

# Effect of Temperature on Gas Permeation of Polymer Blends. I. Poly(ethylene Oxide) / Copolyester–Polyurethane

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## Synopsis

The transport behavior of H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, and CO<sub>2</sub>, was studied for blends of poly(ethylene oxide) (PEO) with a copolyester–polyurethane (PU) at various temperatures from 20 to 80°C. It was found that there was an abrupt change in slope or discontinuity around the melting point of PEO in Arrhenius plot of the permeability vs. temperature. The relationships between the logarithm of gas permeability and blend composition were strongly dependent on the temperature and showed very different shapes at temperature below and above the melting point of PEO. The activation energy of gas permeation for the blends had different values below and above the melting temperature of PEO.

## INTRODUCTION

Gas permeability of polymer blends has been extensively studied.<sup>1</sup> Most of the works discussed the difference between the mixing rules for gas permeability of miscible and immiscible blends. For miscible blends, a linear relationship is usually observed when the logarithm of the gas permeability is plotted vs. blend composition, while S-shaped curves are found for immiscible two phase blends. The gas permeability of a polymer blend is intensively dependent on the phase structure which the blend has; and a gas molecule is basically a probe by which the phase behavior can be determined by its influence on the transport properties. Shur and Ranby<sup>2-7</sup> pioneered in using gas permeation data to elucidate the structure of various poly(vinyl chloride) blends. Good agreement of this technique for characterizing blend phase behavior was noted by comparison with other accepted techniques. Paul<sup>8</sup> has developed mixing rules for homogeneous miscible polymer blends from both the activated state and free volume theories of transport, and his theoretical results were examined by gas permeation measurement in some blend systems and especially in a carefully chosen miscible poly(methyl acrylate)/polyepichlorohydrin blend system.<sup>9</sup>

It should be pointed out that the changes in phase structure in a polymer blend may be brought about mainly by variations in temperature. Thus, the

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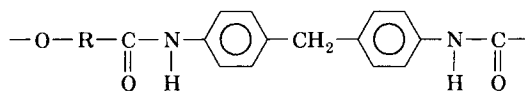
relationship between gas permeability and blend composition will change as temperature changes. In this article, the blends of poly(ethylene oxide) (PEO) with an amorphous copolyester-polyurethane (PU) have been studied at a variety of temperatures from 20 to 80°C. The blends used throughout this study are all with lower PEO content (up to 30 wt %) and composed of a continuous, amorphous, PU-rich phase and a crystalline PEO dispersed phase at room temperature. Once temperature is elevated over the melting point of PEO in the blend, the crystallized PEO dispersions become molten and the changes in phase structure occur. As a result, the relationships between gas permeability and blend composition should be different below and above the melting point of PEO. The purpose of this series of studies is to measure the permeability of different gases in the blends of interest at various temperatures and then to examine how the relationship between permeability and blend composition changes with temperature.

## EXPERIMENTAL

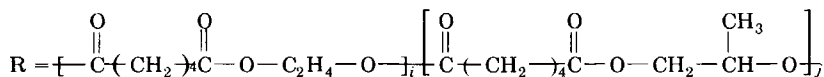
### Materials

The PEO is a commercial product (Polysciences Inc.) with number average molecular weight  $\bar{M}_n = 20,000$ , and the copolyester-polyurethane (PU), commercially obtained from Yantai Synthetic Material Factory (China), has a weight average molecular weight  $\bar{M}_w = 180,000$  and a glass transition temperature  $T_g = -22^\circ\text{C}$ . The soft segment of PU consists of aliphatic copolyester diol and 4,4'-diphenylmethane diisocyanate (MDI). The hard segment is composed of alternating MDI and butanediol units.

