

Thermal Behavior, Morphology, and the Determination of the Flory–Huggins Interaction Parameter of Polycarbonate–Polystyrene Blends

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Synopsis

Blends of bisphenol-A polycarbonate (PC) and polystyrene (PS) prepared by screw extrusion and solution casting have been investigated with weight fractions of PC in the blends varying from 0.95 to 0.05. From the measured glass transition temperatures (T_g) and specific heat increments (ΔC_p) at the T_g , the polystyrene appears to dissolve more in the PC phase than does the PC in the PS phase. The blend appears to be near equilibrium under extrusion conditions so that the polymer–polymer interaction parameter of PC/PS blends was calculated and found to be 0.038 ± 0.004 for extruded blends at 250°C. Scanning electron microscopy supports the conclusion that the compatibility increases more in the regions of PS-rich compositions than in the regions of PC-rich compositions of the PC/PS blends.

INTRODUCTION

Thermal analysis of polymer blends has shown that, for perfectly miscible systems and for partially miscible systems, the glass transition temperature (T_g) of each component shifts with variation of the composition. A miscible polymer blend will exhibit a single glass transition between the T_g 's of the components while for partially miscible systems the T_g 's approach each other but do not become identical.^{1–3} Recently, some investigators^{3–8} have also used the specific heat increment (ΔC_p) at the T_g to investigate the polymer–polymer compatibility by differential scanning calorimetry (DSC).

The blending of polycarbonate (PC) with various polymers has been the subject of some interest in recent years. The polymer blends which have been reported have contained polyethylene,^{9,10} polypropylene,^{11,12} polystyrene,^{9,12–17} poly(methyl methacrylate),¹⁸ poly(styrene-co-acrylonitrile),¹⁶ poly(acrylonitrile–butadiene–styrene),¹⁹ and some polyesters.^{20–22}

Polycarbonate (PC) and polystyrene (PS) are known to be partially miscible,^{9,12–17} and two glass transition regions are observed. Kunori and Geil⁹ have studied morphology–property relationships, and Bye and Miles¹⁴ and Lipatov et al.¹⁵ have investigated the viscoelastic properties of PC/PS blends. Rudin and Brathwaite¹² have studied the melt properties and some mechani-

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cal properties of PC/PS blends. Keitz et al.¹⁶ and Wisniewski et al.¹⁷ have studied the glass transition behavior of PC/PS blends, and reported two T_g 's.

The method of determining the polymer-polymer interaction parameter between component polymers in a miscible blend has been studied widely.²³⁻³¹ Several techniques can be used to determine the thermodynamic polymer-polymer interaction parameter (χ) such as melting point depression,²³⁻²⁵ vapor sorption,^{25,26} inverse-phase gas chromatography,²⁷⁻²⁹ and some light-scattering methods.³⁰⁻³² Only a few methods have been developed which can be applied in incompatible polymer blend systems, however, and most of these are ternary solution methods.³³⁻³⁵

In our present study we are examining the miscibility of blends of PC and PS by determining experimentally the glass transition temperature (T_g) and the specific heat increment (ΔC_p) at T_g of the blends by thermal analysis. Also, a method is presented to determine the polymer-polymer interaction parameter (χ_{12}) in partially miscible systems by using the experimentally determined glass transition temperature. Since the interaction parameter is an equilibrium property, experimental tests were carried out to show that the extruded blends are close to their equilibrium conditions.

EXPERIMENTAL

Polymers

The polymers used in this study were obtained from commercial sources. The characteristics and sources of the bisphenol-A polycarbonate (PC) and polystyrene (PS) polymers are shown in Table I. Molecular weights for the polymers were measured by gel permeation chromatography (GPC) at 25°C in tetrahydrofuran (THF). The universal calibration method^{36,37} based on hydrodynamic volume was used for the PC. The polystyrene molecular weight was measured by GPC using the Chang-Huang correction method.³⁸ Mark-Houwink constants of $K = 3.89 \times 10^{-4}$ dL/g and $\alpha = 0.766$ for the PC³⁹ were used in the universal calibration curve. For the PS, the Mark-Houwink constants used were $K = 6.82 \times 10^{-5}$ dL/g and $\alpha = 0.766$ in THF at 25°C.⁴⁰ The sample designated PC 101 was Lexan polycarbonate, supplied by General Electric Co., and the PS was supplied by Polysciences, Inc.

TABLE I
Characteristics of Polymer Samples Used in PC/PS Blends

Sample	\bar{M}_w^a	\bar{M}_n	\bar{M}_w/\bar{M}_n	T_g (K) ^b	ΔC_p (J g ⁻¹ K ⁻¹) ^b
PC 101 ^c	29,000	12,300	2.36	421.5	0.222
PS ^d	237,700	98,600	2.41	373.5	0.282

^aMeasured in our laboratory by GPC.

^bMeasured in our laboratory by DSC.

^cSupplied by General Electric Co.

^dSupplied by Polysciences, Inc.

The glass transition temperature (T_g) and specific heat increment (ΔC_p) at T_g were measured by differential scanning calorimetry (DSC), using procedures reported earlier.³ Methylene chloride, used as solvent for the preparation of cast films, was spectroquality grade, supplied by Matheson, Coleman, and Bell.

Blend Preparations

Blends were prepared by both solution casting and screw extrusion. For solution casting, a total of 0.6 g of PC/PS mixtures in weight fractions of PC of 1.00, 0.90, 0.80, 0.70, 0.60, 0.50, 0.40, 0.30, 0.20, 0.10, and 0.00 was dissolved in 20 mL of methylene chloride at room temperature [3.0% (w/v) solution] for at least 1 day. Blends were cast on glass plates, and all film samples were dried under vacuum for 15 days at room temperature. Cast film thickness was $15 \pm 3 \mu\text{m}$. To prepare melt blends, all polymers were dried in a vacuum oven at 80°C for 2 days before use. Blends were prepared using a 0.5 in. (12.7 mm) diameter laboratory scale screw extruder, with a 27:1 length-to-diameter screw.¹² The length to diameter (L/D) ratio of the circular die was 19.0 with a diameter of 0.32 mm. Temperatures of the extruder were set at 250°C in each zone (die, die head, and barrel zones) for the pure PC material. The temperature was gradually decreased for the weight fraction of PC of 0.40, 0.30, 0.20, and 0.10 to 230°C. In order to minimize hydrolysis, the extruder hopper was connected to a desiccating dryer that pumped warm, dry air through the mixtures.

Scanning Electron Microscopy (SEM)

The morphology of the cross section of extrudate and solution cast films was examined by SEM in a JOEL Model JSM-840 microscope at 15 kV accelerating voltage after gold sputter coating (500 Å). The fractured surface of both the extrudate and the cast films was prepared by cryogenic fracturing.

Differential Scanning Calorimetry Measurements

The thermal properties of all samples were measured calorimetrically using a Perkin-Elmer differential scanning calorimeter, Model DSC-4, with a Perkin-Elmer thermal analysis data station, Model TADS-101. Temperature calibration was performed using indium ($T_m = 156.60^\circ\text{C}$, $\Delta H_f = 28.5 \text{ J/g}$). The heating rate and cooling rate of the sample were 20 and 135 K min^{-1} , respectively, with a sample size between 10 and 17 mg using standard aluminum sample pans. The sample was surrounded by a helium atmosphere. Following the convention used in other thermal analysis studies, the T_g was taken as the temperature at which the heat capacity reached one half of the entire step change as observed on the thermogram. All glass transition temperatures were measured by this midpoint method.⁵ From our experiments, we have found that the choice of tangent placements allows an uncertainty of approximately $\pm 0.5 \text{ K}$ in T_g and approximately $\pm 0.015 \text{ J g}^{-1} \text{ K}^{-1}$ in ΔC_p of the blended polymers.

