Polymer Vol. 38 No. 11, pp. 2807–2811, 1997
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0032-3861/97/$17.00 + 0.00

PII: S0032-3861(96)00857-9

Characterization and CO_2 sorption behaviour of polystyrene/polycarbonate blend system

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(Received 21 February 1996; revised 1 August 1996)

The CO_2 sorption isotherms of samples of polystyrene/polycarbonate blends with different compositions which were prepared by casting from 1,4-dioxane solutions were obtained as a function of composition of the polymer blend at 25°C using a Cahn-sorption apparatus. The characterization of the polymer blend system was obtained from the point of thermal behaviour such as differential scanning calorimetry, X-ray diffraction, and ^{13}C CP/MAS n.m.r. From the characterization of the polymer blend, it was confirmed that there was a small amount of crystallinity of polycarbonate. Basically the polymer blend system studied here is heterogeneous (i.e. phase-separated) but it was found that a small amount of polystyrene is partly miscible with polycarbonate and this probably disrupts the crystallization of polycarbonate especially at the higher polystyrene content. CO_2 sorption isotherms of the blend system including two homopolymers appeared to obey the dual mode sorption isotherm, which is a characteristic of the glassy state. The change of the CO_2 sorption amount for the polymer blend was mainly explained by the amount of the crystallite of polycarbonate, indicating that the effect of the partly miscible region on the CO_2 sorption behaviour is very small. © 1997 Elsevier Science Ltd.

(Keywords: polystyrene/polycarbonate polymer blend; phase-separated; sorption)

INTRODUCTION

Extensive studies of the properties of polymer blends have been carried out. Although high performance of a polymer blend has been correlated with higher order structure–properties relationships, there are relatively few reports on the membranes of polymer blends. Fundamental research reported in the field of membranes composed of polymer blends is given in refs 1–5. Sorption, diffusion, and permeation behaviour of the polymer blend have been related to the composition. It is well known that different sorption behaviour appears according to the miscibility of polymer blend[6–10]. Phase separated polymer blends in general demonstrate a simple additive rule of the sorption amounts or solubility coefficients, while miscible polymer blends show a negative deviation from the simple additivity rule, dependent on the interaction between the two polymers.

The polystyrene (PS)/polycarbonate (PC) blend system is well known to be partly miscible. When the molecular weight of the PS component is low, this blend system has a lower critical solution temperature type phase diagram[11]. However, high molecular weight PS is not miscible with PC. On the other hand, it had been reported that crystallization of PC occurred readily when cast from its solution with some organic solvents, immersed into the solvents, and stood under the vapour of the solvents[12–14]. If the PS/PC blend system prepared by casting has a crystalline part, therefore, the gas sorption properties of this system should be explained with the influence of the crystallite together the miscibility, morphology, composition and so on. Here, the CO_2 sorption behaviour of the PS/PC blend system prepared by casting from 1,4-dioxane solution was examined from the standpoint of the miscibility as well as the characterization in terms of thermal behaviour, X-ray diffraction, and solid state n.m.r. methods[15–17].

EXPERIMENTAL

Materials

Bisphenol-A-polycarbonate (PC: $M_w = 20\,000$) and atactic polystyrene (PS: $M_w = 280\,000$) were purchased from Aldrich Chemical Co. Ltd. The PS/PC blend and pure PS or PC films were prepared by casting the solution on a glass petri dish at 100°C then the films were dried at room temperature for 1 week. 1,4-Dioxane was used as a common solvent for the PS and PC. The solvent was completely removed by heating the film at 160°C under vacuum. CO_2 used in this study was at least 99.9% pure and used without further purification.

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Measurement

Differential scanning calorimetry (d.s.c.) measurements were made using a DSC7 calorimeter (Perkin Elmer Co.). D.s.c. thermograms were obtained at a heating rate of 10°C min^{-1} from 25 to 260°C in an atmosphere of dry N_2. The glass transition temperature (T_g) was determined as the midpoint temperature with variation of the heat capacity in the glassy state to that in the rubbery state.

