Effect of Temperature on Gas Permeation of Polymer Blends. II. Copolyester/Copolyester–Polyurethane

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Synopsis

The transport behavior of H_2, N_2, O_2, and CO_2 was studied for blends of an aliphatic copolyester with a copolyester–polyurethane (PU) at various temperatures from 20 to 80°C. It was found that there was an abrupt change in slope near the melting point of the copolyester in Arrhenius plot of the permeability vs. temperature. This was considered to be due to the phase changes in the blends. The relationships between the logarithm of gas permeability and blend composition were only slightly dependent on temperature owing to the low degree of crystallinity of the copolyester; however, the activation energy of gas permeation for the blends had different values below and above the melting temperature of copolyester. The T_g measurements by DSC suggested that the copolyester/PU blends are miscible. However, the gas permeation measurements revealed the blends are not molecularly homogeneous. The miscibility of the blends did not extend to the ångstrom level.

INTRODUCTION

Gas permeability of polymer blends has been extensively studied.[1] 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[2-7] 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. However, little work has been done to study the effect of temperature on gas permeation of polymer blends. 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 relationship between gas permeability and blend composition will change as temperature

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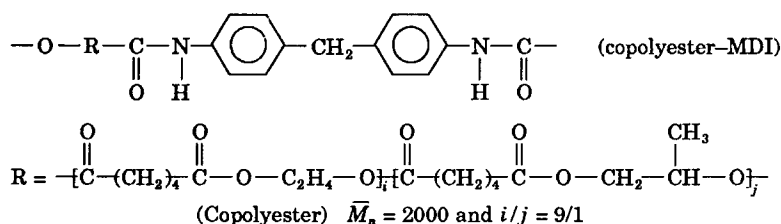† Department of Polymer Science, Beijing Institute of Chemical Technology, Beijing, People's Republic of China.

changes. In the previous paper,[8] the transport behavior of some gases 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 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. In this paper, the blends of a low crystalline aliphatic copolyester with an amorphous copolyester-polyurethane (PU) have been investigated at a variety of temperatures from 20 to 80°C. The crystallinity of the copolyester is rather low due to the irregularity of chain structure. The aim of this study is to clarify the influence of temperature on the gas permeation of polymer blends containing low crystalline component. Furthermore, by comparison with the previous results, the difference of effect of differing degree of crystallinity will be discussed.
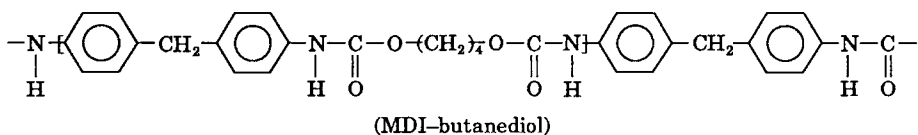
EXPERIMENTAL

Materials

The copolyester–polyurethane (PU) with weight-average molecular weight $\bar{M}_w = 180{,}000$ and a density of 1.267 g/cm^3 at 25°C was supplied by the Yantai Synthetic Material Factory, Yantai, Sandong, China. 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:

$$-O-R-\underset{\underset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-\hspace{-2pt}\langle\bigcirc\rangle\hspace{-2pt}-CH_2-\hspace{-2pt}\langle\bigcirc\rangle\hspace{-2pt}-\underset{\underset{H}{|}}{N}-\underset{\underset{O}{\|}}{C}-\quad\text{(copolyester–MDI)}$$

$$R = -[\underset{\underset{O}{\|}}{C}-(CH_2)_4-\underset{\underset{O}{\|}}{C}-O-C_2H_4-O]_i-[\underset{\underset{O}{\|}}{C}-(CH_2)_4-\underset{\underset{O}{\|}}{C}-O-CH_2-\underset{\underset{CH_3}{|}}{CH}-O]_j-$$

(Copolyester) $\bar{M}_n = 2000$ and $i/j = 9/1$

Hard segment:

$$-\underset{\underset{H}{|}}{N}-[\langle\bigcirc\rangle-CH_2-\langle\bigcirc\rangle-\underset{\underset{H}{|}}{N}-\underset{\underset{O}{\|}}{C}-O-(CH_2)_4-O-\underset{\underset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}]-\langle\bigcirc\rangle-CH_2-\langle\bigcirc\rangle-\underset{\underset{H}{|}}{N}-\underset{\underset{O}{\|}}{C}-$$

(MDI–butanediol)

The PU contains 27 wt % of the hard segment and does not exhibit any detectable crystallinity. The copolyester with the same structure and average molecular weight as that in the soft segment of PU was also commercially obtained from the same factory. It has a density of 1.261 g/cm^3 at 25°C and was used to blend with PU. 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 copolyester and PU with weight ratios of 0/100, 10/90, 25/75, 40/60 50/50, 75/25, 90/10, and 100/0 were prepared by solution-casting onto a Teflon model from DMF and drying under vacuum at room temperature to remove residual solvent.

