

Dynamic Analysis of the Permeability of d-Limonene Vapor in Polymeric Sealant Films.^{a)}

by Shin-ichi OSANAI^{b)}, Tohru KANNO^{c)}
and Masayoshi KOBAYASHI^{c)}

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Abstract

The permeability of d-limonene vapor was measured in various polymeric sealant films at a temperature range of 25–45°C, by using a flow-type diffusion cell newly developed for measuring gas permeation under atmospheric pressure. The transmission rate profile curves describing the transport of d-limonene through all polymer membranes could basically be analyzed by the isostatic method. The data obtained provided information necessary for the estimation of the storage quality of a packaged polymeric sealant film whose quality could be related to the crystallinity of film.

1. INTRODUCTION

A large number of polymeric packaging materials have been developed and used with recent progress of the technology of making thin film. A serious attention is paid into the sorption of flavor compounds or "scalping" as one of the most important compatibility problems. As is well known, Foster¹⁾ demonstrated that polyolefins could selectively sorb certain flavor constituents from products. Durr and Schobinger²⁾ reported that 40% of the total quantity of d-limonene in orange juice is decreased because of absorption into a polyethylene lining materials. Generally speaking, low density polyethylene (LDPE) was found to have strong affinity for d-limonene as has been reported by Hirose et al³⁾, Kwapong and Hotchkiss⁴⁾, Iwaki, Harte and Giaiein⁵⁾ and Yamada, Mita, Yoshida and Ishiya⁶⁾.

In the present study, the major objects were to: (1) develop a measuring procedure of the permeability of d-limonene in polymeric sealant films, and (2) demonstrate reasonable relation between permeability and crystallinity of films.

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^{b)} Chemical Environmental Engineering.

^{c)} Department of Industrial Chemistry.

2. EXPERIMENTAL

2-1. Materials

Analytical grade d-limonene, obtained from Wako Pure Chemical Co. was used and no any impurities were detected by a gas chromatograph (FID). The molecular structure of d-limonene (1,8(9)-p-menthadiene) is given in Fig. 1 and the molecular size is about 10 Å.

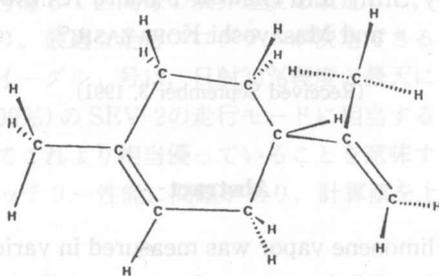


Fig. 1 Molecular structure of d-limonene.

Six polymeric films all of which were typically used as cereal package liners were employed. The detail of the physical nature of the films used is given in Table 1.

Table 1. The membranes used in this study.

Membrane	Mark	Thickness
Low density polyethylene	LDPE	60 μ m
Liner low density polyethylene	LLDPE	60 μ m
High density polyethylene	HDPE	55 μ m
Ethylene vinylacetate copolymer (amount of vinylacetate is 5wt%)	EVA5	70 μ m
Ethylene vinylacetate copolymer (amount of vinylacetate is 7wt%)	EVA7	70 μ m
poly-acrylonitrile copolymer	PAN	30 μ m

The Electron Probe Microanalyzer (EPMA) photographs of low density polyethylene (LDPE), high density polyethylene (HDPE) and polyacrylonitrile copolymer (PAN) membranes are shown in Fig. 2. Fig. 3 illustrates the crystal structure of polyethylene.

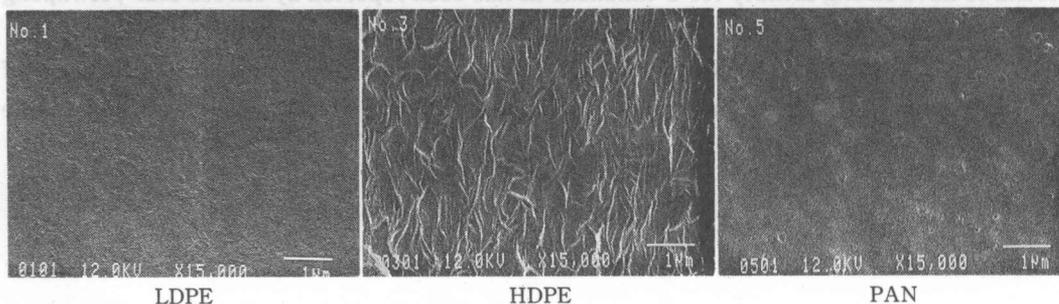


Fig. 2 The EPMA photographs of LDPE, HDPE and PAN.

