 0.04 | 9            | 0.06 |
| 12           | 0.04 | 10           | 0.04 |
|              |      | 11           | 0.05 |
|              |      | 12           | 0.04 |

\* Measurement error, this data point was omitted.

Table A5.3 SD of apparent viscosities of RSCM ST 2 stored at 50°C

| High shear   |      | Low shear    |      |
|--------------|------|--------------|------|
| Storage week | SD   | Storage week | SD   |
| 0            | 0.13 | 0            | 0.08 |
| 0.5          | 0.10 | 0.5*         | -    |
| 1            | 0.03 | 1            | 0.05 |
| 1.5          | 0.21 | 1.5          | 0.08 |
| 2            | 0.03 | 3.5          | 0.07 |
| 2.5          | 0.08 | 4.5          | 0.11 |
| 4            | 0.04 | 5.5          | 0.07 |
| 5            | 0.05 | 6            | 0.07 |
| 6            | 0.07 | 7            | 0.00 |
| 7            | 0.10 |              |      |

\* Measurement error, this data point was omitted.

*SD of HLA over 12 weeks storage*

Each SD was calculated on the basis of triplicate measurement.

Table A5.4 SD of HLA of RSCM ST 2 stored at 30°C

| High shear   |       | Low shear    |      |
|--------------|-------|--------------|------|
| Storage week | SD    | Storage week | SD   |
| 0            | 9.16  | 0            | 3.05 |
| 2            | 16.54 | 1            | 0.58 |
| 3            | 4.25  | 2            | 3.14 |
| 4            | 10.27 | 4            | 4.18 |
| 6            | 9.82  | 5**          | -    |
| 7            | 2.82  | 6            | 5.08 |
| 8            | 12.38 | 7            | 5.07 |
| 9            | 1.21  | 8            | 5.83 |
| 10           | 1.01  | 9            | 1.11 |
| 11           | 4.41  | 10           | 2.24 |
| 12           | 3.07  | 11           | 1.38 |
|              |       | 12           | 7.53 |

\*\* This data point was omitted because the flow curve was not smooth.

Table A5.5 SD of HLA of RSCM ST 2 stored at 40°C

| High shear   |       | Low shear    |       |
|--------------|-------|--------------|-------|
| Storage week | SD    | Storage week | SD    |
| 0            | 13.60 | 0            | 12.00 |
| 2            | 17.03 | 1            | 6.58  |
| 3            | 5.60  | 1.5          | 13.50 |
| 4            | 3.73  | 2            | 1.05  |
| 6            | 1.23  | 4            | 6.10  |
| 7            | 12.77 | 5            | 3.97  |
| 8**          | -     | 6.5          | 6.69  |
| 9            | 6.49  | 7*           | -     |
| 10           | 3.40  | 8            | 3.19  |
| 11           | 2.82  | 9            | 7.15  |
| 12           | 3.49  | 10           | 6.98  |
|              |       | 11           | 1.98  |
|              |       | 12           | 1.81  |

\*\* This data point was omitted because the flow curve was not smooth.

\* Measurement error, this data point was omitted.

Table A5.6 SD of HLA of RSCM ST 2 stored at 50°C

| High shear   |       | Low shear    |       |
|--------------|-------|--------------|-------|
| Storage week | SD    | Storage week | SD    |
| 0            | 26.87 | 0            | 5.07  |
| 0.5          | 25.48 | 0.5*         | -     |
| 1            | 6.47  | 1            | 9.73  |
| 1.5          | 38.13 | 1.5          | 13.36 |
| 2            | 13.81 | 3.5          | 15.40 |
| 2.5          | 13.17 | 4.5          | 14.35 |
| 4            | 6.03  | 5.5          | 2.78  |
| 5            | 18.18 | 6**          | -     |
| 6            | 12.95 | 7            | 17.89 |
| 7            | 3.65  |              |       |

\* Measurement error, this data point was omitted.

\*\* This data point was omitted because the flow curve was not smooth.

*SD of L, a and b values represented the changes of RSCM colour over 12 weeks storage*

Each SD was calculated from measurement at 3 random locations and each location was measured in triplicates.

Table A5.7 SD of colour parameters (L, a and b) of RSCM ST 2 stored at 30°C

| High shear   |      |      |      |
|--------------|------|------|------|
| Storage week | SD   |      |      |
|              | L    | a    | b    |
| 0            | 0.63 | 0.21 | 0.64 |
| 2            | 0.29 | 0.37 | 0.96 |
| 3            | 0.50 | 0.39 | 1.09 |
| 4            | 0.57 | 0.21 | 0.63 |
| 6            | 0.39 | 0.41 | 1.02 |
| 7            | 0.50 | 0.30 | 0.76 |
| 8            | 0.26 | 0.27 | 0.92 |
| 9            | 0.27 | 0.27 | 1.47 |
| 10           | 0.44 | 0.30 | 0.89 |
| 11           | 0.32 | 0.24 | 0.75 |
| 12           | 0.32 | 0.32 | 1.06 |

