NOTE

Temperature Dependence on Gas Permeability and Permselectivity of Poly(lactic acid) Blend Membranes

By Tomomi KOMATSUKA[1] and Kazukiyo NAGAI[1,*]

Poly(lactic acid) (PLA, Scheme) is an environmentally friendly and biodegradable polymer substance (1). Due to the advantages it offers including better biological degradation behavior for bio-recyclable materials, PLA is expected to become a replacement material for petroleum-based plastics, such as polyethylene, polyvinylchloride, and poly(ethylene terephthalate). At present, PLA is popularly used in the manufacture of packaging materials (*e.g.*, films, membranes), foaming materials (*e.g.*, containers), and resins. These materials are expected to be used at high temperatures in several applications such as in films and containers for heating frozen foods in microwave ovens and a retort in boiling water, and in resins for the bodies of electronic products (*e.g.*, computers and mobile phones). Toward further improvements, it is important to emphasize that the mechanical, thermal, and barrier properties are important in designing these materials.

There are some studies about temperature dependence on gas permeability and permselectivity of PLA homopolymers below their glass transition temperature (*i.e.*, glassy state) (2,3). However, there has been no research to date on the gas permeability and permselectivity of PLA homopolymers and blends above their glass transition temperature (*i.e.*, rubbery state). The same is the case for gas permeation and separation behavior across the glass transition of PLA homopolymers and blends.

In this study, the temperature dependence on gas permeability and permselectivity of PLA blends across their glass transition temperatures is therefore investigated for the first time. PLA is an interesting polymer whose oxygen permeability is not significantly affected by its isomer ratio and crystallinity (2–4). In the ranges of the L:D donor ratio of 98.7:1.3–50:50 and crystallinity of 0–25%, the oxygen permeability coefficients of the PLA samples were located in the values between 1.7×10^{-11} and 3.4×10^{-11} cm^3(STP)cm/(cm^2 s cmHg) at 30–35 °C. The PLA samples used in this study were those with properties within above ranges.

EXPERIMENTAL

Materials

The PLA membranes we used were the same samples
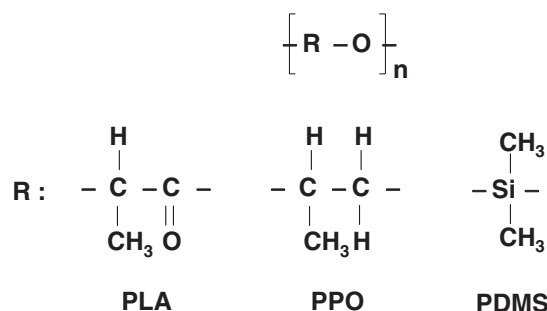
Scheme 1.

employed in our previous study (4). These were kindly prepared by Asahi Kasei Life & Living Co., Ltd., Suzuka, Japan. The base PLA polymers were $L_{96}D_4$ (L-donor 96 mol %, D-donor 4 mol %) and $L_{88}D_{12}$ (L-donor 88 mol %, D-donor 12 mol %). PLA membranes with different crystallinities were prepared by blending these two polymers; Blend 8/2 ($L_{96}D_4$:$L_{88}D_{12}$ = 8:2, Thickness: $24 \pm 1 \mu$m) and Blend 10/0 ($L_{96}D_4$ homopolymer, $L_{96}D_4$:$L_{88}D_{12}$ = 10:0, Thickness: $27 \pm 2 \mu$m).

The glass transition temperature (T_g) values of the Blend 10/0 and Blend 8/2 membranes were 62.3 °C and 60.5 °C, respectively. The crystallization temperature (T_c) values of the Blend 10/0 and Blend 8/2 membranes were 117 °C and 116 °C, respectively. The melting temperature (T_m) value of both blend membranes was 149 °C. The crystallinity (X_c) value, which was determined from differential scanning calorimeter of the Blend 10/0 membrane, was 24.8%, while that of the Blend 8/2 membrane was 7.4%.

Gas Permeation Measurements

The permeability coefficient (P) of pure gases (*i.e.*, hydrogen (H$_2$), oxygen (O$_2$), nitrogen (N$_2$), and carbon dioxide (CO$_2$)) in the PLA blend membranes was determined using a constant-volume/variable-pressure method according to the literature (5). The operating temperature was raised from 35 ± 1 to 85 ± 1 °C, which was much below T_c (*i.e.*, there was only the glass transition for PLA in this temperature range.). The feed pressure was between 39 and 75 cmHg and the

[1]Department of Applied Chemistry, Meiji University, 1-1-1 Higashi-mita, Tama-ku, Kawasaki 214-8571, Japan
*To whom correspondence should be addressed (Tel: +81-44-934-7211, Fax: +81-44-934-7906, E-mail: nagai@isc.meiji.ac.jp).

permeate side was maintained under vacuum. All permeation data were determined for at least three samples to ensure the reproducibility of the experimental results. In addition, the experiments were repeated at least thrice for each sample at a given temperature to confirm the reproducibility.

