

Permeation of CO₂ through Polyurethane

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Synopsis

The permeability of CO₂ through polyurethane was investigated. It is found that the permeability increases with the decrease of hard segment content and the increase of soft segment length; however, no change of activation energy is involved. The permeability increases with the elevation of annealing temperature. The temperature dependence of permeability observes the Arrhenius equation at temperatures below 60–80°C, but it deviates at temperatures above this range. This deviation would be attributed to the increase of mixing of hard and soft segments as a result of the dissociation of short-range order in hard segment domains.

INTRODUCTION

It is well known that the gas permeation through a dense polymer membrane is a solution–diffusion process. The gas permeability depends on the nature of polymer and its morphology in a scale comparable to the size of the gas molecule permeated. Thus, the determination of gas permeability can provide information about the nature of polymer microstructure and the mobility of polymer chain.¹

Polyurethane is a linear segmented block copolymer. It undergoes phase separation in which the urethane and the macroglycol segments cluster into hard and soft domains, respectively, due to the incompatibility of the two dissimilar types of segment. The hard domains act as physical crosslinks or filler particles in the rubbery soft domains. Their morphology is sensitive to both chemical structure and thermal history. It is found that the polyurethanes exhibit excellent physical properties and blood compatibility, which are attributed to their two-phase morphology. Considerable studies have been worked out to investigate the structure-property relationship of polyurethanes,² but little work has been reported on its gas permeation property.^{3,4} In this paper, we present studies on the relationship between the gas permeation behavior and the change of microstructure by using CO₂ as permeate.

EXPERIMENTAL

Polyurethanes were synthesized by a two-step solution polymerization process.⁵ The soft segments of polyether urethane and polyester urethane were poly(propyl oxide) (PPO) and poly(tetramethylene adipate glycol) (PTMAG) respectively. The hard segments were derived from 4,4'-diphenylmethane diisocyanate chains extended with 1,4-butanediol. Table I shows their chemical characterization. The polyurethanes in 5% DMF solution were cast into films

TABLE I
Chemical Parameters of Polyurethanes Studied

Sample	Soft segment	Volume fraction of hard segment (%)	Molecular weight of soft segment (g/mol)
ET-35-1	PPO	31.9	1095
ET-40-1	PPO	36.6	1095
ET-46-1	PPO	42.6	1095
ET-54-1	PPO	50.5	1095
ET-60-1	PPO	56.4	1095
ET-68-1	PPO	64.8	1095
ET-40-2	PPO	40.0	2235
ES-40-2	PTMAG	40.0	1860

on glass plate. The solvent was evaporated at 70°C, and the films were then dried at 40°C for 72 h under vacuum.

The permeability of CO₂ in polyurethane films was measured by gas chromatography (Gas Chromatography 102, made by Shanghai Instrument Factory). Hydrogen was used as the carrier gas. A stainless steel column of 1 m in length and 3 mm inner diameter was filled with 60–80 mesh GPX-401 support, porous polydivinylbenzene (from Chemical Reagent Co., Shanghai, China). The detector was a thermal conductive cell.

A small film was tightly sealed on a permeation cell. The downstream face of the cell was connected to the GC column through a triple valve. The CO₂ pressure was 0.8 kg/cm². The volume of gas permeated per unit time was measured from the peak area of chromatogram, from which the permeability of CO₂ under standard condition can be calculated by

$$P_g = T_0 P V l / 76 P_0 T A t \quad (1)$$

where P_0 and T_0 are the pressure and temperature under standard condition, P and T are the experimental pressure and temperature, V is the volume of CO₂ permeated through the film, l is the film thickness, A is the area of film, and t is the time of permeation.

DSC measurement was performed with 10 mg sample using a DuPont 1090B thermal analyzer. The heating rate was 20°C/min over the temperature range –80–0°C and 10°C/min over the temperature range 0–250°C.

Two kinds of thermal treatment of films were performed in a specially designed electric oven controllable to ± 1°C under continuous purge of dry nitrogen. The annealing-quenching treatments were performed on sample ET-68-1, which was annealed for 20 min at 20, 40, 60, 80, and 100°C, respectively, and then quenched in liquid nitrogen for DSC measurements or on cool metal surface for gas permeability measurements. These measurements were taken at once after quenching. The samples ET-46-1, ET-68-1, and ES-40-2, which were annealed at different temperatures and then cooled very slowly, were treated similarly. None of the specimens were reused after each experiment.