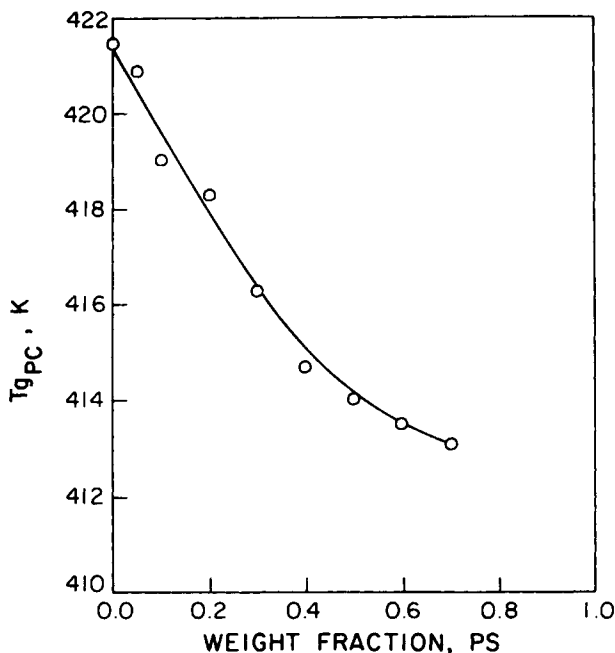


Fig. 1. Effect of blend composition on the $T_g(\text{PC})$ for PC/PS blends from screw extrusion.

RESULTS AND DISCUSSION

T_g of PC/PS Blends

Polycarbonate (PC) and polystyrene (PS) are known to be partially miscible^{9,12-17} and two glass transition regions are observed which we designate as $T_g(\text{PC})$, associated with PC-rich regions, and $T_g(\text{PS})$, associated with PS-rich regions.

In Figures 1-4, we see the two T_g 's for the various compositions. In Figures 1 and 2, the T_g of polycarbonate for screw-extruded blends and solution-cast blends, respectively, is seen to decrease almost linearly with an increase in the PS weight fraction. For a composition of 0.7 weight fraction of PS, the T_g is seen to decrease by about 8 K for the screw-extruded blend and 2 K for the solution-cast blend.

The T_g 's of polystyrene for the PC/PS screw-extruded blends and solution-cast blends are shown to increase linearly with PC weight fraction in Figures 3 and 4, respectively. For a composition of 0.2 weight fraction of PS, the T_g is seen to increase by about 3 K for the screw-extruded blend and about 1.5 K for the solution-cast blend.

The observation that the decrease of $T_g(\text{PC})$ and the increase of $T_g(\text{PS})$ are larger in screw-extruded blends than in the solution-cast blends will be discussed later in terms of the amounts of PC and PS dissolving in the opposite phases. One explanation is that in solution-cast blends, the polymer chains do not have sufficient time or mobility to intermix as the solvent evaporates, which could lead to more facile phase separation in the final dry film.^{41,42}

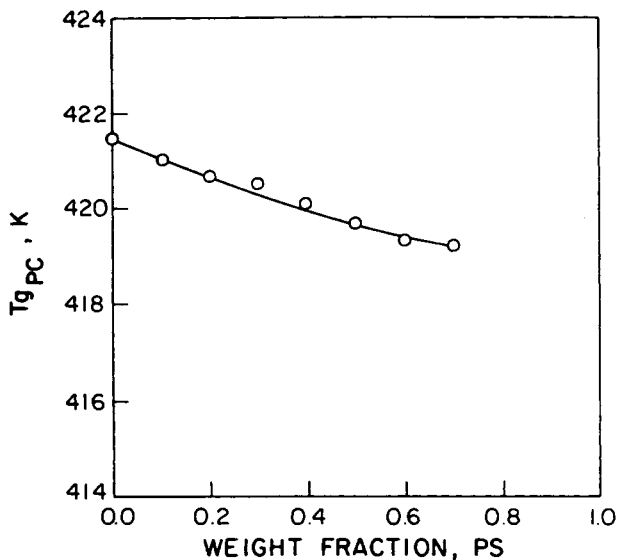


Fig. 2. Effect of blend composition on the T_g (PC) for PC/PS blends by solution casting from 3.0% (w/v) methylene chloride solution.

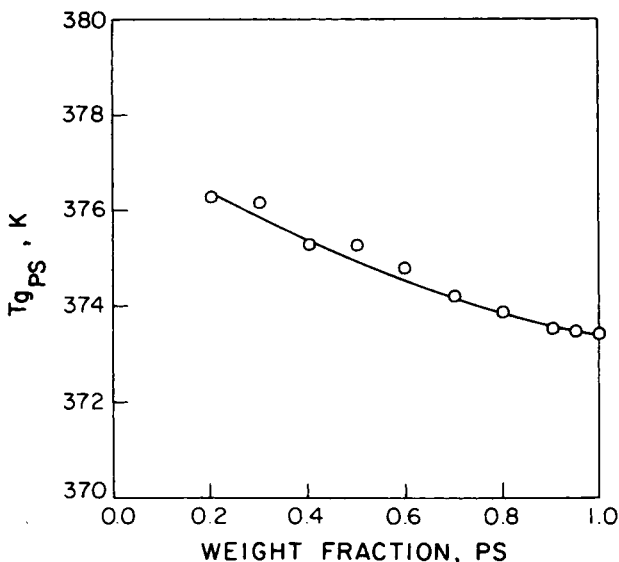


Fig. 3. Effect of blend composition on the T_g (PS) for PC/PS blends from screw extrusion.

From the glass transition temperatures of PC and PS in the PC/PS blends, we can estimate the apparent weight fractions of PC and PS dissolved in the PC-rich phase and the PS-rich phase, respectively. In the study of blends of bisphenol-A polycarbonate (PC) and poly(methyl methacrylate) (PMMA) blends, Gardlund¹⁸ has found two T_g 's in PC/PMMA blends by DSC. The apparent weight fractions of PC were determined in the PC-rich phase and the PMMA-rich phase by the following empirical equation, which is often used to describe the dependence of T_g on composition in random copolymers

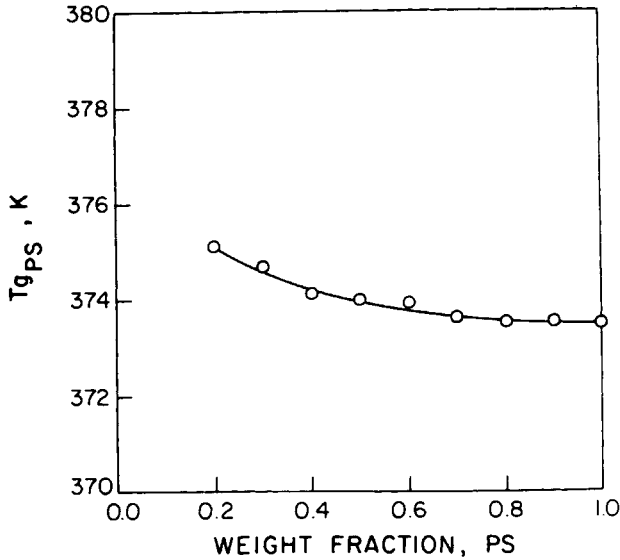


Fig. 4. Effect of blend composition on the $T_g(\text{PS})$ for PC/PS blends by solution casting from 3.0% (w/v) methylene chloride solution.

and plasticized systems⁴³

$$T_g = w_1 T_{g_1} + w_2 T_{g_2} \quad (1)$$

where T_g is the observed T_g of the copolymer, w_1 is the weight fraction of homopolymer 1 having T_{g_1} and w_2 is the weight fraction of homopolymer 2 having T_{g_2} . Equation (1) may be rearranged to⁴⁴

$$w'_1 = \frac{T_{g_1, b} - T_{g_2}}{T_{g_1} - T_{g_2}} \quad (2)$$

where w'_1 is the apparent weight fraction of polymer 1 in the polymer 1-rich phase, $T_{g_1, b}$ is the observed T_g of polymer 1 in the blends, and T_{g_1} and T_{g_2} are the T_g 's of homopolymer 1 and homopolymer 2, respectively.