The ideal permselectivity of Gas A over Gas B ($\alpha(A/B)$) was expressed as the ratio of the permeability coefficient of Gas A over that of Gas B.

$$\alpha(A/B) = \frac{P(A)}{P(B)} \tag{1}$$

RESULTS AND DISCUSSION

Figure 1 presents the temperature dependence on the permeability coefficients for H_2, O_2, and N_2, and CO_2 in Blend 10/0 and Blend 8/2 membranes. During the experiments in this study, any hysteresis in the permeation data in both Blend 10/0 and Blend 8/2 membranes was not observed. In the whole temperature range used, the order of the permeability coefficients was the same for all gases for both Blend 10/0 and Blend 8/2 membranes: $H_2 > CO_2 > O_2 > N_2$. Additionally, as the temperature increased, all gas permeability coefficients increased.

In the region without any transition in polymers (*e.g.*, glass transition) and penetrant (*e.g.*, boiling point), the temperature dependence on gas transport through a polymer membrane generally follows Arrhenius rule (6). That is, there is a linear relationship between a transport parameter logarithm and the reciprocal of absolute temperature (T). P is expressed as

$$P = P_0 \exp\left(-\frac{E_P}{RT}\right) \tag{2}$$

where P_0 is the pre-exponential factor of permeation, E_P is the activation energy for permeation, and R is the gas constant. Across polymer T_g, there appears a transition on gas permeation. Therefore, the E_P value of gases in polymers is either larger or smaller above T_g than below T_g. Sometimes, no transition is observed; that is, the E_P values at above T_g and below T_g are the same with each other.

In Figure 1, both Blend 10/0 and Blend 8/2 membranes followed Arrhenius rule for all gases tested in this study. When experimental uncertainty was considered, it was difficult to indicate a distinct transition of gas permeability at T_g. Otherwise, the uncertainties might mask a small transition on permeation. We have found that Blend 10/0 and Blend 8/2 membranes belong to a family of polymers whose gas permeation is not significantly affected by a change in chain mobility at glass transition.

Table I summarizes the permeability coefficients at around room temperature ($P(T)$), P_0, and E_P for H_2, O_2, and N_2, and CO_2 in Blend 10/0 and Blend 8/2 membranes with some data from the literature (2,3,7,8). All literature data on PLA homopolymers were recorded below T_g. There were no data for hydrogen in PLA homopolymers from the literature. We estimated the P_0 and E_P values of our samples through the
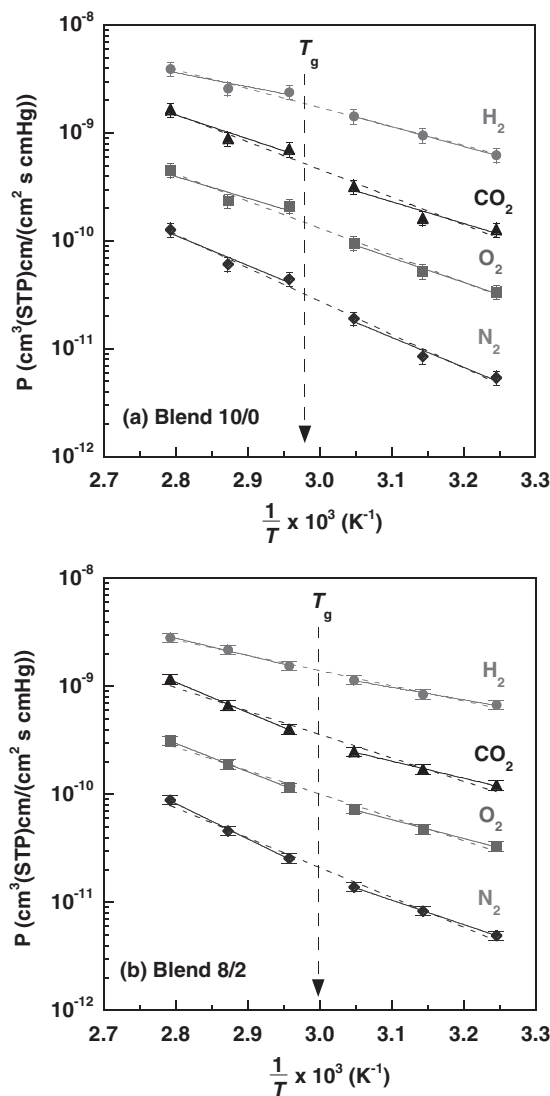
Figure 1. Temperature dependence on gas permeability (P) in (a) Blend 10/0 and (b) Blend 8/2 poly(lactic acid) (PLA) membranes. Gases: ●, H_2; ▲, CO_2; ■, O_2; ◆, N_2.

