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Analysis method

Investigation of multiple-component diffusion through LLDPE film using an FTIR-ATR technique

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ABSTRACT

An FTIR-ATR technique was developed to investigate the multiple-component diffusion properties of 2-octanone, hexyl acetate, octanal, limonene and linalool (equal volume mixture) in a linear low density polyethylene film. Diffusion coefficient (D) values determined for these compounds in the mixture were 7.02×10^{-10}, 2.86×10^{-9}, 1.09×10^{-9}, 7.49×10^{-9} and 5.81×10^{-9} cm^2/s, respectively. Compared with the diffusion of the individual permeants (1:4 permeant:ethanol, v/v), the *D* values of 2-octanone, hexyl acetate and limonene were lower in the mixture solution, while those of octanal and linalool were higher. Hansen solubility parameters (HSP) were used to elucidate the solubility properties of the permeants. Two-dimensional FTIR data analysis showed that diffusion of the test permeants in LLDPE occurred in the following sequence: limonene (first) → linalool → hexyl acetate → octanal → 2-octanone (last).

1. Introduction

Thermoplastic polymers are widely used in food, cosmetic and pharmaceutical packaging applications [1,2]. However, since polymers are permeable to small molecules, it is important to characterize the barrier properties of the packaging materials to ensure that the packaged products are adequately protected [3,4].

Diffusion coefficient (D) reflects the ease of movement of the absorbed molecules through the polymer matrix [5]. The conventional methods of determining D of an organic compound in a polymer film are typically based on GC or gravimetric techniques [6]. Other techniques involve NMR spectroscopy and laser interferometry [7,8]. Although these techniques are useful for mass transport investigation, they do not provide real-time information on permeant-polymer interaction during diffusion. Furthermore, some of these techniques are expensive and the equipment involved is difficult to operate.

Fourier transformed infrared - attenuated total reflection (FTIR-ATR) spectroscopy is a simple and non-destructive technique that has been recently adapted for studying diffusion of permeants in thermoplastic polymers [9–14]. In a typical experimental setup, one side of the film specimen is exposed to the permeant, while the opposite side is pressed against an ATR crystal. The infrared (IR) spectrum of the film that is in contact with the ATR crystal is recorded as a function of time. The time-resolved spectral data are then used for calculating the D values by fitting with diffusion models.

To date, the majority of the published diffusion studies have been focused on the single-component diffusion process without considering the effects of other permeants. This approach does not reflect the actual mass transport conditions wherein diffusion of multiple components often exists. For instance, studies have shown that absorption of limonene in low and high density polyethylene films could enhance the diffusion of other aroma compounds present in permeant mixtures. This phenomenon has been

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attributed to the plasticization and swelling effects of limonene [9,15]. In their studies involving the sorption of limonene and carvone in polypropylene film, Letinski and Halek reported that the mixture of these compounds resulted in a lower amount of permeant sorbed as compared to limonene or carvone alone. These observations were attributed to the competition of the two permeants for sorption sites on the surface and within the polymer [16]. These examples highlight the importance of considering multi-component effects during a permeation study.

The main objective of the current study is to develop an FTIR-ATR method for the analysis of diffusion of multiple flavor compounds (hexyl acetate, 2-octanone, octanal, (±)-linalool and (R)-(+)-limonene) in a linear low density polyethylene (LLDPE) film, and in which multiple film samples could be tested. LLDPE polymer was chosen in this study because it is one of the most commonly used sealant polymers in contact with packaged food products. The second objective of this study is to elucidate multi-component effects on the diffusion of individual permeants.

2. Materials and methods

2.1. Materials

2.1.1. Film samples

LLDPE film (thickness 55 ± 1 μm, density 0.924 g/cm^3; melt flow index 0.674 dg/min) was donated by E.I. DuPont Canada Company (Kingston, Canada). The refractive index of the film ($n_2 = 1.39$) was determined according to the method by Harrick [18]. Crystallinity of the LLDPE film was 80%, based on the FTIR peak height ratios for the crystalline band at 731 cm^{-1} and the amorphous band at 719 cm^{-1} [19–21].