Sorption isotherms of CO_2 in the films at 25°C were obtained using a gravimetric sorption apparatus with an electromicrobalance 2000 (Cahn-Instruments Inc.). After sufficient drying of the films under about 10^{-4} mmHg, the net sorption amount of CO_2 in the film at a fixed pressure was corrected by subtracting a buoyancy contribution.

The ^{13}C cross-polarization and magic angle spinning (CP/MAS) n.m.r. spectra were recorded on a UNITY 400 plus n.m.r. spectrometer (Varian Co. Inc.) operating at 100.579 MHz and room temperature. The spinning rate, 90° pulse width for ^1H and the contact and repetition times were about 5 kHz, 4.5 μs, 2 ms, and 5 s, respectively. The spin-lattice relaxation time of ^1H (T_1^H) was indirectly determined by the inversion recovery method from ^{13}C signals.

The wide angle X-ray diffraction profiles at room temperature were obtained using a RAD-RC (Rigaku Co., Inc.) with a nickel-filtered copper K_α irradiation with the power of 40 kV × 80 mA.

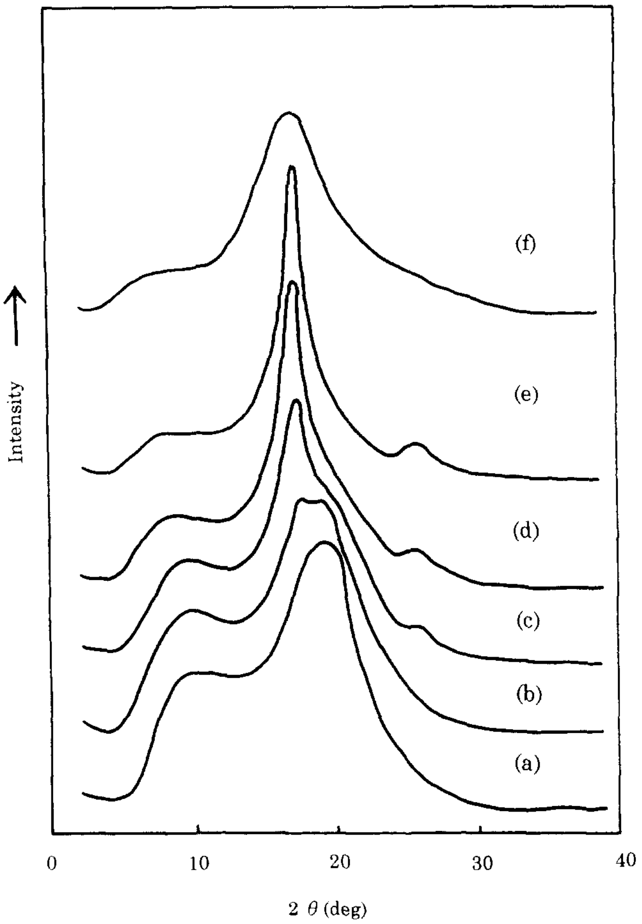

Figure 1 Wide angle X-ray scattering profiles of the films cast from 1,4-dioxane solutions of (a) PS, (b) PS/PC (80/20), (c) PS/PC (50/50), (d) PS/PC (20/80), (e) PC, and (f) as cast PC film quenched from 245°C

RESULTS AND DISCUSSION

Characterization

Wide angle X-ray scattering profiles of the PS/PC blend films with different compositions are shown in *Figure 1* together with those of the pure PS and PC films. The PC film and the blend films as cast demonstrate the appearance of a crystalline peak at about $2\theta = 18°$ which is coincident with the report of Filippo *et al.*[13]. The crystalline peak of PC of the PS/PC blend becomes much sharper with increasing volume fraction of PC. While the PC as cast film exhibits crystallinity, the PC film quenched from 245°C above the melting temperature of the PC crystallites (T_m) demonstrates no crystallinity as shown in *Figure 1f*. Compression-moulded PC is also observed to be amorphous.