entire experimental temperature range (*i.e.*, 35–85 °C), because we could not observe a distinct transition on gas permeation at their T_g. This means that these P_0 and E_P values above T_g were the same as those below T_g. Gas permeability is significantly influenced by measurement temperature and feed gas pressure. Moreover, although a simple comparison between our blend data and the homopolymer values in the literature was difficult, for O_2, and N_2, and CO_2, Blend 10/0 and Blend 8/2 membranes had larger P_0 and E_P values compared with those of glassy PLA homopolymers.

The following empirical equation describes the relationship between $\log P_0$ and E_P/R (9).

$$\log P_0 = \frac{E_P}{R} \times 10^{-3} + Z \tag{3}$$

Regardless of the chemical structures of common polymers, the plot of $\log P_0$ and E_P/R provides the slope of 1×10^{-3} and the

Table I. Permeation parameters of hydrogen (H_2), oxygen (O_2), nitrogen (N_2), and carbon dioxide (CO_2)
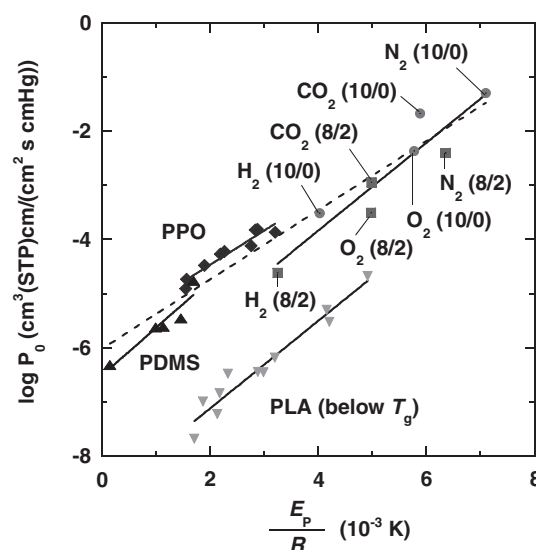of Blend 10/0 and Blend 8/2 poly(lactic acid) (PLA) and related polymers