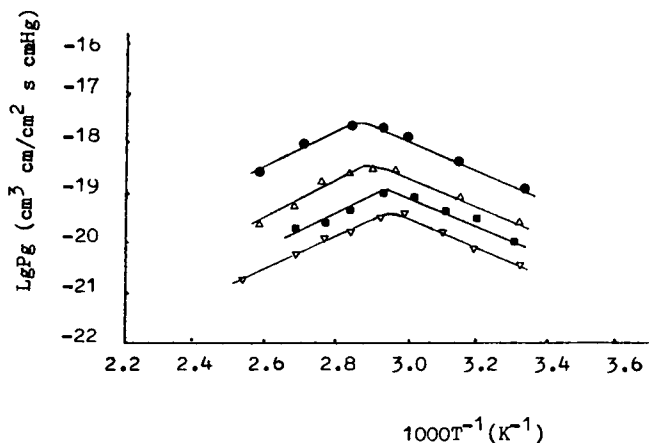


Fig. 1. Arrhenius plot for CO₂ permeation through: (●) ET-46-1; (Δ) ET-54-1; (■) ET-60-1; (▽) ET-68-1.

RESULTS AND DISCUSSION

Figure 1 shows the data plotted with $\ln P_g$ vs. $1/T$. A linear relationship between $\ln P_g$ and $1/T$ below the temperature range of 60–80°C is obtained; this indicates that the Arrhenius expression governs the temperature dependency of permeation for polyurethane under study. It is typical in the diffusion process. The permeability coefficients at 26°C and the activation energies for permeation are listed in Table II. For polyether urethane, both the increasing of the hard segment content and the decreasing of the soft segment length result in a decrease of permeability coefficients, but it makes no difference to the activation energy, implying the permeation route is similar.

Figure 2 is a plot of P_g vs. the content of hard segment at 26°C for the polyether urethane with soft segment of molecular weight 1095. The relationship between P_g and hard segment content is linear. Extrapolating this line to zero percentage of hard segment provides a theoretical permeability of the soft segment in the absence of hard segment. Table III shows the extrapolated permeability of pure soft segment at several temperatures. The value of activation

TABLE II
Permeability Coefficient and Activation Energy

Sample	$P_g \times 10^9$ (cm ³ cm/cm ² s cm Hg)	E (kJ/mol)
ET-35-1	8.81	19.5
ET-40-1	7.35	19.2
ET-46-1	6.46	19.8
ET-54-1	3.57	19.4
ET-60-1	2.53	19.4
ET-68-1	1.31	20.1
ET-40-2	13.1	19.8

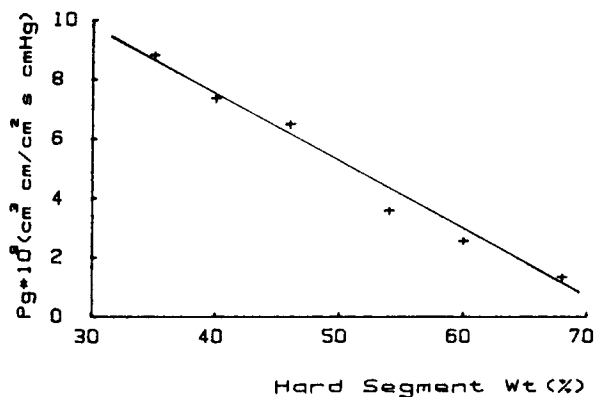


Fig. 2. Plot of CO₂ permeability vs. content of hard segment for polyurethane with 1095 molecular weight of polyether soft segment.

energy of pure soft segment thus obtained is 19.5 kJ/mol, which is the same as that of polyurethane listed in Table II. This suggests that, in polyurethane, the gas permeation occurs primarily through the “nearly pure” soft segment domains in which the chain mobility of soft segments is not influenced by the presence hard segment, and the hard segments act only as nonpermeable filler particles. Similar results have been reported by Micheal and Bixler for semi-crystalline PE.⁶