D.s.c. thermograms of the PS/PC blend films as cast all exhibited an endothermic peak appearing at approximately 220°C which was assigned to the T_m of PC crystallites, corresponding to the presence of the crystalline peak in the wide angle X-ray scattering profile. In addition, two typical heat capacity jumps were observed due to the glass transition temperatures, corresponding to two phases of the PS/PC blend system.

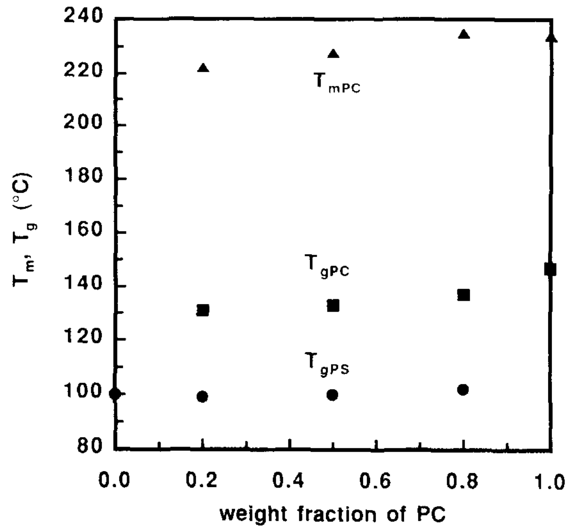

Figure 2 The melting temperature of PC crystallites (T_{mPC}; ▲) and glass transition temperatures of two phases of the phase-separated PS/PC blend (T_{gPC}; ■ and T_{gPS}; ●) determined by d.s.c. as a function of the weight fraction of PC

Figure 2 shows the T_m of the PC crystallites and T_g of the two phases of the phase-separated PS/PC blends determined by d.s.c. as a function of the PC composition. The T_m of the PC crystallites and the T_g of the PC in the phase-separated phase decrease with decrease in the PC composition, indicative of miscibility of small amount of PS into the PC phase[18]. On the other hand, the T_g of the PS phase does not vary noticeably and remains almost constant with the composition. This suggests that the PS/PC blend system basically provides two phases; one phase is composed of pure PS and the other phase is composed of PC containing a small amount of PS. The PS/PC blend system appears to be partially miscible.

Figure 3 shows a plot of the degree of crystallinity in the PC phase of the PS/PC blend system against the PC

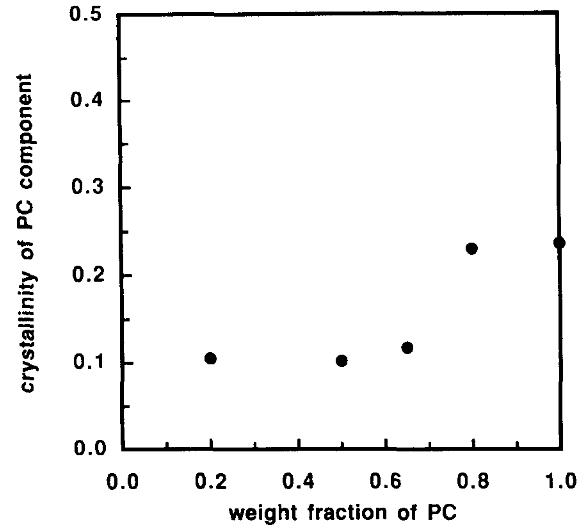

Figure 3 The degree of crystallinity in PC phase of the phase-separated PC/PS blend as a function of the weight fraction of PC