The apparent weight fraction of PC and PS components can be also determined by using the Fox equation⁴⁵ and the Couchman equation,^{46,47} which are used to predict T_g 's for miscible polymer blends. The Fox equation is

$$\frac{1}{T_g} = \frac{w_1}{T_{g_1}} + \frac{w_2}{T_{g_2}} \quad (3)$$

where w_1 and w_2 represent the weight fraction of the components, and T_g , T_{g_1} , and T_{g_2} are the T_g 's of the blend, components 1 and 2, respectively. Equation (3) may be rearranged to

$$w'_1 = \frac{T_{g_1}(T_{g_1, b} - T_{g_2})}{T_{g_1, b}(T_{g_1} - T_{g_2})} \quad (4)$$

TABLE II
 Apparent Weight Fraction (w) and Apparent Volume Fraction (ϕ) of PC and PS components in the PC-Rich Phase and the PS-Rich Phase, and the Polymer-Polymer Interaction Parameter (χ_{12}) of Extruded PC/PS Blends

Blend ^a	T_{g_1} (K)	T_{g_2} (K)	PC-rich ^b		PS-rich ^b		PC-rich		PS-rich		χ_{12} ^c
			w'_1	w'_2	w''_1	w''_2	ϕ'_1	ϕ'_2	ϕ''_1	ϕ''_2	
1.00	421.5	—	1.0000	—	—	—	1.0000	—	—	—	—
0.80	418.3	376.3	0.9497	0.0503	0.0772	0.9228	0.9429	0.0571	—	0.0682	0.9318
0.70	416.3	376.2	0.9173	0.0827	0.0745	0.9225	0.9066	0.0934	—	0.0658	0.9342
0.60	414.7	375.4	0.8910	0.1090	0.0527	0.9473	0.8773	0.1227	—	0.0464	0.9536
0.50	414.0	375.3	0.8793	0.1207	0.0500	0.9500	0.8644	0.1356	—	0.0440	0.9560
0.40	413.5	374.8	0.8709	0.1291	0.0362	0.9638	0.8551	0.1449	—	0.0318	0.9682
0.00	—	373.5	—	—	—	1.0000	—	—	—	—	1.0000

^a Blend composition given as the overall weight fraction PC in the PC/PS blend.

^b Single prime and double prime denote PC-rich phase and PS-rich phase, respectively, and subscripts 1 and 2 denote PC and PS components, respectively. All w 's calculated from eq. (6).

^c All χ_{12} 's calculated from eq. (16).

where w'_1 is the apparent weight fraction of polymer 1 in the polymer 1-rich phase, and $T_{g_1, b}$ is the observed T_g of polymer 1 in the blends. The Couchman relation which yields T_g 's for miscible polymer blends for values of T_g and ΔC_p at T_g for the unblended polymer components is given by the equation

$$\ln T_g = \frac{w_1 \Delta C_{p_1} \ln T_{g_1} + w_2 \Delta C_{p_2} \ln T_{g_2}}{w_1 \Delta C_{p_1} + w_2 \Delta C_{p_2}} \quad (5)$$

where $\Delta C_p = C_p^l(T_g) - C_p^s(T_g) =$ difference in molar heat capacity at T_g , where $C_p^l(T_g)$ is the molar heat capacity of the liquid at T_g , and $C_p^s(T_g)$ is the molar heat capacity of the solid at T_g .

Equation (5) may be rearranged to

$$w'_1 = \frac{\Delta C_{p_2} (\ln T_{g_1, b} - \ln T_{g_2})}{\Delta C_{p_1} (\ln T_{g_1} - \ln T_{g_1, b}) + \Delta C_{p_2} (\ln T_{g_1, b} - \ln T_{g_2})} \quad (6)$$

where w'_1 is the apparent weight fraction of polymer 1 in the polymer 1-rich phase, and $T_{g_1, b}$ is the observed T_g of polymer 1 in the blend.

Applying eq. (6) to the DSC results of $T_g(\text{PC})$ and $T_g(\text{PS})$ in PC/PS blends, we have calculated the apparent weight fraction of PC and PS in the PC-rich phase and in the PS-rich phase, which are shown in Table II. Using the apparent weight fractions which we have calculated from the glass transition temperatures of the blends, we can then estimate the Flory-Huggins polymer-polymer interaction parameter (χ_{12}), provided that the system is at equilibrium or nearly so.

ΔC_p of PC/PS Blends

The values of ΔC_p for polycarbonate and polystyrene in PC/PS blends prepared by screw extrusion and solution casting are presented in Figures 5-8.

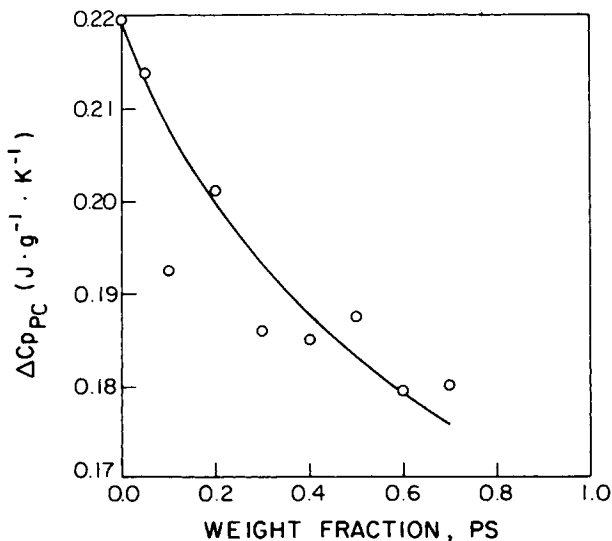


Fig. 5. Specific heat increment (ΔC_p) at the T_g of polycarbonate for PC/PS blends from screw extrusion.