Gas	Polymer	Crystallinity (%)	Temperature for P(T) (°C)	$P(T)$ $\left(\frac{cm^3(STP)cm}{cm^2 \cdot s \cdot cmHg}\right)$	Temperature range (°C)	P_0 $\left(\frac{cm^3(STP)cm}{cm^2 \cdot s \cdot cmHg}\right)$	E_P (kJ/mol)	Reference
H_2	PLA (Blend 10/0)	24.8	35	6.23×10^{-10}	35–85	3.09×10^{-4}	33.5	This work
	PLA (Blend 8/2)	7.4	35	6.77×10^{-10}	35–85	2.43×10^{-5}	27.0	This work
	PPO	0	30	1.26×10^{-8}	30–80	1.49×10^{-4}	23.6	7
	PDMS	0	25	5.73×10^{-8}	25–125	1.73×10^{-5}	14.1	8
CO_2	PLA (Blend 10/0)	24.8	35	1.27×10^{-10}	35–85	2.13×10^{-2}	48.9	This work
	PLA (Blend 8/2)	7.4	35	1.21×10^{-10}	35–85	1.14×10^{-3}	41.5	This work
	PLA (L:D = 98.7:1.3)	< 4%	30	1.10×10^{-10}	22.8–45.0	1.46×10^{-7}*	18.1	3
	PLA (L:D = 80:20)	0	30	5.1×10^{-11}	22.8–45.0	6.0×10^{-8}*	17.8	3
	PLA (L:D = 50:50)	0	30	7.1×10^{-11}	22.8–45.0	2.1×10^{-8}*	14.3	3
	PLA (L:D = 98:2)	40	35	2.32×10^{-10}	25–45	1.03×10^{-7}*	15.6	2
	PLA (L:D = 94:6)	25	35	1.71×10^{-10}	25–45	3.35×10^{-7}*	19.4	2
	PPO	0	30	7.06×10^{-8}	30–80	1.23×10^{-5}	13.0	7
	PDMS	0	25	2.85×10^{-7}	25–125	4.81×10^{-7}*	1.30	8
O_2	PLA (Blend 10/0)	24.8	35	3.36×10^{-11}	35–85	4.27×10^{-3}	47.9	This work
	PLA (Blend 8/2)	7.4	35	3.31×10^{-11}	35–85	3.12×10^{-4}	41.4	This work
	PLA (L:D = 98.7:1.3)	< 4%	30	2.6×10^{-11}	22.8–45.0	3.59×10^{-7}*	24.0	3
	PLA (L:D = 80:20)	0	30	1.8×10^{-11}	22.8–45.0	3.55×10^{-7}*	24.9	3
	PLA (L:D = 50:50)	0	30	1.7×10^{-11}	22.8–45.0	6.58×10^{-7}*	26.6	3
	PPO	0	30	8.29×10^{-9}	30–80	7.70×10^{-5}	23.0	7
	PDMS	0	25	5.33×10^{-8}	25–125	2.46×10^{-6}*	9.49	8
N_2	PLA (Blend 10/0)	24.8	35	5.40×10^{-12}	35–85	4.97×10^{-2}	59.0	This work
	PLA (Blend 8/2)	7.4	35	4.96×10^{-12}	35–85	3.99×10^{-3}	52.8	This work
	PLA (L:D = 98.7:1.3)	< 4%	30	5×10^{-12}	22.8–45.0	5×10^{-6}*	34.6	3
	PLA (L:D = 80:20)	0	30	2×10^{-12}	22.8–45.0	2×10^{-5}*	40.9	3
	PLA (L:D = 50:50)	0	30	3×10^{-12}	22.8–45.0	3×10^{-6}*	35.0	3
	PPO	0	30	3.34×10^{-9}	30–80	1.36×10^{-4}	26.7	7
	PDMS	0	25	2.50×10^{-8}	25–125	3.46×10^{-6}*	12.2	8

*These P_0 values were not listed in the original articles. We estimated them using Equation 2 for this study.

average Z value is −7.0 for rubbery polymers and −8.2 for glassy polymers. These Z values were determined by van Krevelen using mainly permeation data on polymers sourced from the literature (9). This trend reveals the importance that temperature dependence plays on the gas permeability of most polymers, which is changed at glass transition because the Z values below and above T_g are different from one another. We found that PLA is a rare polymer whose temperature dependence on gas permeability is the same across T_g.

In commercial applications, polymer materials are used either below or above T_g. They are never used at the conditions appearing in any transitions of polymers such as glass transition. The PLA used in this study was an interesting polymer whose temperature dependence on gas permeability was not significantly affected by T_g, crystallinity, and L/D composition. As compared to other polymers, this is a good characteristic especially for industrial application, because it indicates that the quality control for PLA products can be more easily achieved than that for others.

Figure 2 presents the P_0 value of the polymers listed in Table I as a function of the E_P value. In this figure, the data of two rubbery polymers whose chemical structures contain an ether group in the main chain like PLA (*i.e.*, poly(propylene oxide) (PPO) and polydimethylsiloxane (PDMS); Scheme) are also plotted. The data of both Blend 10/0 and Blend 8/2 membranes were gathered around the line of rubbery polymers

Figure 2. The preexponential constant (P_0) of Blend 10/0 (●) and Blend 8/2 (■) poly(lactic acid) (PLA) membranes, glassy PLA homopolymers (▼) (2,3), poly(propylene oxide) (PPO) (◆) (7), and polydimethylsiloxane (PDMS) (▲) (7,8) as a function of the activation energy of gas permeation (E_P).