Gas Permeability Tests

The measurements of H_2, N_2, O_2, and CO_2 permeability at various temperatures were made on films of the blends (as prepared above with thickness about 0.4 mm) by a dynamic gas chromatographic method as described by Caskey.[9] The temperature controlled apparatus (precision 0.1°C) employed a thermoconductivity detector instead of a helium analyzer which Caskey used. N_2 was used as reference gas for measuring the permeability of H_2 through the films, and H_2 for N_2, O_2, and CO_2.

WAXS Measurement

The crystallinity of the blends was studied by a Rigaku diffractometer with Cu-K_α radiation at room temperature.

Differential Scanning Calorimetry

The calorimetric measurements were made on a Perkin-Elmer DSC-2C differential scanning calorimeter. All samples were first heated to 97°C to melt any crystallinity, followed by quenching to −133°C. A heating rate of 10°C/min was used in all cases. The glass transition temperature (T_g) was taken as the midpoint of the transition of the second scan, while the melting point temperature (T_m) as the maximum of the endothermic transition of the first scan.

RESULTS AND DISCUSSION

The copolyester/PU blends with low copolyester content were transparent at room temperature. The blends with high copolyester content were opaque but became clear just above the melting point of the copolyester. The DSC study revealed a single glass transition temperature for each blend which varied with blend composition as shown in Figure 1. These suggests that the blend presents a homogeneous single amorphous phase, i.e., the two components are miscible in the amorphous phase and in the melt.

Several theoretical and empirical equations have been used to describe the T_g–composition dependence of miscible blends. One of these, the Fox equation,[10] is written as

$$1/T_g(\text{blend}) = W(\text{copolyester})/T_g(\text{copolyester}) + W(\text{PU})/T_g(\text{PU}) \quad (1)$$

where $T_g(\text{blend})$ is the glass transition temperature of the blend, T_g(copolyester) and T_g(PU) are those of the plain copolyester and PU, and
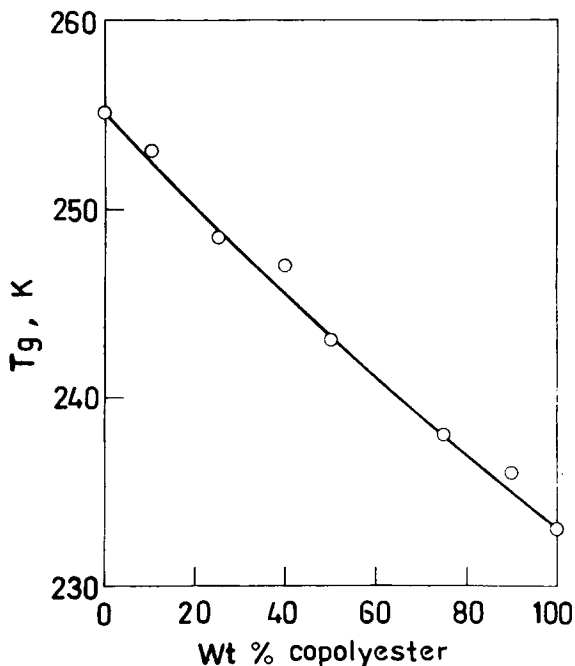
Fig. 1. Glass transition temperatures for the copolyester/PU blends plotted vs. blend composition. The curve is as predicted by the Fox equation.

W (copolyester) and W (PU) are the corresponding weight fractions. Equation (1), as shown by Figure 1, fits the experimental T_g data quite well.