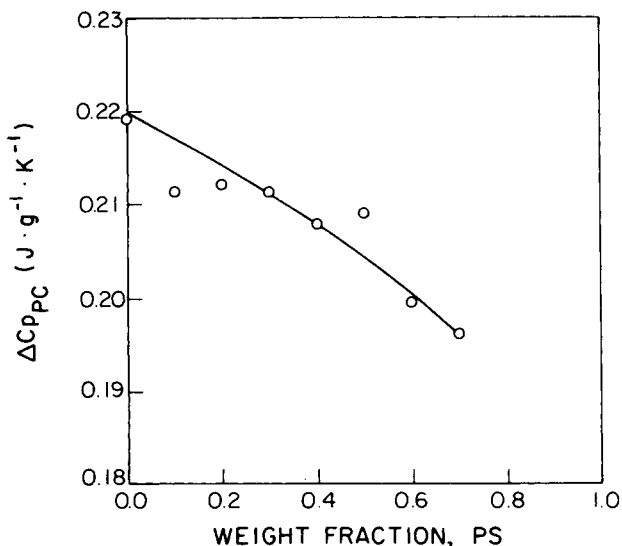


Fig. 6. Specific heat increment (ΔC_p) at the T_g of polycarbonate for PC/PS blends by solution casting from 3.0% (w/v) methylene chloride solution.

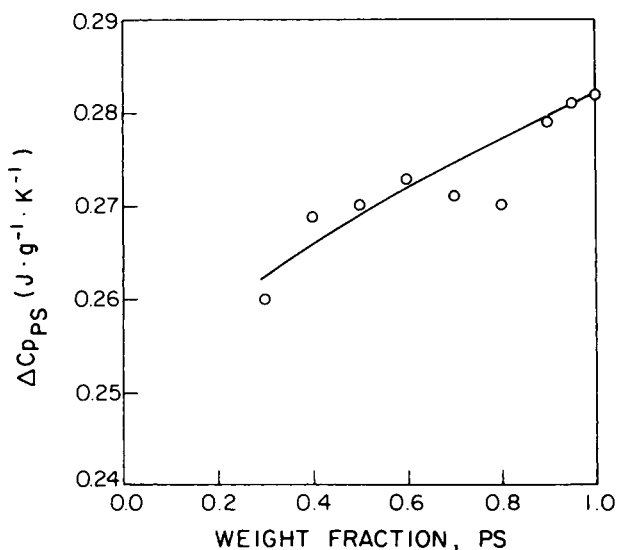


Fig. 7. Specific heat increment (ΔC_p) at the T_g of polystyrene for PC/PS blends from screw extrusion.

In Figures 5 and 6, the ΔC_p of PC is seen to decrease linearly with composition of polystyrene in PC/PS blends. Observedly, the decrease of ΔC_p of PC is larger in screw-extruded blends than in solution-cast blends.

Two explanations have been proposed for the decrease of specific heat increment (ΔC_p) at T_g of polycarbonate.⁴⁸ One explanation is that the size of the dispersed phase is very small so that the magnitude of the specific heat increment (ΔC_p) of each phase is decreased somewhat. The other explanation proposed is that both polycarbonate and polystyrene phases diffuse into an

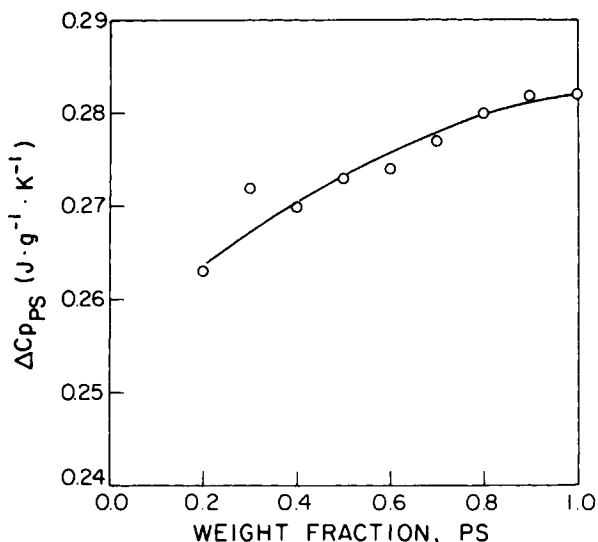


Fig. 8. Specific heat increment (ΔC_p) at the T_g of polystyrene for PC/PS blends by solution casting from 3.0% (w/v) methylene chloride solution.

interfacial region. If the interfacial region were to be established, then the magnitude of the specific heat increment (ΔC_p) is decreased. Thus the undissolved part of the blends would show a reduced ΔC_p by DSC.

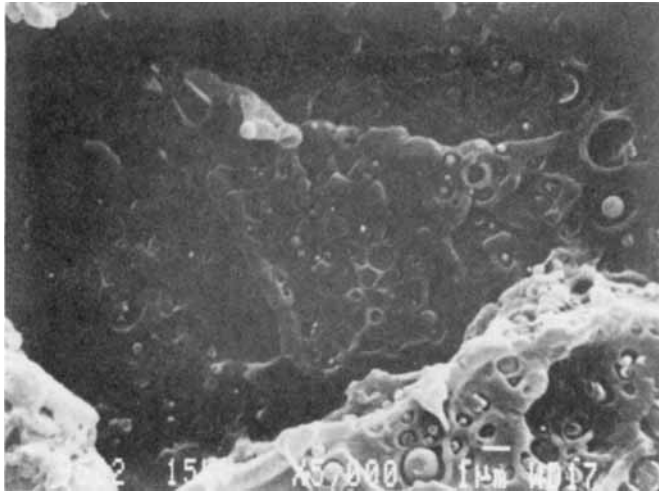
In our earlier paper,³ we attributed the reduction in the ΔC_p at T_g of each component to the dissolution of that component in the conjugate phase. The results in Figures 5 and 6, then, would indicate that some of the PC is dissolving in the PS-rich phase with greater dissolution occurring in the screw-extruded blend.

In Figures 7 and 8 are presented the ΔC_p values for polystyrene of screw-extruded and solution-cast blends, respectively. From Figures 7 and 8, the ΔC_p of polystyrene is seen to increase linearly with composition of polystyrene in PC/PS blends.

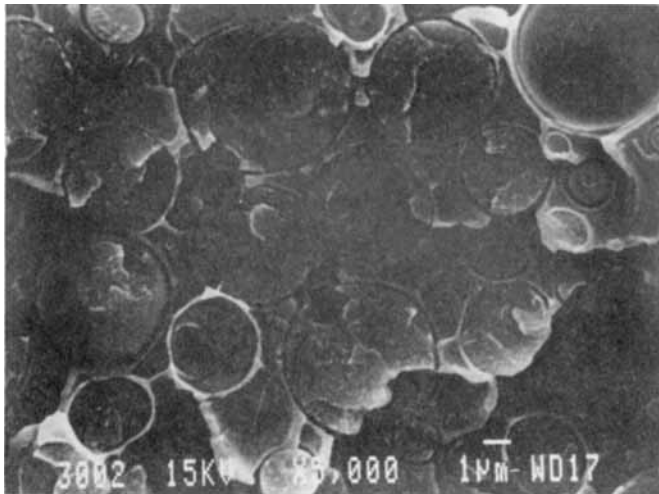
In the extruded blends of Figures 1 and 3, we can see that the decrease of $T_g(\text{PC})$ with weight fraction of PS is more significant than the increase of $T_g(\text{PS})$ with weight fraction of PC. This behavior can be explained quantitatively in Table II, which shows that the weight fraction of polystyrene dissolved in the PC-rich phase (w_2') is higher than the weight fraction of polycarbonate component dissolved in the PS-rich phase (w_1''). This result is consistent with the behavior of ΔC_p in Figures 5 and 7. These results suggest that the polystyrene dissolves more in the polycarbonate phase than does the polycarbonate in the polystyrene phase.