It could be found that, from Figure 1, the gas permeability decreases with the rising of temperature above 60–80°C, indicating that there is a remarkable deviation from the the Arrhenius temperature dependency determined below this range. The deviation observed in this study is similar to the results obtained from SBS block copolymer by Odani et al.,⁷ which shows that the permeability of CO₂ tends to decrease when it is above the glass transition temperature of PS hard segment. This is a challenging problem which may be associated with the multiphase character of block copolymer. By the morphological model proposed by Wilkes et al.,^{8,9} the hard and soft segments in polyurethane are clustered into separate domains, and there are interfaces which are the phase boundary and the junction of hard and soft segments in which the chain mobility of soft segment is restricted by hard segments. Thus it would lose some of pure domain which transforms into more mixed system of hard and soft segments during the rise of temperature. Because the “nearly pure” soft segment domains are the main permeate route as mentioned above, it is reasonable to suggest that the soft segment in the interface offers less contribution to the gas permeation, and the decrease of permeability above 60–80°C may be attributed to the decrease of the content of such pure soft domain, as a result of hard and soft segment mixing.

TABLE III
Extrapolated Permeability of Pure PPO Soft Segment

Temperature (°C)	26	30	35	40	45
P _g (cm ³ cm/cm ² s cm Hg) × 10 ⁸	2.3	2.8	3.1	3.4	4.0

TABLE IV
The T_g of Soft Segment of ET-68-1 after Quenching

Annealing temperature (°C)	T_g of soft segment (K)
20	252.9
40	252.7
60	257.6
80	262.4
100	264.1

To detect the temperature dependency of the phase separation, the sample ET-68-1 was annealed at different temperatures, and then quenched to fix the given morphology, which is characterized by the glass transition temperature (T_g) of the soft segment. From Table IV, it could be found that the T_g of soft segment remains the same when the annealing temperature is below 60°C. This implies that, in this temperature range, the mixing of hard and soft segment does not vary significantly with the change of temperature; the morphology is "frozen" so that the gas permeability could be represented by Arrhenius equation. However, when the sample is annealed between 60 and 120°C, the T_g of soft segment tends to be higher when the annealing temperature is elevated, indicating that the hard-soft segment mixing is promoted by the increasing of temperature. The extensive mixed morphology would result in the decrease of the permeability of polyurethane as mentioned above, even though there is an increasing capability of chain mobility of hard segment which might result in an increase in the permeability of hard segments.

DSC study shows that there is an endothermal peak at about 60–80°C (see Table V), which is attributed to the dissociation of short-range order in hard segment domain. From Table V, it is also found that the temperatures at which permeability begins to deviate from Arrhenius temperature dependency are consistent with the dissociation temperature of short-range order in hard segment domain. This implies that the increase of hard-soft segment mixing is the result of significant increasing mobility of some hard segment with the dissociation of short-range order in hard segment domain.

TABLE V
Effect of Dissociation of Short-Range Order on the Temperature Dependence of Permeation of Polyurethane

Sample	Annealing condition	Temp at which permeation deviates (Arrhenius equation) (°C)	Dissociation temp of short-range order (°C)	ΔH_1 (kJ/mol)
ET-46-1	Control	80	80, 90	18
	150°C/4 h	70	70, 80	9
	170°C/4 h	70	80	10
ET-68-1	Control	60	60	11
	150°C/4 h	80	77	10
	190°C/4 h	80	80	11

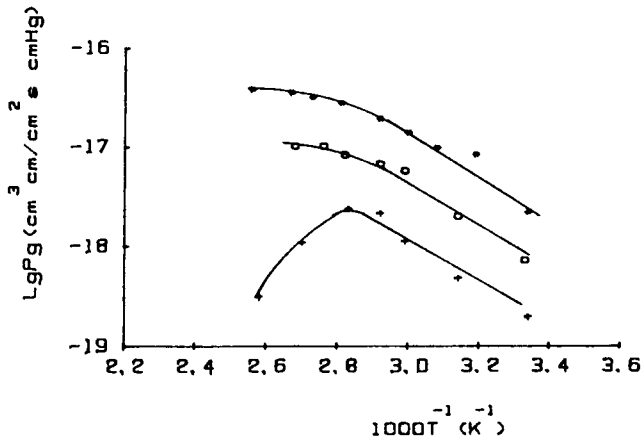


Fig. 3. Arrhenius plot for CO_2 permeation through ET-46-1: (+) control; (O) annealing at 150°C for 4 h; (*) annealing at 170°C for 4 h.