By measuring the areas under the melting peaks, it should be possible to evaluate the heat of fusion and the fractional crystallinity. The crystallinity based on total blend, X_c(blend), and the crystallinity of the copolyester in the blend, X_c(copolyester), were calculated from

$$X_c(\text{blend}) = \Delta H_f(\text{blend})/\Delta H_f^0(\text{PEA}) \qquad (2)$$

$$X_c(\text{copolyester}) = \Delta H_f(\text{copolyester})/\Delta H_f^0(\text{PEA}) \qquad (3)$$

where $\Delta H_f^0(\text{PEA}) = 122$ J/g is the heat of fusion for 100% crystalline poly(ethylene adipate),[11] and $\Delta H_f(\text{blend})$ and $\Delta H_f(\text{copolyester})$ are the observed heat of fusion for the total blend and for the copolyester in the blend, respectively. The results so obtained with the other resulting thermal properties from the DSC scans are presented in Table I. It can be seen that the values of X_c(copolyester) is rather low. Particularly, for the pure copolyester, X_c(copolyester) = 27.1%. And for the blend, the crystallinity based on total blend, X_c(blend) is even lower. The low crystallinity of the copolyester and the blends was also verified by X-ray diffraction as shown in Figure 2.

The temperature dependence of permeation coefficients of H_2, N_2, O_2, and CO_2 through PU, the copolyester, and the blends, from 20 to 80°C, is shown in the form of Arrhenius plots in Figure 3. For PU a straight line is obtained for all gases, because no transition of PU exists in the above range of temperature

TABLE I
Thermal Properties of Copolyester/PU Blends[a]

Copolyester/PU	T_m (°C)	ΔH_f (blend) (cal/g blend)	ΔH_f (copolyester) (cal/g copolyester)	X_c (blend) (%)	X_c (copolyester) (%)	T_g (K)
0/100		0	0	0	0	255
10/90	43	2.8	28	2.3	23	253
25/75	43	8.9	35.6	7.3	29.2	248.5
40/60	44	14.4	36.0	11.8	29.5	247
50/50	47	18.5	37.1	15.2	30.4	243
75/25	51	27.0	36.0	22.1	29.5	238
90/10	51	32.9	36.6	27.0	30.0	236
100/0	52	33.1	33.1	27.1	27.1	233

[a] Data in columns 2–6 refer to the first scans of as-cast samples; T_g data in the last column refer to the second scan.

[Fig. 3(a)]. For the copolyester, discontinuities of the curves appear near the melting temperature [Fig. 3(b)]. Furthermore, for the blends with low copolyester content up to 40 wt % [Figs. 3(c)–(e)], abrupt changes in slope of the curves are clearly shown. The temperatures where the abrupt changes in slope appeared in Arrhenius plots are indicated in the figure. They approximately
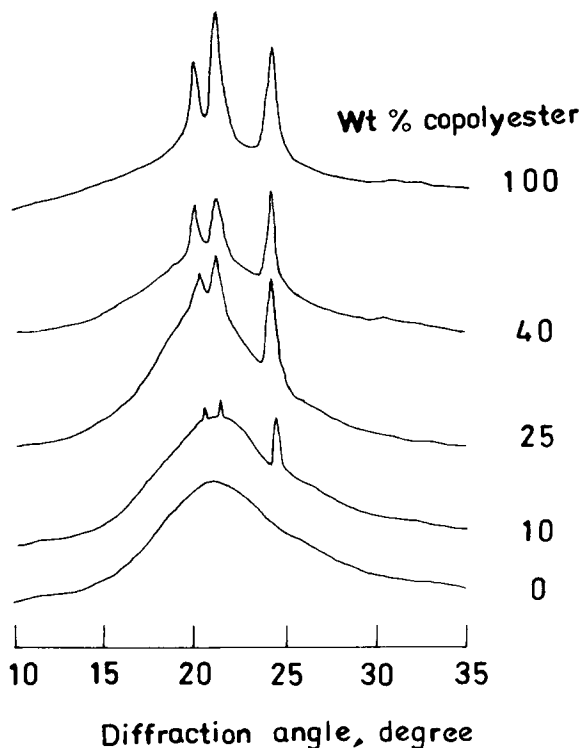
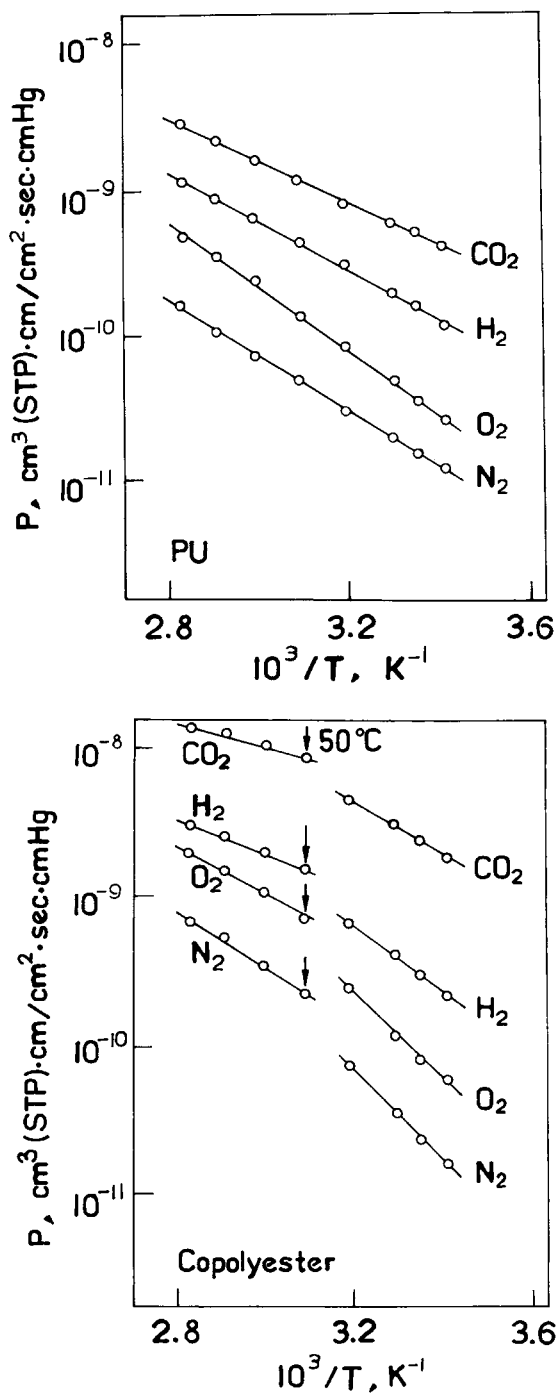Fig. 2.   X-ray diffraction diagram of the copolyester/PU blends.