| Low shear    |      |      |      |
|--------------|------|------|------|
| Storage week | SD   |      |      |
|              | L    | a    | b    |
| 0            | 0.33 | 0.12 | 0.40 |
| 1            | 0.53 | 0.46 | 1.18 |
| 2            | 0.45 | 0.51 | 1.16 |
| 4            | 0.46 | 0.29 | 0.89 |
| 5            | 0.34 | 0.32 | 0.68 |
| 6            | 0.21 | 0.33 | 1.27 |
| 7            | 0.27 | 0.31 | 1.36 |
| 8            | 0.57 | 0.44 | 1.12 |
| 9            | 0.37 | 0.44 | 1.33 |
| 10           | 0.28 | 0.29 | 0.75 |
| 11           | 0.39 | 0.22 | 0.75 |
| 12           | 0.37 | 0.22 | 1.34 |

Table A5.8 SD of colour parameters (L, a and b) of RSCM ST 2 stored at 40°C

| High shear   |      |      |      |
|--------------|------|------|------|
| Storage week | SD   |      |      |
|              | L    | a    | b    |
| 0            | 0.74 | 0.22 | 0.80 |
| 2            | 0.37 | 0.11 | 0.62 |
| 3            | 0.68 | 0.07 | 0.76 |
| 4            | 0.62 | 0.15 | 0.97 |
| 6            | 0.37 | 0.28 | 0.64 |
| 7            | 0.34 | 0.31 | 0.50 |
| 8            | 0.29 | 0.21 | 0.49 |
| 9            | 0.16 | 0.38 | 0.36 |
| 10           | 0.33 | 0.28 | 0.29 |
| 11           | 0.37 | 0.25 | 0.42 |
| 12           | 0.23 | 0.68 | 0.49 |

| Low shear    |      |      |      |
|--------------|------|------|------|
| Storage week | SD   |      |      |
|              | L    | a    | b    |
| 0            | 0.69 | 0.18 | 0.74 |
| 1            | 0.44 | 0.14 | 0.59 |
| 1.5          | 0.61 | 0.15 | 0.75 |
| 2            | 0.82 | 0.13 | 1.12 |
| 4            | 0.48 | 0.12 | 0.51 |
| 5            | 0.36 | 0.40 | 0.36 |
| 6.5          | 0.21 | 0.19 | 0.55 |
| 7            | 0.21 | 0.24 | 0.45 |
| 8            | 0.58 | 0.36 | 0.44 |
| 9            | 0.37 | 0.30 | 0.28 |
| 10           | 0.34 | 0.26 | 0.68 |
| 11           | 0.35 | 0.52 | 0.53 |
| 12           | 0.29 | 0.32 | 0.38 |



Table A5.9 SD of colour parameters (L, a and b) of RSCM ST 2 stored at 50°C

| Storage week | High shear |      |      |
|--------------|------------|------|------|
|              | SD         |      |      |
|              | L          | a    | b    |
| 0            | 0.36       | 0.20 | 0.60 |
| 0.5          | 0.78       | 0.12 | 1.03 |
| 1            | 0.23       | 0.30 | 0.45 |
| 1.5          | 0.41       | 0.25 | 0.27 |
| 2            | 0.49       | 0.42 | 0.27 |
| 2.5          | 0.43       | 0.31 | 0.35 |
| 4            | 0.36       | 0.26 | 0.54 |
| 5            | 0.44       | 0.36 | 0.84 |
| 6            | 0.50       | 0.28 | 0.43 |
| 7            | 0.58       | 0.19 | 0.75 |
| 7.5          | 0.30       | 0.20 | 0.52 |
| 8            | 0.59       | 0.49 | 0.75 |
| 8.5          | 0.60       | 0.31 | 0.87 |
| 10           | 0.20       | 0.41 | 0.35 |

| Storage week | Low shear |      |      |
|--------------|-----------|------|------|
|              | SD        |      |      |
|              | L         | a    | b    |
| 0            | 0.55      | 0.20 | 0.64 |
| 0.5          | 0.46      | 0.17 | 0.56 |
| 1            | 0.37      | 0.14 | 0.44 |
| 1.5          | 0.24      | 0.40 | 0.37 |
| 3.5          | 0.47      | 0.26 | 0.49 |
| 4.5          | 0.74      | 0.26 | 0.81 |
| 5.5          | 0.36      | 0.22 | 0.42 |
| 6            | 0.50      | 0.28 | 0.66 |
| 7            | 0.61      | 0.31 | 0.95 |
| 8            | 0.27      | 0.41 | 0.57 |
| 9            | 0.49      | 0.39 | 0.70 |
| 9.5          | 0.35      | 0.64 | 0.28 |
| 10           | 0.63      | 0.61 | 0.99 |