PPO and PDMS. On the other hand, those of the glassy PLA homopolymers were located below the line of rubbery polymers.
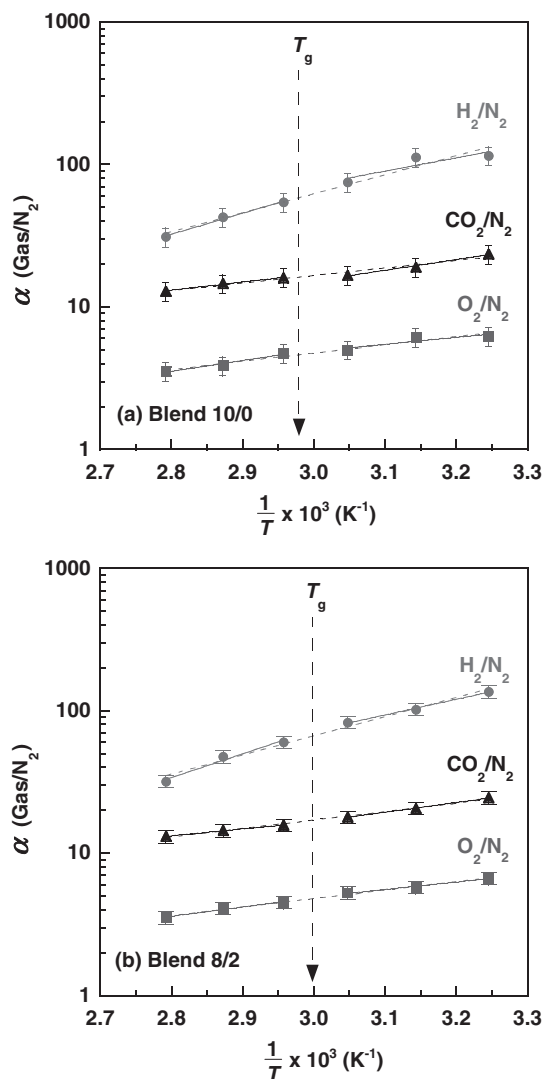
Figure 3. Temperature dependence on gas permselectivity (α) in (a) Blend 10/0 and (b) Blend 8/2 poly(lactic acid) (PLA) membranes. Gas pairs: ●, H_2/N_2; ▲, CO_2/N_2; ■, O_2/N_2.

In Equation 3, the slope was $0.81 \pm 0.12 \times 10^{-3}$ for Blend 10/0 and Blend 8/2 membranes, $0.63 \pm 0.07 \times 10^{-3}$ for PPO (7), $0.88 \pm 0.18 \times 10^{-3}$ for PDMS (7), and $0.81 \pm 0.07 \times 10^{-3}$ for the glassy PLA homopolymers. All values were smaller than the value of Equation 3 (*i.e.*, 1×10^{-3}). The Z value was -7.1 ± 0.7 for Blend 10/0 and Blend 8/2 membranes, -5.7 ± 0.2 for PPO (7), -6.5 ± 0.2 for PDMS (7), and -8.7 ± 0.2 for the PLA homopolymers. The Z value of Blend 10/0 and Blend 8/2 membranes, PPO, and PDMS was similar to that of rubbery polymers (*i.e.*, -7.0), while that of glassy PLA homopolymers was close to that of glassy polymers (*i.e.*, -8.2). Finally, when the slope and Z values were estimated using all the data of rubbery polymers containing an ether group in the main chain (*i.e.*, Blend 10/0 and Blend 8/2 membranes, PPO, and PDMS), the slope and Z values were $0.64 \pm 0.04 \times 10^{-3}$ and -6.0 ± 0.2, respectively.

Figure 3 presents the temperature dependence on the permselectivity of Gas over N_2 in Blend 10/0 and Blend 8/2

membranes. As expected from the order of gas permeability, the ranking of permselectivity of both membranes was $H_2/N_2 > CO_2/N_2 > O_2/N_2$. Additionally, as the temperature increased, all gas permselectivities decreased.

Using eqs 1 and 2, the permselectivity of Gas over N_2 ($\alpha(\mathrm{Gas}/N_2)$) is defined from the following.

$$\begin{aligned}\alpha(\mathrm{Gas}/N_2) &= \frac{P(\mathrm{Gas})}{P(N_2)} \\ &= \frac{P_0(\mathrm{Gas})}{P_0(N_2)} \exp\left(-\frac{E_P(\mathrm{Gas}) - E_P(N_2)}{RT}\right)\end{aligned} \quad (4)$$

In Figure 3, all gas permselectivities were obeyed by this equation (*i.e.*, Arrhenius rule). Like gas permeability, when experimental uncertainty was considered, it was difficult to indicate a distinct transition of gas permselectivity. We have also found that Blend 10/0 and Blend 8/2 membranes belong to a family of polymers whose gas permselectivity is not significantly affected by a change in chain mobility at glass transition.

CONCLUSION

Our Blend 10/0 and Blend 8/2 PLA membranes belong to a family of polymers whose gas permeability and permselectivity are not significantly affected by a change in chain mobility at glass transition. Interestingly, on the basis of the relationship between P_0 and E_P of polymers, even in the data at glassy state, these PLA membranes followed the trend of rubbery polymers as compared to that of glassy polymers.

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