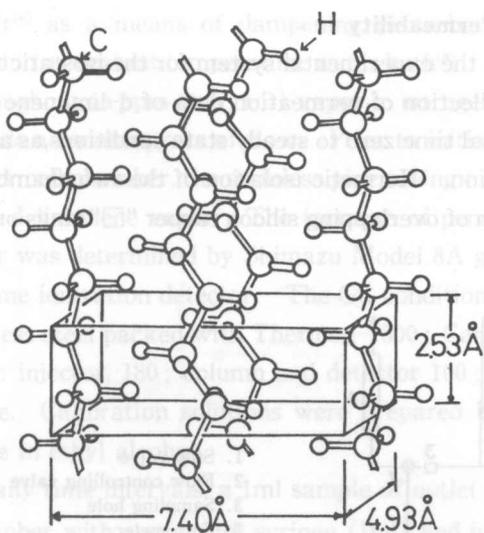


Fig. 3 The crystal structure of polyethylene.

2-2. Methods

The film samples were stored over silica gel at ambient temperature ($25 \pm 3^\circ\text{C}$) prior to testing.

2-3. Permeability cell

Fig. 4 illustrates the schematic drawings of the permeability cell used in this study^{7,8)}. The cell consisted of two flat plates (stainless steel, $9 \times 2 \times 0.5\text{cm}$) in each of which a groove was prepared for the gas flow, and the film was sandwiched between the two plates. The groove of the two plates was divided by the film. The gases in both grooves partly permeated between the two plates through the film, with counter current. The permeation through the film from one side to the other side was visualized in the figure. The permeation area was 18.0cm^2 and the groove volume was 3.6cm^3 . The diffusion cell was put into a water bath the temperature of which was well controlled within the accuracy of $\pm 1^\circ\text{C}$ at the given temperature.

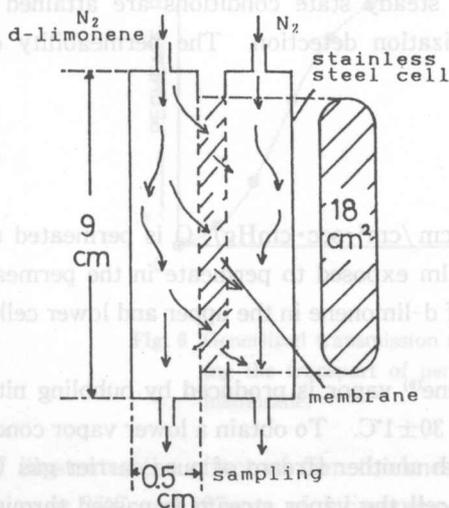


Fig. 4 The diffusion cell used in this study.

2-4. Procedure and Measurements of Permeability

Fig. 5 illustrates the flow diagram of the experimental system for the isostatic method⁷⁾. The measuring system allows for the collection of permeation data of d-limonene vapor or gas through a polymer film from the initial time zero to steady state conditions, as a function of temperature and permeate concentration. Hermetic isolation of the two chambers from each other is achieved by the compression of overlapping silicon rubber "□" rings on the film sample.

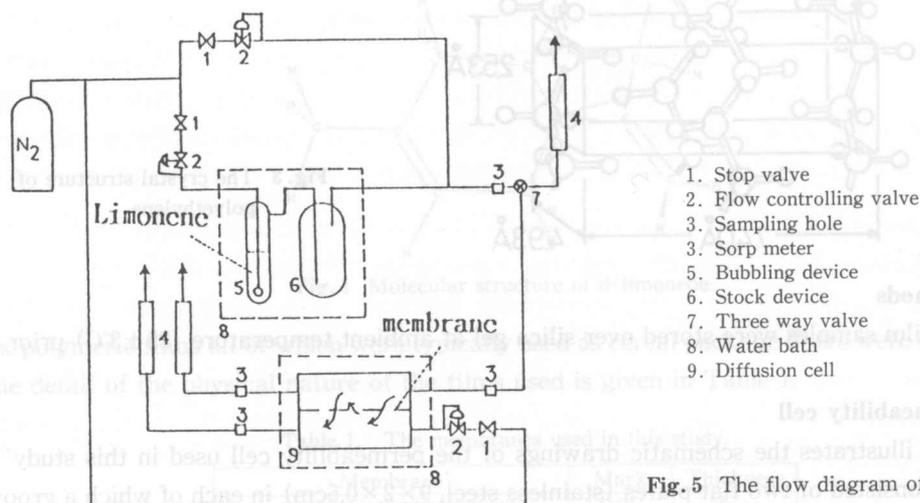


Fig. 5 The flow diagram of the experimental system.