Fig. 3. Arrhenius plots of permeability coefficients for (a) PU, (b) the copolyester, and for their blends containing: (c) 10, (d) 25, and (e) 40 wt % copolyester.

correspond to the melting points (T_m) of the copolyester in the blends and in the pure state determined by DSC as listed in Table I. Thus, the phenomena can be attributed to the changes of phase structure in the blends and in the
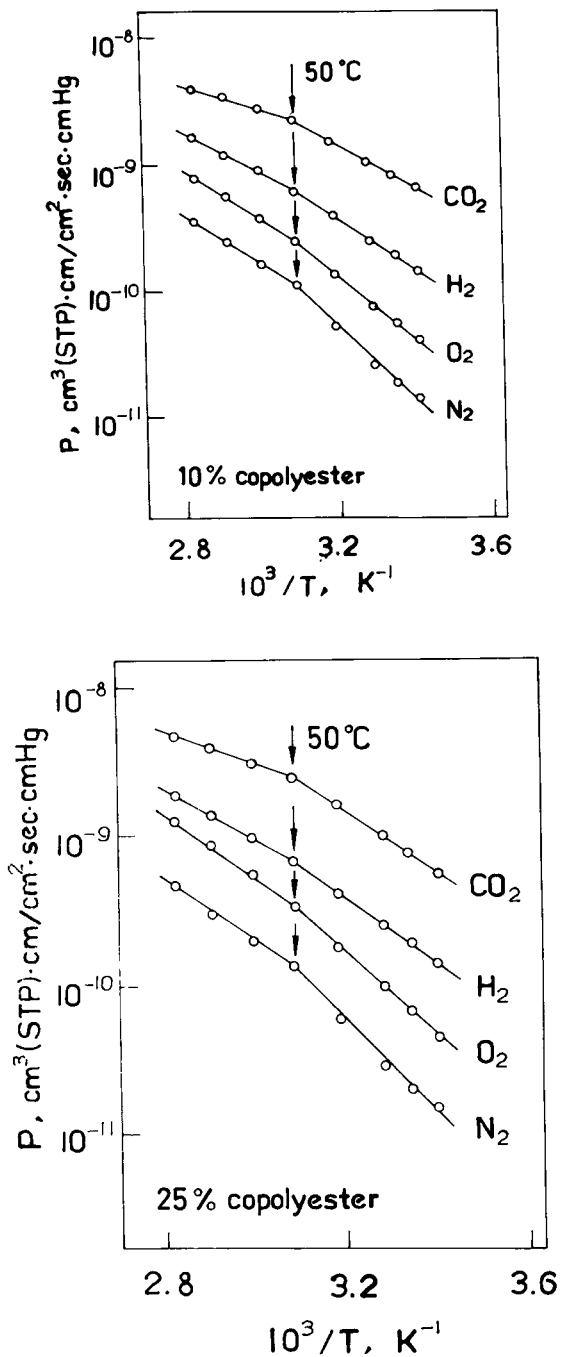
Fig. 3.   (Continued)