Scanning Electron Microscopy of PC/PS Blends

The morphology of PC/PS blends by screw extrusion and solution casting was studied using scanning electron microscopy. In Figures 9–11 are presented micrographs of the cryogenically fractured cross-section surfaces of extrudates and cast films of the blends. The micrographs of 0.95, 0.70 and 0.50, and 0.40,



(a)

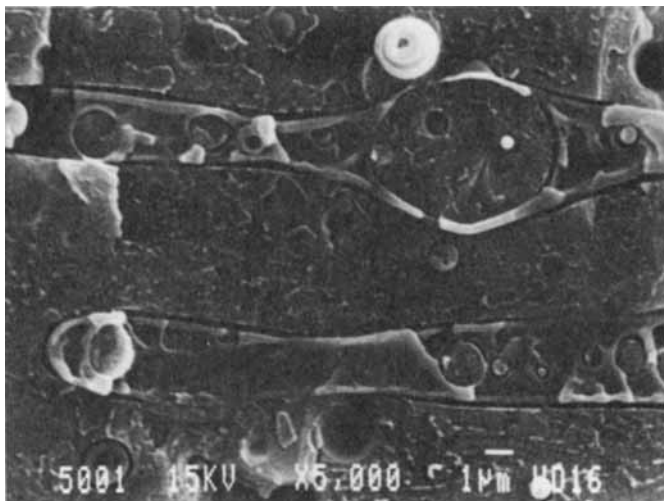


(b)

Fig. 9. Scanning electron micrographs obtained from the cryogenically fractured cross-section surfaces of polycarbonate/polystyrene extruded blends: (a) 95/5; (b) 70/30; (c) 50/50.

0.30 and 0.05 weight fractions of polycarbonate in PC/PS extruded blends are presented in Figures 9 and 10, respectively.

From Figures 9 and 10, we can see that phase separation between the PC-rich phase and the PS-rich phase is more pronounced in the case of 0.95 and 0.70 weight fractions of polycarbonate (PC-rich compositions) than in the 0.30 and 0.05 weight fractions of polycarbonate (PS-rich compositions) in the PC/PS blends. This observation is consistent with the situation that the polystyrene dissolves more in the polycarbonate phase than does the polycarbonate in the polystyrene phase, which has been indicated by the behavior



(c)

Fig. 9. (Continued from the previous page.)

of glass transition temperature and specific heat increment (ΔC_p) at T_g of the PC/PS blends.

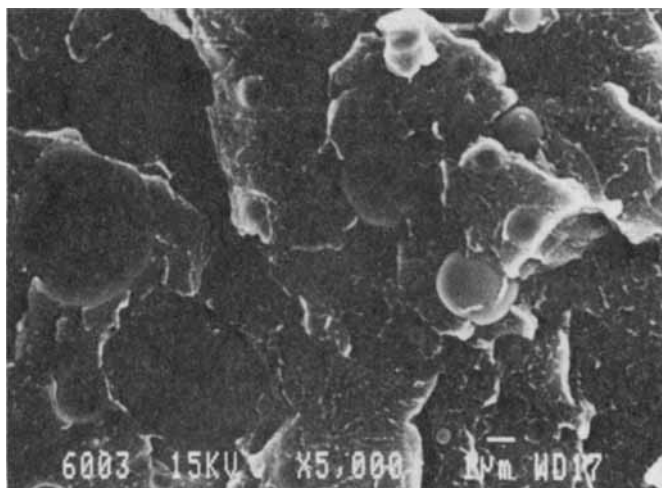
The micrographs of 0.80, 0.20, and 0.10 weight fractions of polycarbonate in PC/PS solution-cast blends are presented in Figure 11. In Figure 11 we can see the continuous phase and dispersed phase for all the compositions. Phase separation between the two phases is more pronounced in the 0.80 weight fraction of polycarbonate (PC-rich composition) than in the 0.20 and 0.10 weight fractions of polycarbonate (PS-rich compositions) in the PC/PS blends. This phase separation behavior is similar to the situation for screw-extruded blends as we have seen in Figures 9 and 10. From the microscopy study, it appears that the compatibility increases more in the regions of PS-rich compositions than in the regions of PC-rich compositions in PC/PS blends.

Polymer–Polymer Interaction Parameter (χ)

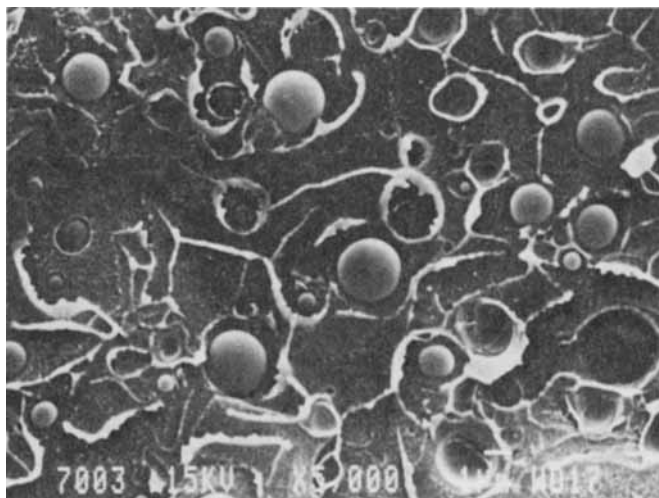
For miscible polymer blends, several techniques^{23–32} have been used to determine the Flory–Huggins polymer–polymer interaction parameter (χ).

Scott⁴⁹ and Tompa⁵⁰ were the first to apply the Flory–Huggins⁵¹ theory of polymer solutions to mixtures of polymers, with and without added solvent, in order to determine the polymer–polymer interaction parameter. For polydisperse polymers, it has been found⁵² that number-average molecular weights can be used in place of monodisperse molecular weights in the modified Flory–Huggins equation with very little effect on the consequent value of χ .

The Flory–Huggins equation was developed for systems at equilibrium. In order to ascertain how close the PC/PS blend system is to equilibrium in the extruder, we have tested the two criteria of equilibria, that the properties are constant with time and that the final state can be approached from opposite directions (see, for example, Ref. 53).



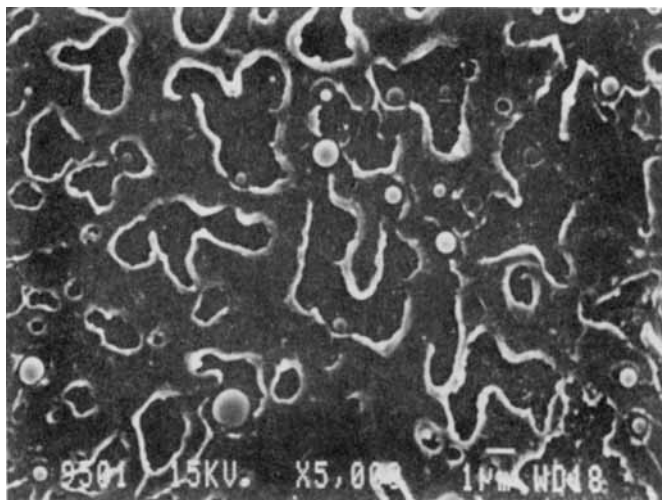
(a)



(b)

Fig. 10. Scanning electron micrographs obtained from the cryogenically fractured cross-section surfaces of polycarbonate/polystyrene extruded blends: (a) 40/60; (b) 30/70; (c) 5/95.

