THE "LAMINATE FILM" METHOD FOR MEASURING THE PERMEATION OF VOLATILE ORGANIC COMPOUNDS THROUGH POLYMER FILMS

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ABSTRACT

The use of barrier polymers for packaging foods has created a need to test the transmission of organic penetrants, such as flavour and aroma compounds, that can be lost from the food to the polymer. Many studies have been carried out on organic penetrants but due to the large number of possible penetrant-polymer combinations and the interactions between these plus the factors that can affect these interactions, there are many conflicting results. In addition, the tests were generally carried out at high penetrant concentrations and the results were not applicable to the low concentrations found in food packages. Traditional methods for measuring permeation of organic compounds are slow and capital intensive, with no standard test method or test conditions existing. A simple, inexpensive method, known as the "laminate film" method was developed by Holland and Santangelo in 1988 in which the transmission of a penetrant is measured by the change in absorbance in a polymer film.

This "laminate film" method was used to measure the sorption of d-limonene and vanillin by low density polyethylene, nylon 6 and polyvinylidene chloride coated nylon 6 at 10, 25, and 40°C and in ethylene-vinyl alcohol films at 25°C and 90% relative humidity. Different thicknesses of the polymers were also tested. The sorption of d-limonene and vanillin was studied over long periods of time up to 8000 hours.

The amounts of vanillin sorbed and the rate of uptake of vanillin were lowest in low density polyethylene and polyvinylidene chloride coated nylon 6. Nylon 6 and moist ethylene-vinyl alcohol films rapidly picked up large amounts of vanillin. Increasing the temperature increased the rate and amount of vanillin sorbed.

Both orientation of the film and increasing the proportion of ethylene in the ethylene-vinyl alcohol films decreased the amount of vanillin sorbed, but increasing the relative humidity increased it.

Increasing the thickness of the films increased the amount of vanillin sorbed but did not affect the rate or method of uptake. Therefore, more layers can be used to accurately estimate small diffusion coefficients without affecting the permeation of the penetrant.

The results became less reproducible with time due to effects such as oxidation of the penetrant, degradation of the polymer film and concentration effects.

Diffusion, partition (or solubility) and permeation coefficients were calculated for all films with vanillin. For low density polyethylene, these were of the order of 10^{-9}cm^{2}/s, 10^{-3}, 10^{-12}cm^{2}/s respectively. For nylon 6, they were 10^{-12}cm^{2}/s, 10^{-2}, 10^{-13}cm^{2}/s; polyvinylidene chloride coated nylon 6 10^{-14}cm^{2}/s, 10^{-2}, 10^{-15}cm^{2}/s and ethylene-vinyl alcohol films 10^{-13}cm^{2}/s, 10^{-2}, 10^{-13}cm^{2}/s. The units used for the coefficients allow for the direct comparison of results for other penetrants as no conversion is necessary when comparing solid, liquid or gaseous penetrants.

D-Limonene was not an appropriate compound to be used with this method as it had a low extinction coefficient and the absorbance was not easily measured.

From this study, there are certain requirements that need to be met ,if this method is to be used as a standard test method. The compound to be tested needs a large extinction coefficient so that sorption of the penetrant can be accurately measured, and the polymer must be transparent. Temperature and relative humidity, (if the film is moisture sensitive), must be controlled as these factors can have dramatic effects on the permeation.

The "laminate film" method would be useful in industry, where a simple and inexpensive method is needed to measure transmission of flavours and aromas in polymer films in order to enable the best barrier film for a packaging application to be chosen.

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1.0 INTRODUCTION

The recent growth in the use of barrier polymers for packaging foods that were previously packaged in glass or metal containers has created a need to develop a better understanding of the transport of gases and low molecular weight compounds into and through polymer films. Barrier polymers are those materials that show a high resistance to the permeation of liquids or vapours through the polymer matrix.

Polymers are less inert than glass or metal and can interact with foods to alter their flavour or aroma in a number of ways. The three important methods of interaction are migration of compounds from the polymer to the food, and sorption and permeation of food components into and through the polymer. Components of the polymer, such as processing additives, may migrate into the food to cause off flavours and odours.

The mechanism of transmission of vapours through polymeric films is either by leakage or permeation. Leakage occurs if there is a discontinuity such as a pinhole, crack or faulty seam in the material. Permeation involves mass transfer across the film and this occurs in three steps (Gilbert et al., 1983). A penetrant molecule must first collide with the surface of the film and dissolve into it. The molecule must then diffuse through voids in the polymer network. Finally, the penetrant molecule must come out of solution and evaporate into the atmosphere on the opposite side of the film. Sorption involves the first two steps of this process, whereas permeation consists of all three (Gilbert et al., 1983; Anon., 1987).