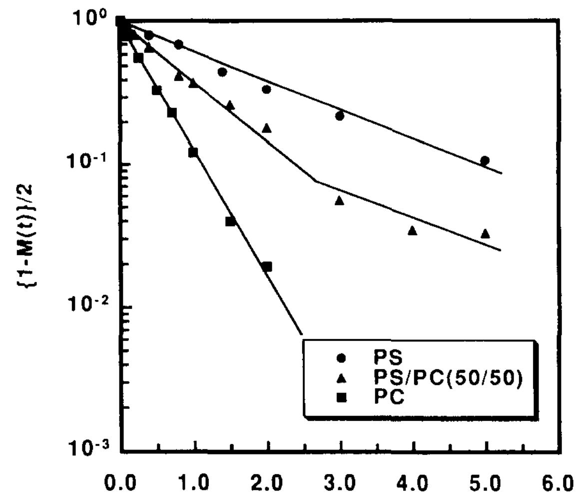

Figure 4 Observed T_1^H recovery curves of PS, PC, and PS/PC (50/50). The solid lines were drawn according to the values in *Table 1*

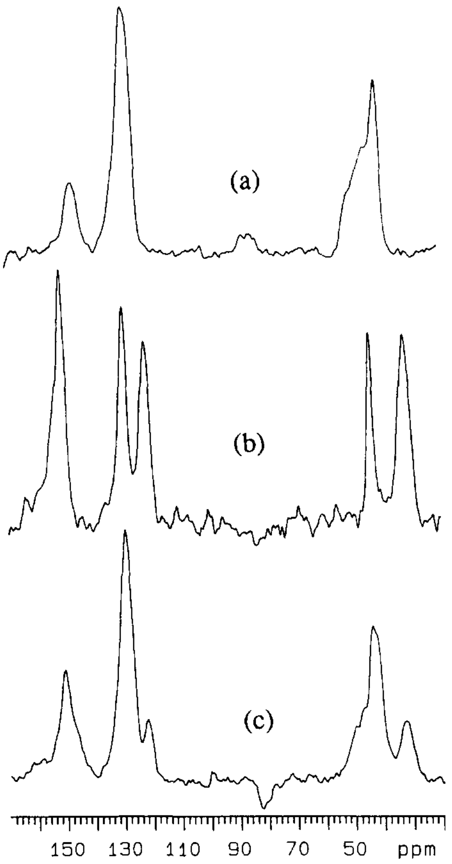

Figure 5 ^{13}C CP/MAS n.m.r. spectra of (a) PS, (b) PC, and (c) PS/PC (50/50) at room temperature

Table 1 The spin-lattice relaxation time of proton, T_1^H determined from the peaks at 129 ppm in the ^{13}C CP/MAS n.m.r. spectra of the pure PS, pure PC, and polymer blend of PS/PC (50/50)

Composition	T_1^H (s)
Pure PS	2.34
PS/PC $(50/50)_{PS}$	2.12
PS/PC $(50/50)_{PC}$	0.80
Pure PC	0.51

composition, which is calculated using the heat of fusion of a perfect PC crystal[19,20]. There is no change in the degree of crystallinity of PC for the PS/PC blend system with high PC composition, but there is a remarkable interruption of PC crystallization in the range of low composition below about 0.60[21–24].

Next, to estimate the domain size of the phase-separated phases, we measured the spin-lattice relaxation time (T_1^H) of ^1H by the inversion-recovery method. The spin-diffusion process via the ^1H dipole–dipole interaction homogenizes the heterogeneous magnetization when the domain size of a phase-separated phase is smaller than the maximum diffusive path-length $\langle L^2\rangle^{1/2}$ of ^1H spin-diffusion for a T_1^H ($\langle L^2\rangle^{1/2} \sim (6DT_1^H)^{1/2}$, where D is the diffusion coefficient). The value of $\langle L^2\rangle^{1/2}$ is several hundred Å for a T_1^H of about 0.4–2 s. Therefore, if the blend system was miscible in this scale, the values of T_1^H for the both of PS and PC should be averaged.