To test the first criterion, we took the extrudate, remelted it in the extruder, and extruded it a second time. In Table III we can see that the $T_g(\text{PC})$ of remelted extrudate is very close to the $T_g(\text{PC})$ of the first extrudate for the 0.90 and 0.80 weight fraction of PC. For the 0.70 and 0.60 weight fractions of PC, the $T_g(\text{PC})$ of remelted extrudate is lower by about 1.0 K compared to the $T_g(\text{PC})$ of the first extrudate. For the 0.50 weight fraction of PC composition, the $T_g(\text{PC})$ of remelted extrudate is lower by about 2.7 K, but the sample showed signs of decomposition. After the DSC measurement of the PC/PS blends for the 0.50 weight fraction PC, we visually compared both



(c)

Fig. 10. (Continued from the previous page.)

samples and found some bubbling indicating that hydrolysis may have occurred in the case of the remelted sample.

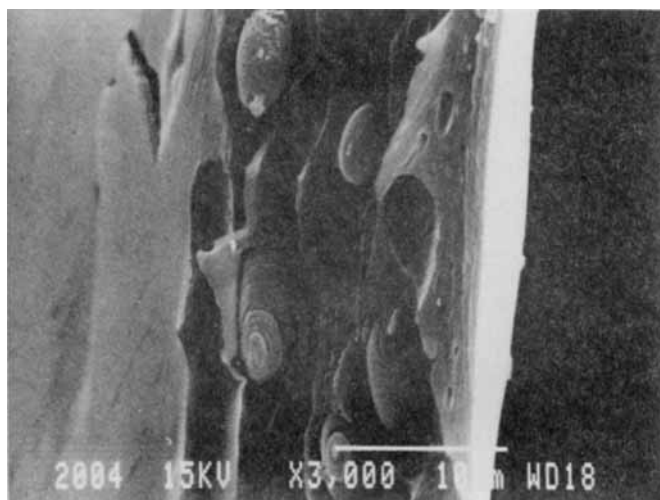
The T_g 's of polystyrene for both the first extrudate and the remelted extrudate are in good agreement throughout the investigated composition range. In Table III we also can see that the T_g 's of PC and PS of the first extrudate are very close to the T_g 's of PC and PS of the repeated extrusion for all the compositions.

The remelted extrudate was further annealed in the DSC for 5 h at 433.2 K, which is 10 K above the T_g of PC, and the T_g 's of PC and PS essentially did not change.

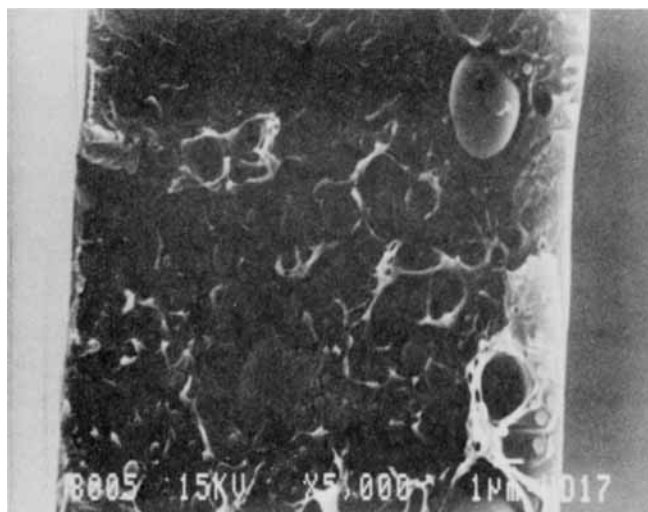
For the second criterion, the extrudate compositions were obtained by blending pure components first with each other and second with previously blended components to the same final compositions. The results are shown in Table IV. The T_g 's of PC and PS are compared between the first extrudate and remelted extrudates which have been formulated by adding pure polycarbonate to the first extrudate. The values of T_g 's of PC and PS are seen to be in good agreement for both samples. From these results in Tables III and IV, it can be concluded that the PC/PS blend system in the extruder is very close to an equilibrium condition.

For this case, then, an expression can be developed to determine the Flory-Huggins polymer-polymer interaction parameter (χ_{12}) of the mixture without solvent in partially miscible blends, similar to the earlier work of Scott.⁴⁹ Let us consider a mixture of two polymers in the absence of solvent and assume that equilibrium is reached. From the Flory-Huggins theory,⁵¹ the Gibbs' free energy of mixing, ΔG_m , for a system consisting of two polymers can be written as follows:⁵⁰

$$\frac{\Delta G_m}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + \chi_{12} \phi_1 \phi_2 (m_1 n_1 + m_2 n_2) \quad (7)$$



(a)



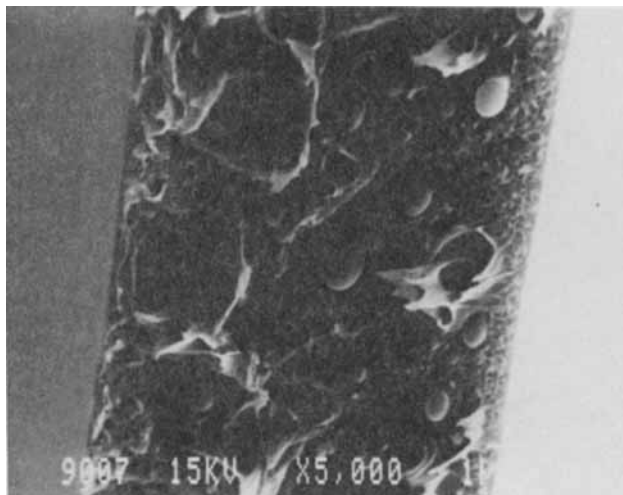
(b)

Fig. 11. Scanning electron micrographs obtained from the cryogenically fractured cross-section surfaces of solution cast films of polycarbonate/polystyrene blends: (a) 80/20; (b) 20/80; (c) 10/90.

where n_i is the number of moles of the i th component in the mixture and $\phi_i = m_i n_i / (m_i n_i + m_j n_j)$, which is the volume fraction of the i th component ($i, j = 1, 2$ and $i \neq j$). χ_{12} is the Flory-Huggins interaction parameter. Subscripts 1 and 2 denote polymers 1 and 2. m_i is essentially the degree of polymerization, relating the molar volumes V_1 and V_2 of the polymers to a fictitious molar volume V_0 of one submolecule of polymer:

$$m_1 = V_1/V_0 \quad (8)$$

$$m_2 = V_2/V_0 \quad (9)$$



(c)

Fig. 11. (Continued from the previous page.)

TABLE III
Glass Transition Temperatures (T_g) of the First Extrudate, Remelted Extrudate in the Extruder,
and Repeated Blending Experiment of PC/PS Blends

Blend ^a	First extrudate ^b		Remelted extrudate ^c		Repeated experiment ^d	
	T_{g_1} (K)	T_{g_2} (K)	T_{g_1} (K)	T_{g_2} (K)	T_{g_1} (K)	T_{g_2} (K)
1.0	421.5	—	421.5	—	421.5	—
0.9	419.0	—	418.9	—	419.1	—
0.8	418.3	376.3	418.2	376.6	418.5	376.4
0.7	416.3	376.2	415.2	375.9	417.0	376.2
0.6	414.7	375.4	413.8	375.5	414.2	375.9
0.5	414.0	375.3	411.3	375.4	413.7	375.2
0.4	413.5	374.8	—	—	413.1	375.1
0.0	—	373.5	—	373.5	—	373.5

^aBlend designation given as overall weight fraction PC in PC/PS blend.