*Soft segment:*

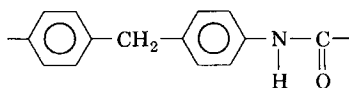
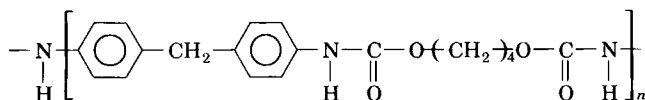


(copolyester-MDI)



(copolyester)  $\bar{M}_n = 2,000$  and  $i/j = 9/1$

*Hard segment:*



(MDI-butanediol)

The PU contains 27 wt % of the hard segment and does not exhibit any detectable crystallinity, *N,N'*-dimethyl formamide (DMF) is analytically pure. The gases used in this experiment were > 99% pure and were used as received.

### Preparation of Samples

Blends of PEO and PU with weight ratios of 0/100, 10/90, 20/80, and 30/70 were prepared by solution casting onto a polytetrafluoroethylene model from DMF and drying under vacuum at room temperature to remove residual solvent.

### Gas Permeability Tests

The measurements of H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, and CO<sub>2</sub> permeability at various temperatures were made on films of the blends (prepared above with thickness about 0.4 mm) by a dynamic gas chromatographic method as described by Caskey.<sup>10</sup> The temperature controlled apparatus (precision 0.1°C) employed a thermoconductivity detector instead of a helium analyzer which Caskey used. N<sub>2</sub> was used as reference gas for measuring the permeability of H<sub>2</sub> through the films, and H<sub>2</sub> for N<sub>2</sub>, O<sub>2</sub>, and CO<sub>2</sub>.

### WAXS Measurement

The crystallinity of the blends was studied by a Rigaku diffractometer with Cu-K<sub>α</sub> radiation at room temperature.

### Differential Scanning Calorimetry

A Perkin-Elmer DSC-2C differential scanning calorimeter was used to measure the melting point of PEO in the blends. The heating rate was 10°C/min. The maximum in the endothermic peak was taken as the melting point.

## RESULTS AND DISCUSSION

The temperature dependence of permeation coefficients of H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, and CO<sub>2</sub> through PU and the blends, from 20 to 80°C, is shown in the form of Arrhenius plots in Figure 1. For PU a straight line is obtained for all gases, because no transition of PU exists in above range of temperature [Fig. 1(a)]. However, for blends containing 10 wt % PEO [Fig. 1(b)], changes in slope at the melting point of PEO are clearly shown. Furthermore, the blends with higher PEO content (20 and 30 wt %) have discontinuities occurring around the melting point of PEO [Figs. 1(c) and 1(d)]. These are attributed to the changes of phase structure in the blends when temperature is elevated over the melting point of PEO. The changes in phase structure may strongly affect the transport behavior of gas through the blends. Different values for activation energy of permeation ( $E_p$ ) above and below the melting point of PEO are shown in Figure 2. The figure displays two types of activation energy-composition curves for below [Fig. 2(a)] and above [Fig. 2(b)] the melting point of PEO.