2.1.2. Permeants

Ethyl acetate, hexyl acetate and 2-octanone, all 99% purity, were purchased from Fisher Scientific (Ottawa, Canada). Octanal (99%), (±)-linalool (95.0%) and (R)-(+)-limonene (98%) were purchased from Sigma–Aldrich (Oakville, Canada).

2.2. Experimental setup and design

An IRPrestige-21 FTIR spectrometer (Shimadzu Corp., Tokyo, Japan) equipped with a MIRacle ATR accessory (Pike Technologies, Madison, USA) was used for detecting the spectral changes of LLDPE film during the diffusion study. The ATR accessory is equipped with a diamond/ZnSe crystal ($n_1 = 2.4$) with a 45°angle of incidence. To prepare the sample for the diffusion experiment, an LLDPE film was placed on top of the thread finish of a vial containing the test permeant solution (Fig. 1). The film was sealed over the vial opening by securely screwing the Teflon-lined closure onto the thread finish. To start the diffusion test, the vials were quickly inverted to allow the LLDPE film to come in contact with the liquid permeant. At predetermined time intervals, the polymer film was removed from the vial, and the side of film that was facing the Teflon liner was pressed immediately against the ATR crystal using a MIRacle micrometer clamp (Pike Technologies). The film was scanned at 4 cm^{-1} resolution in 600–4000 cm^{-1} frequency

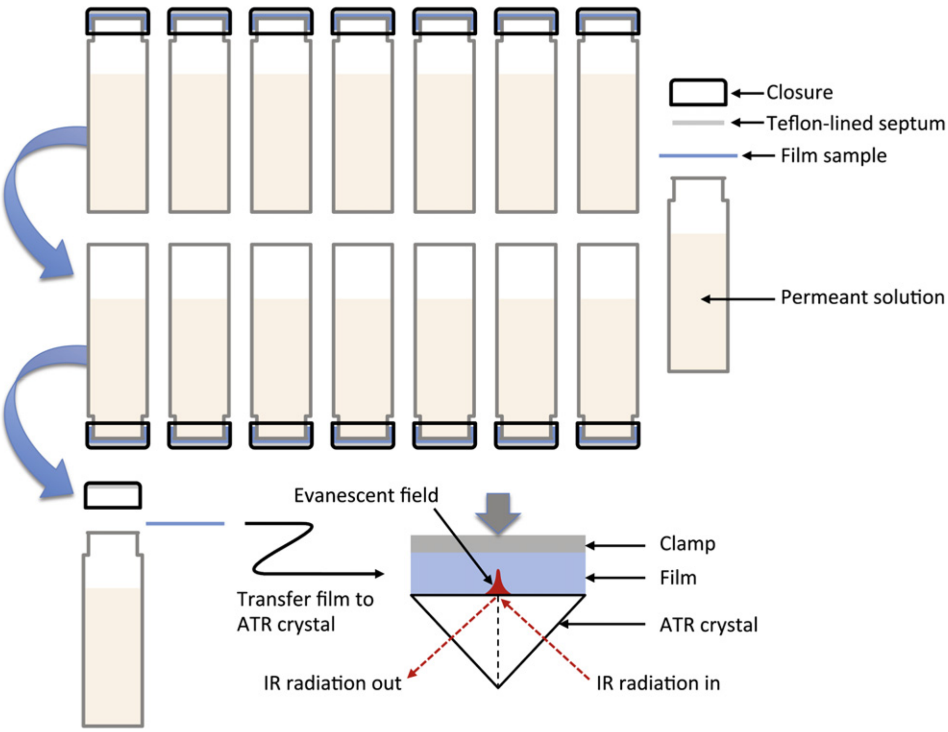

Fig. 1. Experimental scheme used for evaluating the diffusion of flavor compounds in LLDPE film.