The polymer may absorb or adsorb compounds thereby reducing the total volatile content of the food. Absorption involves matrix dissolution. It refers to the case of penetration by the molecules into the bulk structure of the polymer such that a mixture similar to that of a true solution is created. Adsorption refers to surface attraction and applies to cases where the molecules remain on the surface of the polymer. The packaging may also selectively absorb key compounds which contribute to the aroma of the food, and thus alter the characteristic odour of the food. As well, the package surface can act as a catalyst or co-reactant to chemically change a component of the food.

Foreign odours from the environment may pass through the package wall to the food. Alternatively, flavour compounds may be lost by permeation through the plastic to the environment. Figure 1.1 shows some possible interactions between the polymer, the product and the environment.

Figure 1.1 Possible Interactions Between the Polymer, the Product and the Environment

FOOD	<------------------- ------------------->	**POLYMER**	<------------ ------------>	**ENVIRONMENT**
FOOD CHANGE				FOOD CHANGE
Discolouration, Nutrient Degradation	<-----	Light Penetration		
Flavour, Toxicity	Additives, Monomer <-----	Polymer Migration		
Oxidation	O_2 <-----	Gas Permeation	CO_2 ----->	Carbonation loss
Texture change, Microorganisms	H_2O <-----	Water Permeation	H_2O ----->	Drying
Undesirable Odours	Volatiles <-----	Odour Permeation	Volatiles ----->	Loss of Intensity
Loss of Intensity	Volatiles ----->	Aroma Sorption		

When dealing with the loss of compounds from food, the important mechanisms of interaction are both sorption and permeation as losses occur to both the polymer and the environment.

The transport of penetrants such as oxygen, carbon dioxide and water vapour through polymer structures has been the subject of numerous investigations and standard test methods are available for these penetrants. However, while the transport of organic penetrants through polymeric materials has been the subject of several studies, there is a lack of data available in this area. Permeation is more complex for organic compounds in contact with polymers because:

- the materials concerned are not simple gases;
- polymers are complex structures which are not homogeneous, particularly multilayer structures;
- major chemical and physical affinities exist of which the most important is tendency to solution (Briston and Katan, 1974b).

The organic penetrant/polymer interactions and the ways in which various factors affect these interactions is not fully understood. There are complications due to the large number of flavour compounds and the wide variety of available polymeric films. A vast number of combinations need to be investigated before these interactions are completely understood.

In the studies of organic penetrants, there are many conflicting observations and many different test methods, which makes comparison of the results difficult. In addition, a large proportion of the published work has involved the use of saturated vapours and it is generally not valid to use this data to estimate the permeation rates at the lower levels encountered in typical retailing situations. No standard methods for the measurement of odour permeation exist. Many of the test methods currently used are only suitable for use with high concentrations of vapours.

The need is therefore for a test method that can be used at the low concentrations found in food packages. Baner et al., 1986; Landois-Garza et al., 1988; Mohney et al., 1988 and Zobel, 1982, 1985; have carried out studies at low concentrations. Their work has found that permeation behaviour can be accurately predicted from theory at these levels.

Traditional methods for measuring the interaction of organic compounds with polymers could be time consuming and capital intensive. A novel, simple and inexpensive method was developed by Holland and Santangelo, 1988; and is known as the "laminate film" method. The important difference is that a concentration gradient not a pressure gradient drives the penetrant through the film. In this method, the usual gas or liquid supply and collector systems are replaced by completely solid state systems. The procedure is quite general as it is independent of vapour pressure, and also applies to non-volatile diffusants. In food packages, flavour and aroma molecules are absorbed largely from the liquid or solid food rather than from the headspace so this method is more closely attuned to the practical situation.

This present research continues Holland's work. It also studies vanillin but includes another flavour compound, d-limonene. The polymers studied were low density polyethylene, nylon 6, polyvinylidene chloride coated nylon 6 and ethylene-vinyl alcohol copolymers. The polymers were chosen as typical examples of food packaging materials. D-Limonene and vanillin were used as examples of common food flavours. D-Limonene was also chosen as it has already been extensively studied using existing techniques. It is also an important flavour that is often lost to the packaging material.

The aim of this research was to determine if the "laminate film" method was a suitable method to use to test the permeation of flavour and aroma compounds and the applications and limitations of this method. This would be particularly useful in industry where a simple, cheap method is needed.