The assemble cell⁽⁹⁾ is placed horizontally in a constant temperature water bath⁽⁸⁾, and a constant concentration of d-limonene vapor is continuously flowed through the upper cell chamber. Concurrently, a constant flow of nitrogen is passed through the lower cell chamber removing permeate vapor. At preselected time intervals the concentration of penetrant in the nitrogen stream flowing through the low concentration cell chamber is determined, and the transmission rate is monitored until steady state conditions are attained by a gas chromatograph equipped with flame ionization detection. The permeability coefficient value are then computed by equation (1).

$$P = \frac{Q}{A} \cdot \frac{L}{p_1 - p_2} \quad (1)$$

P is permeation coefficient (cm^3 (STP) \cdot cm / $\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}$), Q is permeated amount at steady state (cm^3/sec), A is area of the film exposed to permeate in the permeability cell (cm^2), p_1 and p_2 are the partial pressure of d-limonene in the upper and lower cell chambers (cmHg), and L is film thickness (cm).

A constant concentration of d-limonene⁽⁵⁾ vapor is produced by bubbling nitrogen gas through liquid d-limonene which is kept at $30 \pm 1^\circ\text{C}$. To obtain a lower vapor concentration, the d-limonene vapor stream is mixed with another stream of pure carrier gas (nitrogen). Before being directed to the permeation cell the vapor stream is passed through a glass

reservoir⁽⁶⁾ as a means of dampening perturbations. The vapor generator system was mounted in a constant temperature water bath⁽⁸⁾. D-limonene vapor concentration is expressed throughout as ppm (v/v, 1/1) vapor in nitrogen. Fine flow controlling valves were used to provide a constant rate of flow. Prior to initialing a run, special care was taken to purge the lower cell chamber, the stainless pipe tubing interfacing the cell and the sampling hole of residual d-limonene vapor. The increase of penetrant level in the low concentration cell chamber was determined by Shimazu Model 8A gas chromatograph (GC), equipped with a dual flame ionization detector. The GC conditions were as follows : column, 100×0.3cm O. D. stainless steel packed with Thermon-1500 ; Carrier gas, nitrogen at 30ml/min ; Temperature, °C : injector, 180 ; column and detector 100 ; to give a retention time of 40 sec for d-limonene. Calibration solutions were prepared by dissolution of known quantities of d-limonene in ethyl alcohol.

At any time intervals, a 1ml sample of outlet was removed from the low concentration cell chamber with a gas tight syringe (1ml) and injected directly into the GC. The syringe has no grease because of protecting the absorption of d-limonene into it and was washed carefully by dry air after the sampling.

3. RESULTS AND DISCUSSION.

3-1. Dynamic Behavior of d-limonene Permeated in Polymer Membranes

Fig. 6 illustrates a generalized transmission rate profile curve describing the transport of a permeate through a polymer membrane by the isostatic method. The volumetric amount of d-limonene permeated for one second is plotted as a function of time.

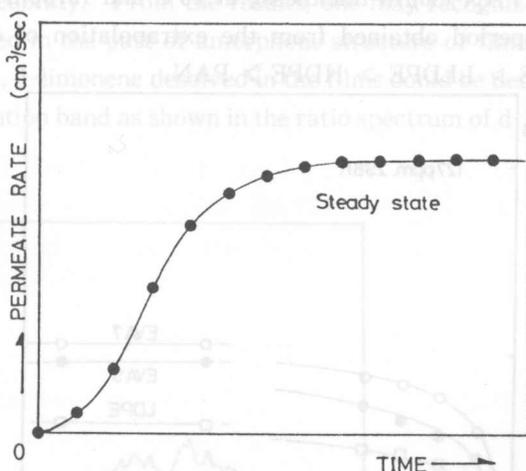


Fig. 6 Generalized transmission rate profile curves describing the transport of permeate through a polymer membrane.

Fig. 7 illustrates the effect of film thickness on the transient behavior of d-limonene transmission at 25°C and 127ppm of d-limonene.

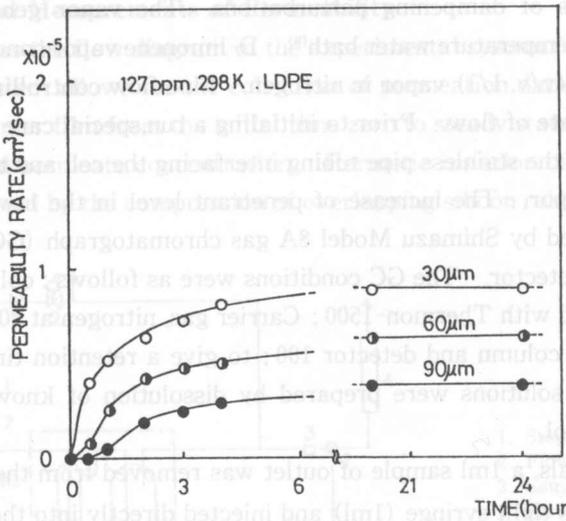


Fig. 7 The effect of film thickness on the transient behavior of d-limonene.