^bSubscripts 1 and 2 denote PC and PS components, respectively.

^cRemelted extrudate after second extrusion.

^dReplicated experiment of blending from pure components.

The choice of a lattice site volume can be rather arbitrary, but once a site volume has been chosen for one of the components, it must be the same for the other component.

The chemical potential of mixing of component i , as discussed by Tompa,⁵⁰ is obtained as the partial derivative of eq. (7) with respect to n_i :

$$\Delta\mu_1/RT = \ln \phi_1 + (1 - m_1/m_2)\phi_2 + m_1\chi_{12}\phi_2^2 \quad (10)$$

$$\Delta\mu_2/RT = \ln \phi_2 + (1 - m_2/m_1)\phi_1 + m_2\chi_{12}\phi_1^2 \quad (11)$$

TABLE IV
Glass Transition Temperatures (T_g) of PC and PS Components after Adding Polycarbonate to the First PC/PS Blend Extrudates

Blend ^a	T_{g_1} (K) ^b	T_{g_2} (K) ^b	Blend ^a	T_{g_1} (K) ^c	T_{g_2} (K) ^c
0.70	416.3	376.2	0.40 → 0.70	416.7	376.1
0.60	414.7	375.4	0.30 → 0.60	414.4	375.8
0.50	414.0	375.3	0.20 → 0.50	414.3	375.6
0.40	413.5	374.8	0.10 → 0.40	413.6	375.1

^aBlend designation given as overall weight fraction PC in PC/PS blend.

^b T_g 's of the first extrudate. Subscripts 1 and 2 denote PC and PS components, respectively.

^c T_g 's of the second extrudate after adding pure polycarbonate.

Equations (10) and (11) are not mathematically independent, but are equivalent to eqs. (1a) and (1b) of Scott,⁴⁹ respectively. From the lattice fluid theory of solutions,^{54,55} Sanchez⁵⁶ has derived an expression of the chemical potential of one component in a binary mixture which leads to expressions similar to eqs. (10) and (11).

At equilibrium the chemical potential of each component must be the same in both phases. Denoting the two conjugate phases by single and double primes, we have

$$\Delta\mu'_1 = \Delta\mu''_1 \quad (12)$$

$$\Delta\mu'_2 = \Delta\mu''_2 \quad (13)$$

Thus, eq. (10) will give

$$\chi_{12} = \frac{\ln(\phi'_1/\phi''_1) + (1 - m_1/m_2)(\phi'_2 - \phi''_2)}{m_1(\phi_2'^2 - \phi_2''^2)} \quad (14)$$

Similarly eq. (11) yields

$$\chi_{12} = \frac{\ln(\phi'_2/\phi''_2) + (1 - m_2/m_1)(\phi'_1 - \phi''_1)}{m_2(\phi_1'^2 - \phi_1''^2)} \quad (15)$$

Although eqs. (14) and (15) should give the same value of χ_{12} , the experimental error involved in the different experimental measurements in each equation leads to slightly different values. To minimize this error in χ_{12} , arithmetic average of the χ values can be made. Adding eqs. (14) and (15), we get

$$\begin{aligned} \chi_{12} = & \{ (\phi_1'^2 - \phi_1''^2) [m_2 \ln(\phi'_1/\phi''_1) + (m_1 - m_2)(\phi'_2 - \phi''_2)] \\ & + (\phi_2'^2 - \phi_2''^2) [m_1 \ln(\phi'_2/\phi''_2) + (m_2 - m_1)(\phi'_1 - \phi''_1)] \} \\ & \times [2m_1m_2(\phi_1'^2 - \phi_1''^2)(\phi_2'^2 - \phi_2''^2)]^{-1} \end{aligned} \quad (16)$$

TABLE V
Comparison of Polymer-Polymer Interaction Parameter (χ_{12}) from Different Values of Apparent Volume Fraction (ϕ) of PC and PS by the Wood, Fox, and Couchman Relations

Blend ^a	T_g (K)	T_g (K)	Wood ^b			Fox ⁴⁵			Couchman ^{46,47}		
			ϕ_1	ϕ_1'	χ_{12}^c	ϕ_1	ϕ_1'	χ_{12}^c	ϕ_1	ϕ_1'	χ_{12}^c
1.00	421.5	—	1.0000	—	—	1.0000	—	—	1.0000	—	—
0.80	418.3	376.3	0.9245	0.0514	0.037	0.9326	0.0576	0.036	0.9429	0.0682	0.035
0.70	416.3	376.2	0.8781	0.0495	0.038	0.8904	0.0556	0.037	0.9066	0.0658	0.035
0.60	414.7	375.4	0.8413	0.0348	0.042	0.8568	0.0391	0.040	0.8773	0.0464	0.038
0.50	414.0	375.3	0.8253	0.0330	0.042	0.8420	0.0370	0.041	0.8644	0.0440	0.039
0.40	413.5	374.8	0.8140	0.0238	0.046	0.8316	0.0268	0.044	0.8551	0.0318	0.042
0.00	—	373.5	—	0.0000	—	—	0.0000	—	—	0.0000	—

^a Blend composition given as overall weight fraction PC in the PC/PS blend.

^b Single prime and double prime denote PC-rich phase and PS-rich phase, respectively, and $\phi_2' = 1 - \phi_1'$ and $\phi_2'' = 1 - \phi_1''$. Subscripts 1 and 2 denote PC and PS components, respectively.

^c All χ_{12} 's calculated from eq. (16).

TABLE VI
 Apparent Weight Fraction (w) and Apparent Volume Fraction (ϕ) of PS and PBD components in PS-Rich Phase and PBD-Rich Phase, and Polymer-Polymer Interaction Parameter (χ_{12}) of PS/PBD Blends

Blend ^a	T_g (K) ^b	T_{g_2} (K) ^b	PS-rich ^c		PBD-rich ^c		PS-rich		PBD-rich		χ_{12} ^d
			w'_1	w'_2	w''_1	w''_2	ϕ'_1	ϕ'_2	ϕ''_1	ϕ''_2	
Solution Casting											
1.00	374.0	—	1.0000	—	—	—	1.0000	—	—	—	—
0.90	368.9	164.4	0.9757	0.0243	0.0005	0.9995	0.9715	0.0285	0.0004	0.9996	0.0078
0.75	370.1	164.4	0.9814	0.0186	0.0005	0.9995	0.9782	0.0218	0.0004	0.9996	0.0080
0.50	371.9	164.4	0.9900	0.0100	0.0005	0.9995	0.9882	0.0118	0.0004	0.9996	0.0086
0.25	373.2	164.4	0.9961	0.0039	0.0005	0.9995	0.9954	0.0046	0.0004	0.9996	0.0095
0.00	—	164.3	—	—	—	1.0000	—	—	—	1.0000	—
Mill Blending											
1.00	374.0	—	1.0000	—	—	—	1.0000	—	—	—	—
0.90	372.6	164.5	0.9933	0.0067	0.0010	0.9990	0.9918	0.0082	0.0008	0.9992	0.0086
0.75	372.3	164.5	0.9919	0.0081	0.0010	0.9990	0.9894	0.0106	0.0008	0.9992	0.0083
0.50	370.0	164.6	0.9809	0.0191	0.0014	0.9986	0.9777	0.0223	0.0017	0.9983	0.0073
0.25	369.7	165.4	0.9795	0.0205	0.0052	0.9948	0.9765	0.0235	0.0048	0.9957	0.0067
0.00	—	164.3	—	—	—	1.0000	—	—	—	1.0000	—

^a Blend composition given as weight fraction PS in the PS/PBD blend.