copolyester when temperature is elevated over the melting point of the copoly-
ester. The changes in phase structure can strongly affect the transport be-
havior of gas through a polymer blend. In general, for crystalline polymers, as
well as polymer blends containing crystalline phase, the phase structure will
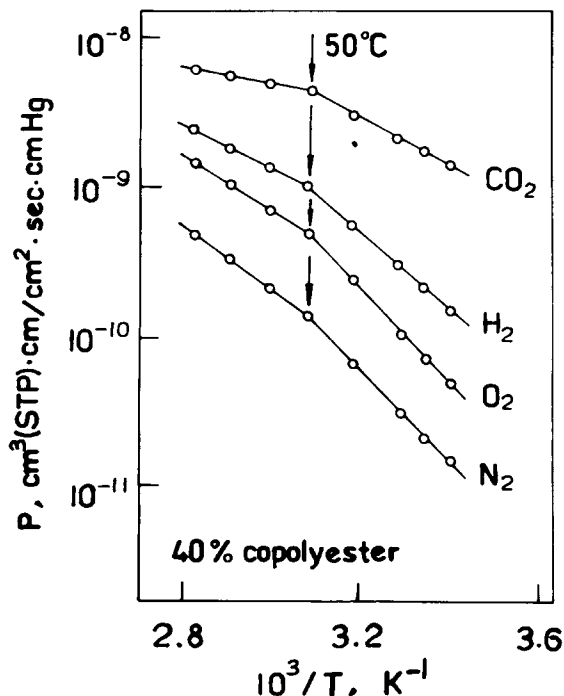
Fig. 3. (Continued)

change when temperature is elevated above T_m. As a result, discontinuities or abrupt change in slope in Arrhenius plot of gas permeability vs. temperature occur, depending on the crystalline level. This has been seen for crystalline homopolymers.[12] Naturally, the case is also expected for polymer blends containing crystalline components. Indeed, it has been confirmed in the miscible PEO/PU blends by our previous work.[8] In the present case, only abrupt changes in slope in Arrhenius plots appear, which is due to the low crystallinity of the blends. For the blend with 40 wt % copolyester, the crystallinity based on total blend, X_c(blend), only reaches 11.8% (Table I).

It can be also seen from Figure 3 that different values for activation energy for permeation, E_p, are expected for above and for below the melting point of the copolyester. The results are shown in Figure 4. The figure displays two types of activation energy-composition curves for below [Fig. 4(a)] and above [Fig. 4(b)] the melting point of the copolyester. The degree of crystallinity within a polymer affects the rate of transport of matter since it has been shown[13,14] that only the amorphous fractions take part in the phenomenon. This, of course, is reflected in lower E_p values above the T_m of the copolyester for the pure copolyester and the blends as shown in Figure 4.