Figure 4 shows the observed T_1^H recovery curves of the peak observed at about 129 ppm for PS/PC (50/50) and the two homopolymers. Not only the PS but also the PC homopolymers demonstrate single exponential recovery curves. This finding shows that the size of the crystallite of the PC is smaller than several hundred Å. On the other hand, the PS/PC (50/50) curve exhibits two components which basically correspond to two phase-separated phases of the polymer blend, because the peak observed at about 129 ppm and assigned to the protonated phenyl carbons of the both PS and PC overlap with each other (see *Figure 5*). This observation shows that the domain size of the phase-separated phases of the blend were at least greater than several hundred Å. The values of T_1^H were determined by the standard procedures[25,26] and these are given in *Table 1*. The long T_1^H of the PS/PC (50/50) agrees with that of the pure PS homopolymer. However, the second value does not agree with that of the pure PC homopolymer and has an intermediate value between those of pure PS and PC homopolymers. This indicates that the PC component of the phase-separated structure contains the small amount of PS and is partially miscible in the range of several hundred Å. This fact agrees with d.s.c. results described above.

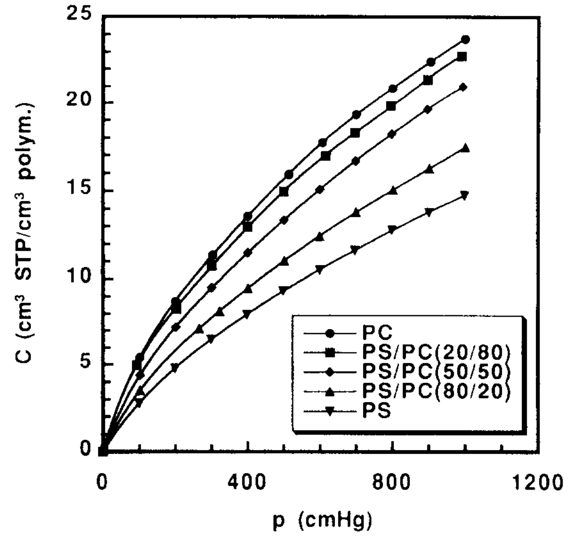

Figure 6 CO_2 sorption isotherms of PS/PC blend system at 25°C: (▼) PS; (▲) PS/PC (80/20); (◆) PS/PC (50/50); (■) PS/PC (20/80); (●) PC

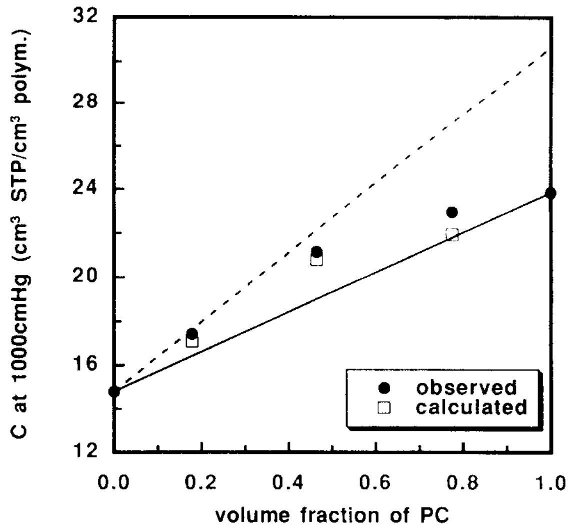

Figure 7 Amounts of CO_2 sorption for PS/PC blend system at 25°C and 1000 cmHg as a function of volume fraction of PC: (●) observed; (□) calculated by considering the crystallinity of PC. The solid and dashed lines indicate the CO_2 sorption amounts predicted by the simple additive rule using the observed and corrected values of the pure PC, respectively. The details of the calculation and correction are described in the text

CO_2 sorption behaviour

CO_2 sorption behaviour was studied for the PS/PC blend system at 25°C. CO_2 sorption isotherms are shown in *Figure 6*. The sorption mechanism for a polymer blend consisting of two glassy phases is complicated but the CO_2 sorption isotherms for the PS/PC blend probably represent an apparent dual mode sorption[24] which is characteristic of a glassy polymer. Both phases are in the glassy state, and, therefore, each phase is assumed to obey the dual mode sorption mechanism as follows:

$$C = \phi_{PS}\left(k_{DPS}\,p + \frac{C'_{HPS}b_{PS}p}{1 + b_{PS}p}\right) + \phi_{PC}\left(k_{DPC}\,p + \frac{C'_{HPC}b_{PC}p}{1 + b_{PC}p}\right) \qquad (1)$$