^b Data from Kim and Burns (Ref. 3).

^c Single prime and double prime denote PS-rich phase and PBD-rich phase, respectively, and subscripts 1 and 2 denote PS and PBD components, respectively. All w 's calculated from eq. (2).

^d All χ_{12} 's calculated from eq. (16).

TABLE VII
 Characteristics of Polymer Samples Used in PS/PBD Blends

Sample	\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n	T_g	ΔC_p
PS 237,700 ^a	237,700	98,600	2.41	373.5	0.282
PS 233,000 ^b	195,000	63,600	3.07	—	—
PBD 270,000 ^a	270,000	45,000	6.00	164.3	0.545

^aData from Ref. 3.

^bData from Ref. 52.

Using eq. (16), we have calculated the polymer-polymer interaction parameter (χ_{12}) from measured volume fractions for PC/PS blend systems (Tables II and V). The volume fraction was obtained from weight fraction divided by densities of each polymer.⁵⁷ The $m_1 = 48.4$ and $m_2 = 443.4$ were used for polycarbonate and polystyrene, respectively (Table I), and a repeat unit of polycarbonate has been chosen as a lattice site volume.

In Table V, the values of χ_{12} are compared with different ways of treatment of apparent weight fraction of PC and PS components by the Wood, Fox, and Couchman relations. From Table V the value of χ_{12} has been found to be 0.038 ± 0.004 at 250°C and the values of χ_{12} are in good agreement among the three different ways of obtaining weight fractions.

The validity of this method for calculating interaction parameters can be checked by reviewing our early studies,³ in which we reported experimentally measured glass transition temperatures in polystyrene (PS) and polybutadiene (PBD) blends using DSC. Applying the values of T_g of PS/PBD blends for mill-blending and solution-casting to eq. (16), we have calculated the polymer-polymer interaction parameter (χ_{12}) of PS/PBD blends, which is shown in Table VI. The $m_1 = 947.2$ and $m_2 = 508.9$ are used for PS 237,700 and PBD 270,000, respectively (Table VII), and a polystyrene repeat unit has been chosen as a site volume.

The χ_{12} values from the solid state which are shown in Table VI can then be compared with the values from solution studies. They are found to be in reasonable agreement with the χ_{23} values (cf. Table VIII) which have been published by Narasimhan et al.⁵² for the PS/PBD blends with solvent using GPC. It should be noted that the PS 233,000 and PBD 270,000 are used for PS/PBD blends with solvent⁵² (Table VII). Also Roe and Zin⁵⁸ have reported χ values ranging from 0.07 to 0.09 at 150°C, and Robledo-Muniz et al.⁵⁹ have

 TABLE VIII
 Interaction Parameters for PS 233,000/PBD 270,000/Toluene^a

Blend ^b	Wt % solvent (mean)	χ_{12}	χ_{13}	χ_{23}
0.50	81.56	0.403	0.448	0.004
0.45	81.55	0.402	0.439	0.005
0.50	84.51	0.404	0.430	0.008
0.50	87.54	0.409	0.034	-0.098

^aFrom Narasimhan et al.⁵²

^bBlend composition given as weight fraction PS in PS/PBD blend.

reported χ values ranging from -0.086 to $+0.012$ in ternary solution at room temperature for PS/PBD blends.

From the values of χ obtained by using the glass transition temperature method and the ternary solution method by Narasimhan et al.,^{33,52} we can say that the glass transition temperature method appears promising and could be applied to other partially miscible polymer blend systems in order to determine the polymer-polymer interaction parameter (χ_{12}). The χ_{12} values which have been calculated using eq. (16) may depend upon the degree of polymerization (m_i).

CONCLUSIONS

In the study of PC/PS blends, two glass transition temperatures have been found, $T_g(\text{PC})$, associated with PC-rich regions, and $T_g(\text{PS})$, associated with PS-rich regions, using differential scanning calorimetry.

In the study of the effect of blend composition on the $T_g(\text{PC})$ for PC/PS blends, the $T_g(\text{PC})$ decreased nearly linearly with increase of the weight fraction of PS. The decrease of $T_g(\text{PC})$ blends of 0.7 weight fraction PS composition is about 8 K for screw-extruded blends, and about 2 K for the solution-cast blends. In the $T_g(\text{PS})$ for PC/PS blends, the $T_g(\text{PS})$ increased linearly with increase of PC weight fraction. The increase of $T_g(\text{PS})$ for blends of 0.2 weight fraction PS composition is about 3 K for screw-extruded blends, and about 1.5 K for solution-cast blends.

In the study of the equilibrium of PC/PS blend systems in the extruder, the T_g 's of PC and PS of the first extrudate and the remelted extrudate are in good agreement within the investigated composition range except for the sample of 0.50 weight fraction of PC. Also the two T_g 's of PC/PS blends of the extrudate from the pure components and the remelted extrudate to which has been added pure polycarbonate are in good agreement for all compositions. From the above results, it can be concluded that the PC/PS blend system is close to equilibrium.

Values of the specific heat increment (ΔC_p) at T_g for PC and PS in PC/PS blends have been determined by DSC. The ΔC_p of polycarbonate decreases linearly with composition of polystyrene. The decrease in the ΔC_p of PC in extruded blends is larger than the decrease in the ΔC_p of PC in solution-cast blends. The ΔC_p of polystyrene also decreases linearly with composition of polycarbonate. The decrease of ΔC_p of polycarbonate is larger than that of polystyrene.

From the experimental T_g 's of PC and PS, we have determined apparent weight fractions of PS and PC components dissolved in the PC-rich phase and in the PS-rich phase. The apparent weight fraction of the PS component dissolved in the PC-rich phase is higher than the apparent weight fraction of the PC component dissolved in the PS-rich phase. This result is consistent with the experimental values of ΔC_p in PC/PS blends. From the above results of T_g and ΔC_p with various blend compositions, it can be concluded that polystyrene dissolves more in the polycarbonate phase than does the polycarbonate in the polystyrene phase.

In the study of morphology by scanning electron microscopy, phase separation between the PC-rich phase and PS-rich phase is more pronounced in

the case of the blends having overall PC-rich compositions than in blends having overall PS-rich compositions. This behavior has been found also in solution-cast PC/PS blends. This behavior is consistent with the experimental measurements of glass transition temperatures of PC/PS blends. From the microscopy study and the behavior of T_g 's of the blends with various compositions, it can be concluded that the compatibility increases more in the regions of PS-rich composition than in the regions of PC-rich composition.

Using the determined apparent weight fractions of the PC-rich phase and the PS-rich phase, the polymer-polymer interaction parameter (χ_{12}) of PC/PS blends with various compositions has been determined based on the Flory-Huggins theory, since the blend appears to be near equilibrium under extrusion conditions. The polymer-polymer interaction parameter of PC/PS blends has been calculated and found to be 0.038 ± 0.004 at 250°C for extruded blends.

By taking PS/PBD blends as a model system, we have been able to compare the values of χ with two different methods, the glass transition temperature method and ternary solution method. The two methods are in good agreement for χ values of PS/PBD blends. It is suggested that the T_g method to determine the polymer-polymer interaction parameter (χ_{12}) may be applied to the other polymer blends which are partially miscible systems.

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