It was found by Cooper et al.^{10,11} that the morphology of polyurethane is strongly dependent on its thermal history. In order to study the morphological effect of sample on its gas permeability, in addition to performing the annealing-quenching treatment as discussed above, a slow-rate cooling ($1\text{--}2^\circ\text{C}/\text{min}$) after annealing in a higher temperature ($150\text{--}190^\circ\text{C}$) was also performed. It is found that the extent of the deviation from Arrhenius equation is influenced by such treatment (see Figs. 3 and 4) and related to the decrease of the amount of short-range order in hard segment domains which can be estimated from its dissociation enthalpy ΔH_1 . From Table V, it is seen that, for sample ET-46-1, the ΔH_1 decrease significantly with annealing, implying that the amount of short-range order, which is reorganized to long-range order or microcrystalline as obtained by Seymour and Cooper¹⁰ decreases in this case. Thus, the increase

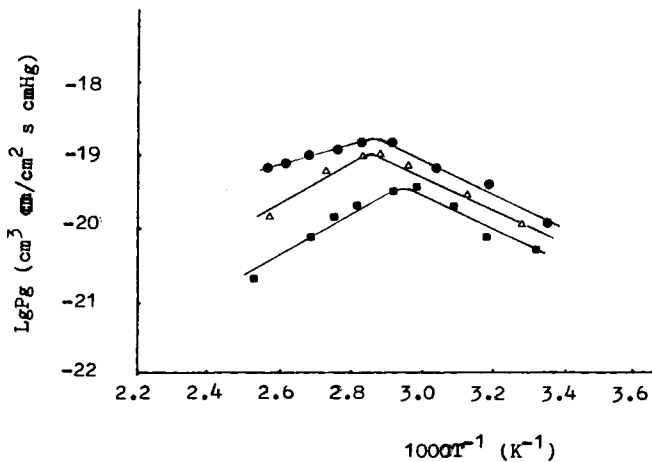


Fig. 4. Arrhenius plot for CO_2 permeation through ET-68-1: (■) control; (Δ) annealing at 150°C for 4 h; (\bullet) annealing at 190°C for 4 h.

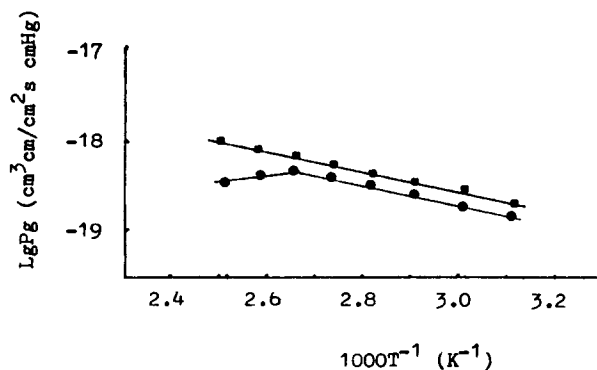


Fig. 5. Arrhenius plot for CO₂ permeation through ES-40-2: (●) control; (■) annealing at 180°C for 4 h.

of hard-soft segment mixing resulted from the dissociation of short-range order is less than that of control sample, so that the extent of deviation is reduced (see Fig. 3). For sample ET-68-1, the ΔH_1 does not change notably with annealing and its dissociation temperature shifts to higher temperature slightly, indicating the amount of short-range order remains roughly constant but becomes more ordered. It is found that the degree of deviation does not change significantly but the temperature at which the deviation begins to shift slightly to higher temperature (see Fig. 4).

It is interesting to note that, from Figure 5, the endothermal peak in DSC spectrum disappears for sample ES-40-2 from 40 to 120°C by annealing at 180°C for 4 h, the short-range order reorganizes completely into the structure of higher order whose dissociation temperature is beyond 120°C. In this temperature range, the rising of temperature does not change the morphology and an Arrhenius temperature dependence is obtained below 120°C. Meanwhile, the permeability of the control sample deviates from the Arrhenius equation when the temperature is beyond 60°C, at which the short-range order begins to dissociate.