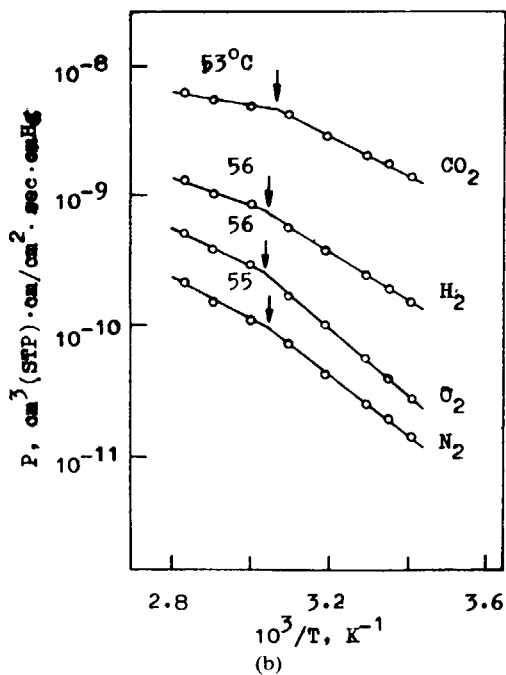
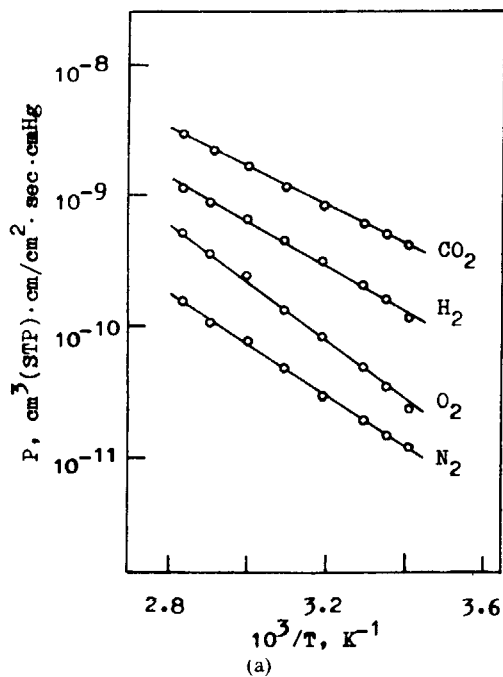
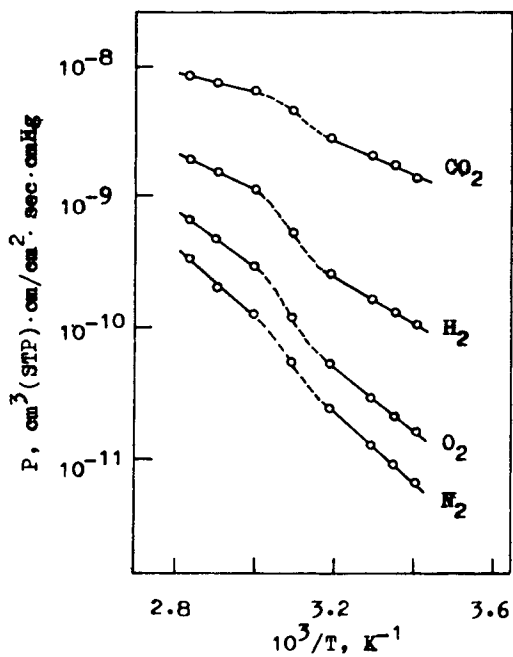
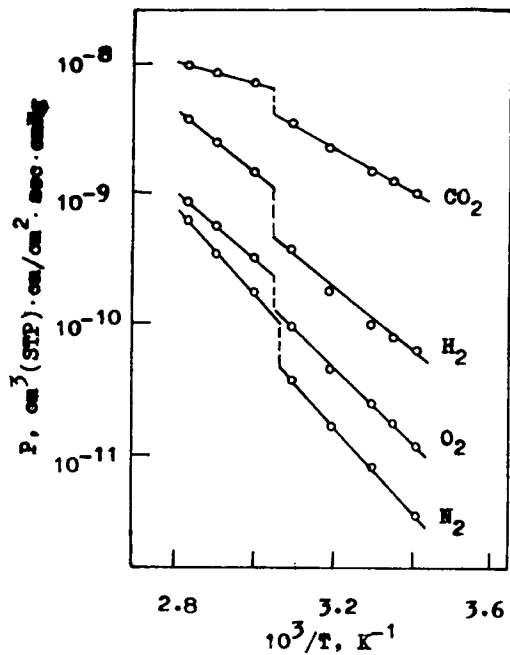


Fig. 1. Arrhenius plots of permeability coefficients for the PEO/PU blends containing: (a) 0, (b) 10, (c) 20, and (d) 30 wt % PEO.



(c)



(d)

Fig. 1. (Continued from the previous page.)