It is generally accepted that the mechanism of gas permeation through polymer films is first the dissolution of the gas at the polymer surface, second the molecular diffusion of the gas through the polymer matrix, and finally the evaporation of the gas at the other polymer-gas interface. The first two steps controlled the rate of the process. It has been known[15] that the permeability
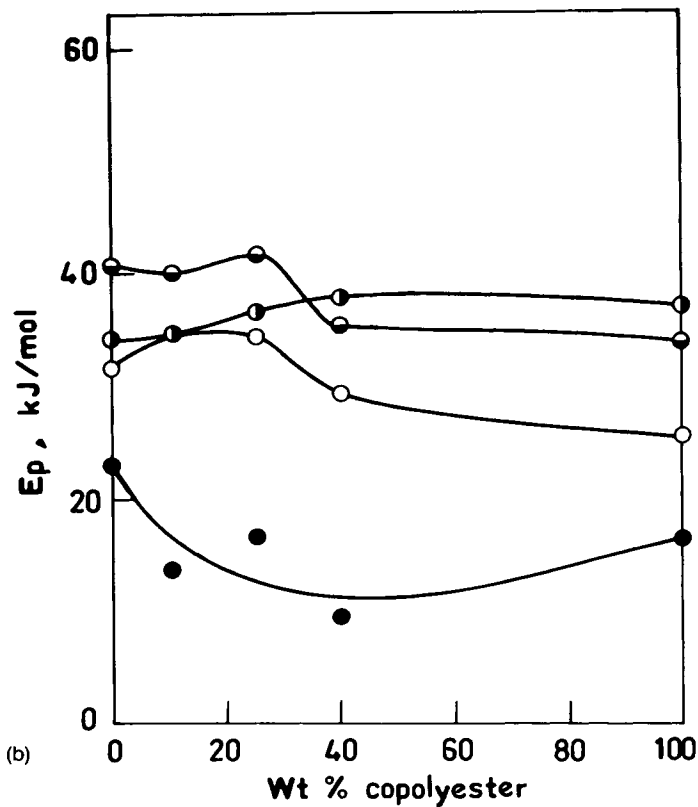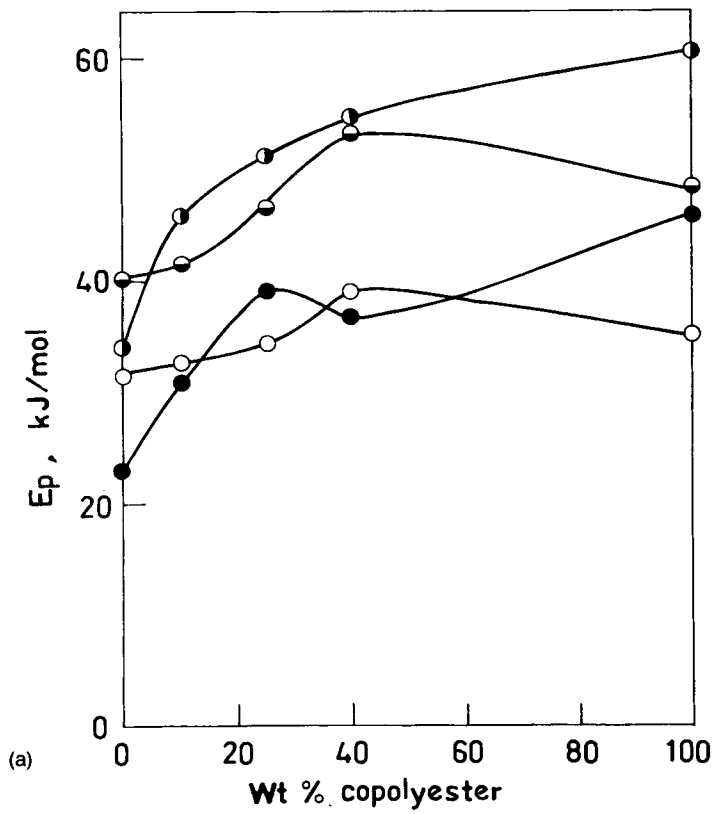