where C, p, and ϕ are the concentration and pressure of CO_2, and the volume fraction, respectively. k_D, b, and C'_H are the dual mode sorption parameters as the Henry solubility coefficient, the affinity constant, and the Langmuir saturation constant, respectively. The subscripts PS and PC represent the PS and PC rich phases of the polymer blend, respectively. The dual mode sorption parameters of the PS rich phase are thought to be approximately the same as those of the pure PS phase, but the dual mode sorption parameters of the PC rich phase are not the same as the pure PC phase because of the slight miscibility of PC with PS as mentioned above. The sorption isotherms in *Figure 6* cannot be used to evaluate analytically the true dual mode sorption parameters of the phase-separated polymer blend. Trial and error fitting can produce the parameters, but there are arbitrary values without physical meaning. Therefore, we did not attempt to obtain the parameters by the method of curve fitting the observed data using equation (1). Instead, we shall examine further the dual mode sorption parameters which are characteristic for each glassy state.

The CO_2 sorption amount at CO_2 pressure of 1000 cmHg is plotted as a function of the PC composition in *Figure 7*. The general trend of sorption amount for a phase-separated polymer blend is well known to obey a simple additive rule[28]. However, the relationship between the CO_2 sorption amount of PS/PC polymer blend and the PC composition is not linear. In *Figure 7*, two simple additive rule lines are drawn. The solid line is obtained by using the observed values of the PS and the PC homopolymers, that is, the additive rule of the purely amorphous PS, C_{PS} and the PC, C_{PC} with a degree of crystallinity of 23.5%. Since crystallites cannot sorb any CO_2, one should consider the CO_2 sorption amount omitting these crystallites. The CO_2 sorption amount of the purely amorphous PC, C_{PC}^{amor} is determined from

$$C_{PC}^{amor} = C_{PC}/(1 - X_C) \qquad (2)$$

where X_C is the degree of crystallinity of the PC. The dotted line indicates the simple additive rule predicted with C_{PS} and C_{PC}^{amor}. From *Figure 7*, it can be seen that the observed value of the blend vary from near the dotted line to the solid one with increasing PC composition, in other words, the degree of crystallinity in the PC component as mentioned above. We try to calculate the CO_2 sorption amount of the PS/PC blend system using the X_C of each blend sample as follows,

$$C = \phi_{PS}C_{PS} + \phi_{PC}C_{PC}^{blend} \qquad (3)$$

where

$$C_{PC}^{blend} = C_{PC}^{amor}(1 - X_C) \qquad (2')$$

The calculated value is shown as (□) in *Figure 7* and agrees well with the observed CO_2 sorption amount. The CO_2 sorption behaviour of the PS/PC blend system would therefore be explained by the simple additive rule corrected for the degree of crystallinity of the PC component, and the effect of the partly miscible region in this system on the sorption behaviour is almost negligible. This finding suggests that the amount of this miscible region is small and/or the interaction is weak in the PS/PC blend studied here.

SUMMARY

In the PS/PC blend prepared by casting from their

1,4-dioxane solution, the semi-miscibility of the PC component with a small amount of the PS component and the existence of the crystalline part in the PC component were confirmed by d.s.c. (the melting of PC crystallites and the glass transition behaviour of the PC and PS components), by wide angle X-ray diffraction, and by the spin-lattice relaxation times of ^{1}H obtained from ^{13}C CP/MAS n.m.r. When the PC composition was smaller than 60 wt%, the amount of crystallite in the PC component was reduced. It was found that the CO_2 sorption behaviour of the PS/PC glassy polymer blend seems to be explained by the dual mode sorption model and the sorption amount of the polymer blend can be calculated considering a true additive rule and the degree of crystallinity.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge partial financial supports from the Grant-in-Aid for science research from the Ministry of Education, Science, and Culture, Japan (06045018), and the British Council.

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