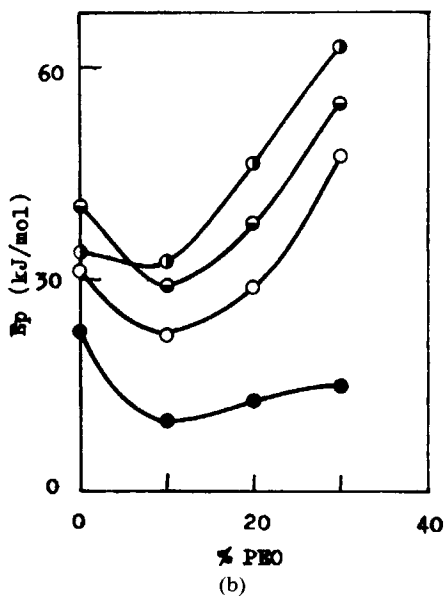
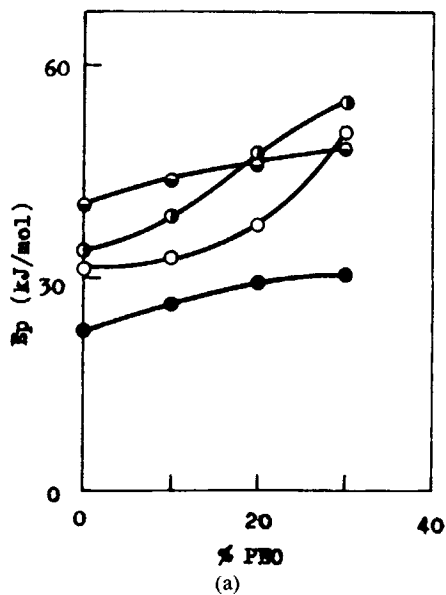


Fig. 2. Activation energy for permeation of H<sub>2</sub> (○), N<sub>2</sub> (◻), O<sub>2</sub> (◻), and CO<sub>2</sub> (●) vs. blend composition: (a) below and (b) above the melting point of PEO.

TABLE I  
 $T_p$  and  $T_m$

PEO/PU	$T_m$ (°C)	$T_p$ (°C)
10/90	53	53-56
20/80	55	40-60
30/70	58	50-60

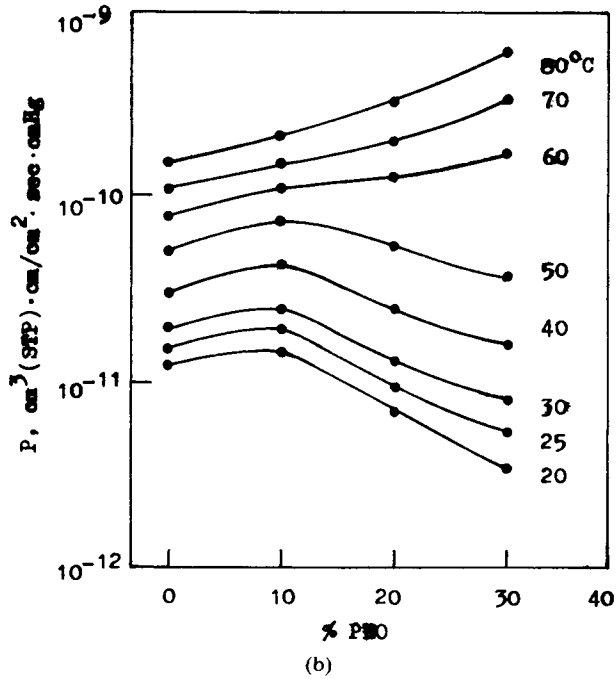
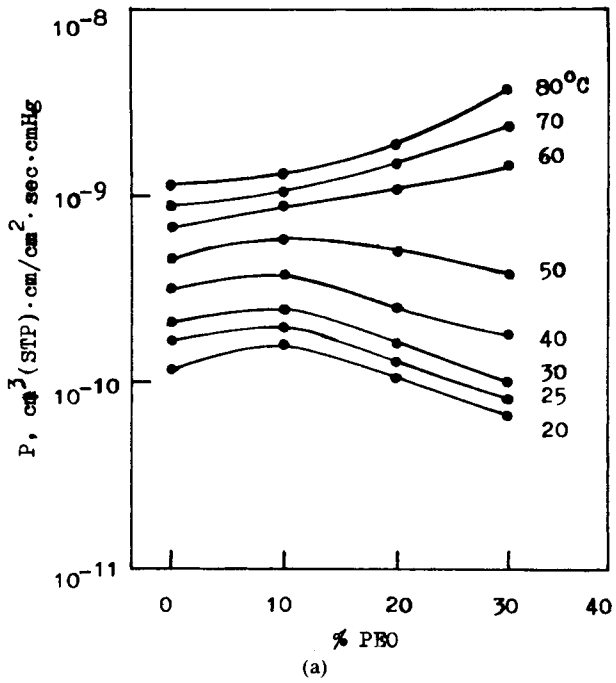