Fig. 4. Activation energy for permeation of H_2 (○), N_2 (◑), O_2 (◒), and CO_2 (●) vs. blend composition: (a) below and (b) above the melting point of copolyester.
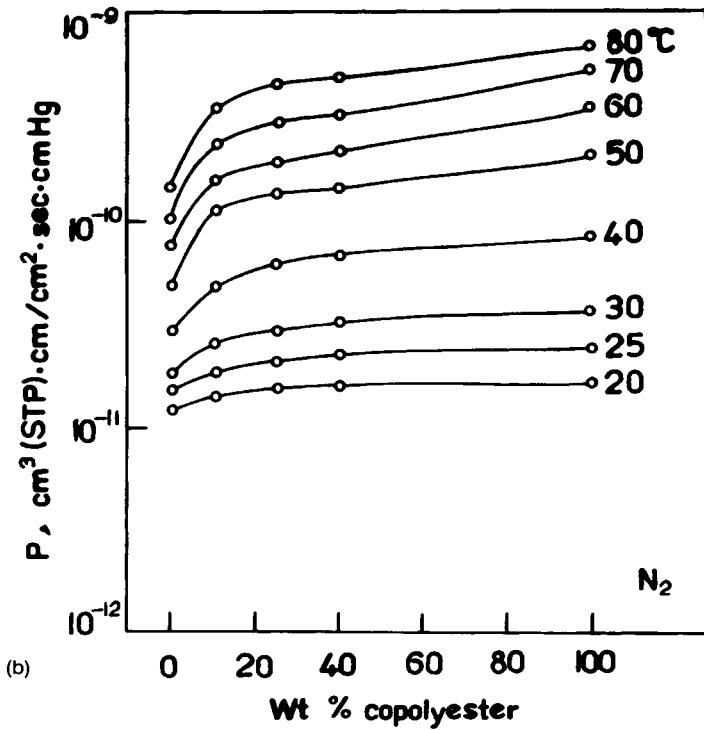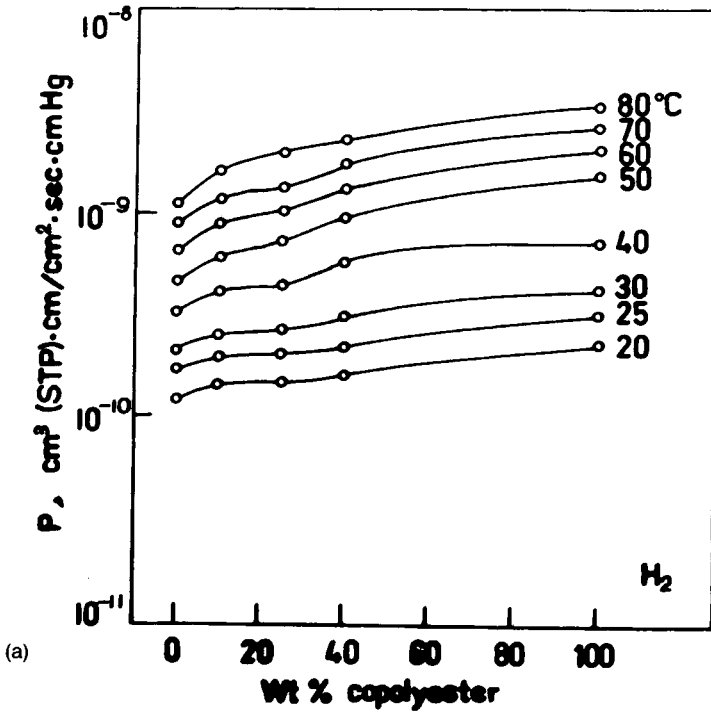
Fig. 5.   Permeability coefficients vs. blend composition: (a) H_2; (b) N_2; (c) O_2; (d) CO_2.
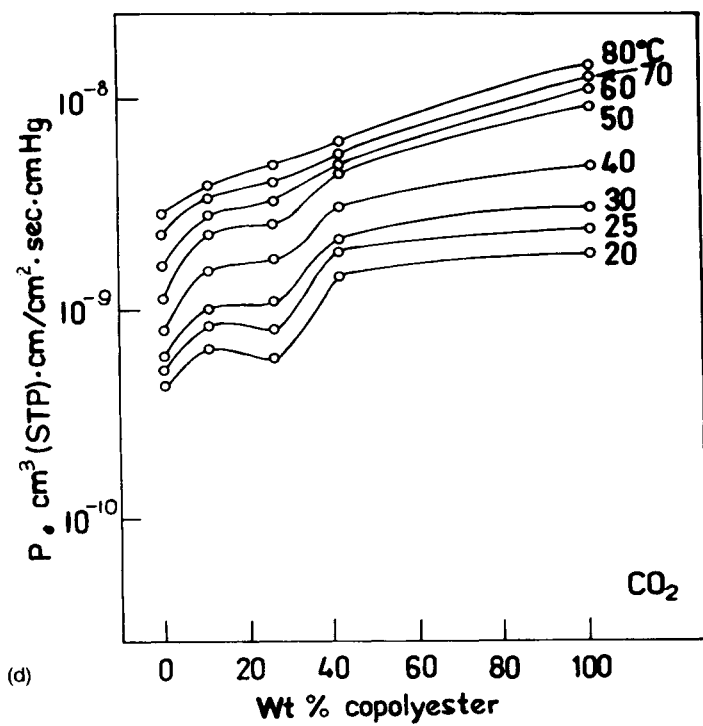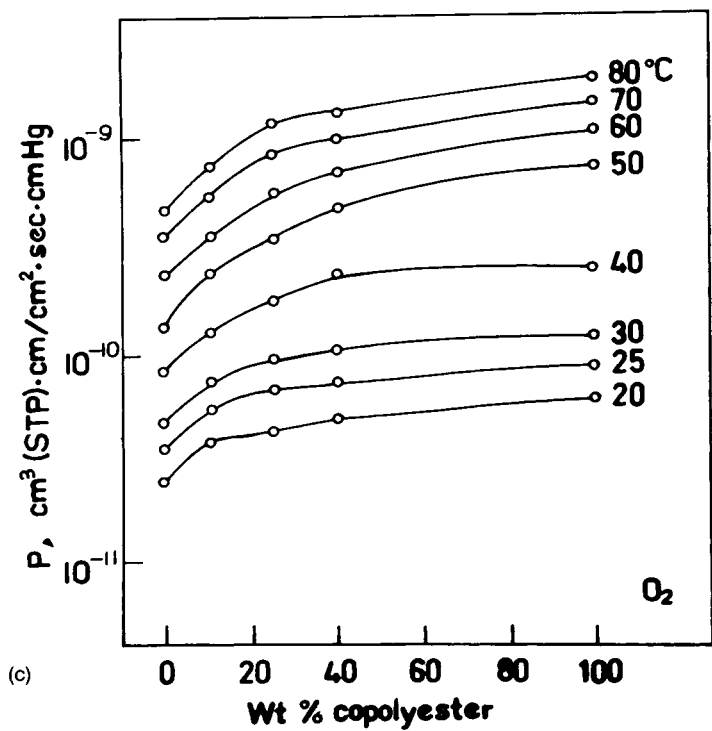
Fig. 5.   (*Continued*)