Table VI lists the permeability and the T_g of soft segment after annealing and slow-rate cooling treatment. It could be seen that permeability of annealed samples is higher than that of control sample and it rises with the increase of annealing temperature; however, the activation energy of permeation remains

TABLE VI
Effect of Annealing on Permeation Behavior of Polyurethane

Sample	Annealing condition	T_g of soft segment (K)	$P_g \times 10^9$ (cm ³ cm/cm ² s cm Hg)	E (kJ/mol)
ET-46-1	Control	246.2	6.46	19.8
	150°C/4 h	240.6	8.34	20.1
	170°C/4 h	234.5	9.60	19.9
ET-68-1	Control	252.9	1.31	20.1
	150°C/4 h	251.5	1.38	20.0
	190°C/4 h	250.1	1.44	20.4

unchanged. Meanwhile, the T_g of soft segment is lower than that of control sample. All of these imply that slow-rate cooling gives enough time to attain better equilibrium, resulting in a more complete phase separation which favors gas permeation.

In order to obtain further morphological information, Barrer's equation is used to analyze the permeability data taking the hard segment domains as nonpermeable filler particle. The equation is¹²

$$P_g = P_{gs} \frac{V_s}{\tau} \quad (2)$$

where P_g is permeability coefficient of polyurethane, P_{gs} is the permeability coefficient of pure soft segment domain with volume fraction V_s , its value is 2.3×10^{-8} ($\text{cm}^3 \text{ cm/cm}^2 \text{ s cm Hg}$), and is commonly called the "tortuous factor," which can be calculated from the expression suggested by Nielson

$$\tau = 1 + 0.5V_h \quad (3)$$

where V_h is the volume fraction of hard segment. Thus, the volume fraction of pure soft segment domain can be obtained from the permeability result. The value $V - V_s$ represents the volume fraction of soft segment in the interface (here V is the total volume fraction of soft segment). It is reasonable to suggest that the value of $(V - V_s)/V$ can be used to denote the degree of microphase separation. From Table VII, it could be seen that its value increases with the increasing of hard segment content; this means that the phase separation decreases.

Table VIII lists the permeability at 26°C for sample ET-68-1, with different annealing-quenching treatment, the permeability remains unchanged when annealing temperature is below 60°C. Beyond this temperature, the higher the annealing temperature, the lower the permeability. The value of $(V - V_s)/V$ increases with the increasing of annealing temperature when it is beyond 60°C. The result is consistent with the result from T_g measurement as mentioned above.

CONCLUSION

The CO_2 permeability coefficients were measured using gas chromatographic method for polyurethane film with different urethane contents and different

TABLE VII
Effect of Hard Segment Content on the Phase Separation of Polyurethane

Sample	$\tau = 1 + 0.5V_h$	$V_s = \tau \times P_g/P_{gs}$ (%)	$(V - V_s)/V$ (%)
ET-35-1	1.16	44.4	31.7
ET-40-1	1.18	37.7	37.0
ET-46-1	1.21	34.0	40.8
ET-54-1	1.25	19.0	57.0
ET-60-1	1.28	14.1	64.8
ET-68-1	1.32	7.5	78.5

TABLE VIII
Effect of Temperature Elevation on the Phase Separation of ET-68-1

Temperature (°C)	$P_g \times 10^9$ (cm ³ cm/cm ² s cm Hg)	$V_s = \tau \times P_g/P_{gs}$ (%)	$(V - V_s)/V$ (%)
26	1.31	7.5	78.7
40	1.30	7.5	78.7
60	1.33	7.6	78.5
80	0.92	5.2	85.2
100	0.71	4.2	88.1
120	0.60	3.4	90.4

types of soft segments. Both the increase of the soft segment length and decrease of the hard segment content result in the increase of permeability, and annealing can improve it as well. Meanwhile the activation energy remains roughly constant, indicating that it makes no change to the permeation route. An Arrhenius expression can describe the temperature dependence of permeation below 60–80°C, and, beyond this temperature range, deviation is found between the Arrhenius equation and the experimental results. The deviation might be associated with the increased mixing of hard and soft segment, or the decreased pure soft segment in soft domain.

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