Fig. 3. Permeability coefficients vs. blend composition: (a) H<sub>2</sub>; (b) N<sub>2</sub>; (c) O<sub>2</sub>; (d) CO<sub>2</sub>.

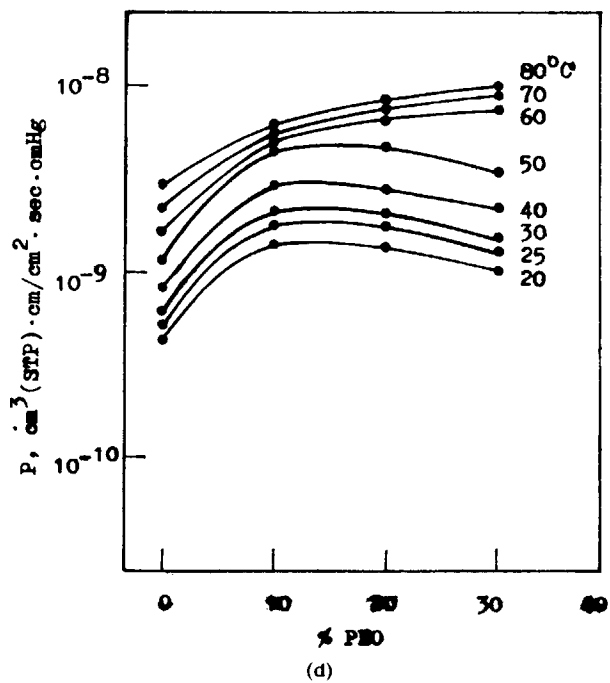
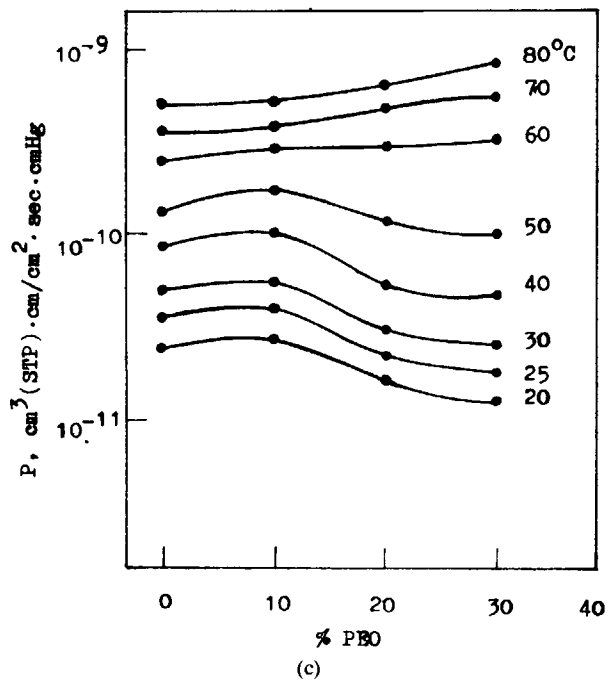


Fig. 3. (Continued from the previous page.)