As can be seen from the figure, all of the permeation behavior had an initial induction period followed by a monotonic increase of permeation rate, and the induction period became longer with increasing the film thickness. Fig. 8 illustrates the permeation behavior of six different films, LDPE (60 μm thickness), LLDPE (60 μm thickness), HDPE (55 μm thickness), EVA7 (amount of vinylacetate is 7wt%, 70 μm thickness), EVA5 (amount of vinylacetate is 5wt%, 70 μm thickness), PAN (30 μm thickness), at 25°C and 127ppm of d-limonene. The length of the induction period obtained from the extrapolation of curves is ordered as EVA7 > EVA5 > LDPE > LLDPE > HDPE >> PAN.

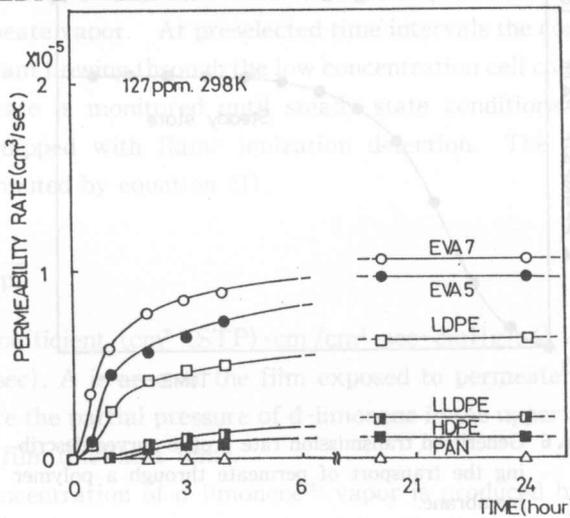


Fig. 8 Permeation behavior of d-limonene for various films.

3-2. Relation between the Permeability and Crystallinity of Polymer Films.

As is well known, melting point (mp) measured by a differential scanning calorimeter (DSC) can be related to crystallinity of polymer films comparing between same raw materials, as the higher DSC mp the better crystallinity.

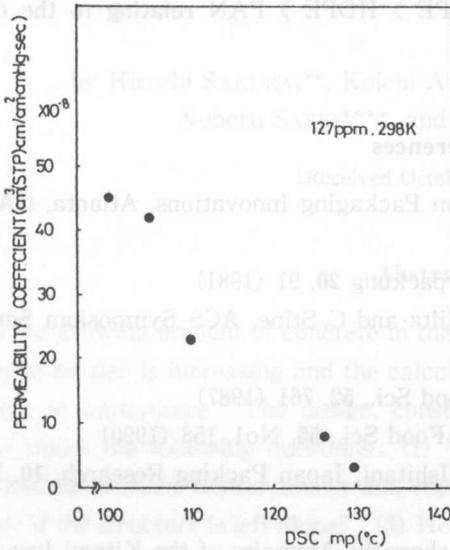


Fig. 9 The plots of permeability vs. DSC melting point.

Fig. 9 illustrates the plots of permeability coefficient vs. crystallinity of films which is shown by DSC-melting point at 25°C and 127ppm of d-limonene. The better permeability is the higher crystallinity, suggesting that the crystallinity is one of the important parameters controlling the permeability. From the results, one may recognize that d-limonene will be preferentially desolved in the part of amorphous structure of films rather than the crystallinity part. Actually, d-limonene desolved in the films could be detected as 1460cm⁻¹ of CH₃ bending for IR absorption band as shown in the ratio spectrum of d-limonene absorbed HDPE Fig. 10.

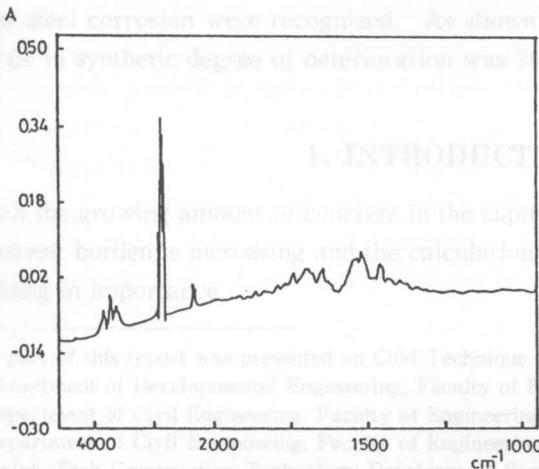


Fig. 10 IR spectra of d-limonene absorbed on HDPE.

4. CONCLUSIONS

The cells newly developed in this study were reconfirmed to be useful for the permeability measurement of polymeric sealant films. The values of permeability coefficient are ordered as EVA7 > EVA5 > LDPE > LLDPE > HDPE > PAN relating to the order of crystallinity.

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