coefficient P is the product of the diffusion and the solubility coefficients, D and S, i.e.,

$$P = DS \qquad (4)$$

and the activation energy for permeation, E_p, is the sum of the activation energy for diffusion, E_D, and the heat of solution, ΔH_s, i.e.,

$$E_p = E_D + \Delta H_s \qquad (5)$$

The E_D was found to be proportional to a certain power of the molecular diameter of the penetrants.[16] For the present case, the E_D for CO_2 should be larger since CO_2 is larger. However, the E_p for CO_2 is so low as shown in Figure 4. This must imply that the condition that the ΔH_s is quite negative for eq. (5) is obeyed.

The relationship between permeability and blend composition is related to the phase structure which the blend has. Since the copolyester/PU blends have different phase structures above and below the melting point of the copolyester, there should be somewhat different types of permeability–composition curves. However, this phenomenon is not evident in Figure 5 as that for the PEO/PU blends,[8] which is because of low crystallinity of the copolyester due to the irregularity of the chain structure. The melting of the so little crystalline copolyester was not able to influence effectively the relation between permeability and blend composition. Rates of gas permeation for the blends slightly increase with increasing copolyester content and log P vs. copolyester content is basically an increasing function. The permeability P of a miscible blend B of polymer 1 and polymer 2 behaves according to

$$\ln P_B = \phi_1 \ln P_1 + \phi_2 \ln P_2 \qquad (6)$$

where ϕ is the volume fraction.[1] The densities of the copolyester and PU are 1.261 and 1.267 g/cm^3, respectively; the volume fractions in eq. (6) thus could be considered approximately as the related weight fractions. The permeability data in Figure 5 exhibit notably positive deviations from eq. (6). This indicates that no favorite interaction energy term or free volume effect exists for this system with forced miscibility at the mer level.[17] The blends are not molecularly homogeneous, although the T_g measurements by DSC suggest the miscibility for the system. The DSC measures a T_g as a change in specific heat that results from long range cooperation of molecules. That long range cooperation is rather greater than 2000 Å. However, gas permeation probes the structure at dimensions much smaller than 2000 Å and responds to the heterogeneity.[18,19] The miscibility of the copolyester/PU blends did not extend to the ångstrom level.

It is also noted that the permeability–composition relationships for CO_2 is somewhat special. The transport mechanism of CO_2 through polymers is generally considered more complex owing to strong interactions between CO_2 molecule and polymers and to usually a higher value for the solubility coefficient.[12,20]

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