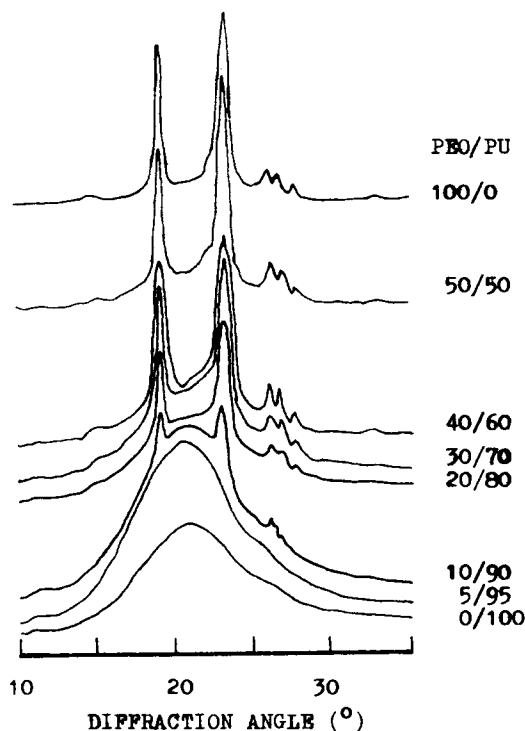


Fig. 4. X-ray diffraction diagram of the PEO/PU blends.

The temperatures ( $T_p$ ) where the abrupt changes in slope or discontinuity appeared in Arrhenius plots as shown in Figure 1 are listed in Table I. They correspond to the melting points ( $T_m$ ) of PEO in the blends determined by DSC.

The relationship between permeability and blend composition is related to the phase structure which the blend has. Since PEO/PU blends have different phase structures above and below the melting point of PEO, there should be different types of permeability-composition curves. This phenomenon is shown in Figure 3. As expected, for all gases ( $H_2$ ,  $N_2$ ,  $O_2$ , and  $CO_2$ ), there exist very different types of permeability-composition curves at temperatures below ( $20$ – $50^\circ C$ ) and above ( $60$ – $80^\circ C$ ) the melting point of PEO. However, for all gases except  $CO_2$ , the permeability-composition curves have almost the same shape provided that temperatures are all above or all below the melting point of PEO. At temperatures in the range of  $20$ – $50^\circ C$ , PEO is a semicrystalline polymer. X-ray diffraction diagrams of PEO/PU blends (Fig. 4) show that the blends with PEO content higher than 10 wt % are crystalline. However, the blend with 5 wt % PEO content is amorphous. A DSC study obtained the same result. At PEO content higher than 10 wt %, rates of gas permeation for the blends decrease and  $\log P$  vs. PEO content is a decreasing function. This result is due to the formation of a separate crystallized PEO phase in the blends. With amounts of PEO higher than 10 wt %, a crystalline phase of PEO develops with the same X-ray diffraction pattern as pure PEO (Fig. 4). A similar permeability-composition relationship was observed by Shur and

Ranby<sup>7</sup> for poly( $\epsilon$ -caprolactone) (PCL)/poly(vinyl chloride) (PVC) blends at room temperature. PCL is a semicrystalline polymer and miscible with PVC.<sup>7,11</sup> At temperature in the range of 60–80°C, the crystallized PEO phase in the blends become molten; our calorimetric study<sup>12</sup> suggested that the PEO/PU blend system is miscible in the melt. Rates of gas permeation for blends increase with increasing PEO content. Negative departures from simple linearity in permeability–composition curves (Fig. 3) imply that there are relatively strong interactions between PEO and PU responsible for miscibility.

It is noted that the permeability–composition relationships for CO<sub>2</sub> is somewhat special. The transport mechanism of CO<sub>2</sub> through polymers is generally considered more complex owing to strong interactions between CO<sub>2</sub> molecule and polymers.<sup>13,14</sup>

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Received October 22, 1988

Accepted April 17, 1989