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Miscibility and mechanical properties of a ternary polymer blend: polystyrene/polycarbonate/tetramethyl polycarbonate

C. J. T. Landry*
Corporate Research Laboratories, Eastman Kodak Company, Rochester, NY 14650, USA

H. Yang*
Imaging/Information Systems Group, Research Laboratories, Eastman Kodak Company, Rochester, NY 14650, USA

and J. S. Machell
Manufacturing Research and Engineering Division, Research Laboratories, Eastman Kodak Company, Rochester, NY 14650, USA

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The phase behaviour and morphology of a ternary blend, consisting of polystyrene (PS), bisphenol A polycarbonate (PC) and tetramethyl bisphenol A polycarbonate (TMPC), are investigated by thermal and mechanical analysis and by transmission electron microscopy. It is shown that the TMPC, which is miscible with each of the other components of the blend, does not solubilize the two immiscible polymers, PS and PC. Two glass transitions are observed for most of the blend compositions. Single phases are obtained only at very high TMPC content. The interaction parameters for the three binary blends were obtained from the literature and utilized to calculate the spinodal for the ternary blend. The theoretical calculation agrees well with the experimental data. It is shown that the relative molecular weights of the polymers have a considerable effect on the phase diagram of the ternary blend.

(Keywords: ternary polymer blends; polystyrene; bisphenol A polycarbonate; tetramethyl bisphenol A polycarbonate; morphology; phase diagram)

INTRODUCTION

The number of pairs of polymers known to form miscible binary blends has increased appreciably in recent years[1–6]. The Flory–Huggins interaction parameter χ is important in quantifying and potentially predicting miscibility in high-molecular-weight polymer blends. The χ value can be measured by small-angle neutron (SANS) or X-ray (SAXS) scattering[7], inverse gas chromatography (i.g.c.)[8] and differential scanning calorimetry (d.s.c.)[9]. Although a considerable number of miscible binary blends have been identified and investigated in detail, only a few studies of ternary polymer blends have been discussed in the literature[10–19]. Multicomponent blends are of significant industrial importance, and therefore it is of great value to investigate the miscibility and morphology of ternary blends.

The phase behaviour of ternary blends can be unique; various morphologies can be produced and optimized to give the desired properties. The concept that a third component, either a homopolymer or a copolymer, in a ternary blend may act as a compatibilizer for two immiscible polymers if this third component is miscible with each of the other polymers has been discussed[6,14,16]. Although the concept has merit, and some degree of compatibilization and enhanced interfacial adhesion often results, the thermodynamic considerations are not straightforward. The question as to whether true molecular miscibility can be induced in this manner is still open. We have chosen a system where one component of the ternary blend is miscible with each of the other components, these being immiscible with each other. The blend consists of polystyrene (PS), bisphenol A polycarbonate (PC) and tetramethyl bisphenol A polycarbonate (TMPC). The morphology of the blend is discussed in terms of the interaction parameters χ_{ij} of the corresponding binary blends. Marin and Monge[19,20] have previously studied the viscoelastic and thermal behaviour of binary and ternary blends of PS, PC and TMPC. They concluded that PS and PC are immiscible, PS and TMPC are miscible, and PC and TMPC are partially miscible up to 70 wt% PC. TMPC does not act as a compatibilizing agent for PS and PC in these ternary blends. The objective of the research presented herein is to explore further the detailed morphology of the PS/PC/TMPC blend using d.s.c., dynamic mechanical spectroscopy (d.m.s.), SANS, optical and transmission electron microscopy (TEM), and to gain deeper insight into the phase behaviour through the calculation of the phase diagram for the ternary system.

Based on the Flory–Huggins (FH) theory for the free energy of mixing, the phase behaviour of ternary systems can be calculated. Expressions for the spinodal and critical points were obtained by Tompa[21] for ternary systems consisting of one polymeric component and two

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*To whom correspondence should be addressed

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solvents. These expressions were later applied by Patterson[22] to systems composed of two polymers and one solvent and then by Su and Fried[23] to blends of three polymeric components. The essential details are summarized below. The free energy of mixing ΔG_m of three monodisperse homopolymers may be expressed in terms of their volume fractions ϕ_i as:

$$\tilde{G} = \left(\frac{\Delta G_m}{kT}\right)\left(\frac{v_0}{V}\right)$$

$$= \left(\frac{\phi_1}{y_1}\right)\ln\phi_1 + \left(\frac{\phi_2}{y_2}\right)\ln\phi_2 + \left(\frac{\phi_3}{y_3}\right)\ln\phi_3 + \chi_{12}\phi_1\phi_2 + \chi_{23}\phi_2\phi_3 + \chi_{31}\phi_3\phi_1 \qquad (1)$$

where v_0 is the volume per lattice site, V is the mixture volume, y_i is the ratio of volume of polymer i to the reference volume (v_0) and χ_{ij} is the interaction parameter between segments of polymers i and j, which is assumed to be composition-independent. For a mixture to be a single phase, the requirement that $\Delta G_m < 0$ must be fulfilled. Additionally, the second derivative of ΔG_m with respect to ϕ_i must be zero or positive. The boundary condition for the spinodal is given by $\partial^2\Delta G_m/\partial\phi_i^2 = 0$. Thus, the spinodal for a ternary blend may be obtained from[21–23]:

$$y_1\phi_1 + y_2\phi_2 + y_3\phi_3 - 2[y_1y_2(\chi_1+\chi_2)\phi_1\phi_2 + y_2y_3(\chi_2+\chi_3)\phi_2\phi_3 + y_3y_1(\chi_3+\chi_1)\phi_1\phi_3] + 4y_1y_2y_3(\chi_1\chi_2+\chi_2\chi_3+\chi_3\chi_1)\phi_1\phi_2\phi_3 = 0 \qquad (2)$$

where

$$\chi_i = (\chi_{ij} + \chi_{ik} - \chi_{jk})/2 \qquad (3)$$

The critical points must satisfy the additional condition:

$$\partial^3\Delta G_m/\partial\phi_i^3 = 0 \qquad (4)$$

Su and Fried[23] have applied this theoretical approach and calculated the phase diagrams (spinodal curves and critical points) for ternary systems, considering various combinations of the binary interaction parameters. One may represent the resulting morphologies (based on the above predictions) by the simplified schematic diagrams shown in *Figure 1*, keeping in mind that many more complex morphologies are possible. We shall consider the requirement for miscibility to be $\chi_c = 0$ for the purpose of this discussion, where χ_c is the threshold value of χ for phase separation.

Structure type 1 represents the simple case where all three binary blends are immiscible ($\chi_{ij} > 0$). Three phases will thus be present, each consisting of the pure component. Many ternary blends show this type of morphology. Structure types 2 and 3 occur when two of the binary blends are either miscible ($\chi_{ij} < 0$) or partially miscible ($\chi_{ij} \simeq 0$), and the third pair is immiscible ($\chi_{ij} > 0$). Thus, depending on the relative χ_{ij} values and the symmetry of the system (a symmetric system is one in which the χ_{ij} values of two or three of the pairs are similar to each other in magnitude and sign), the ternary blend may separate into either two phases (type 3) or three phases (type 2); the glass transition temperatures will be shifted relative to those of the pure components. Single-phase compositions may also occur. When AB and BC are miscible, but CA is marginally miscible or immiscible (type 3), phase separation is predicted[23] to occur in a manner that preserves the most energetically favourable pair interactions. Also, symmetry ($\chi_{AB} = \chi_{BC}$) favours miscibility. In some cases, component B may act as a compatibilizer for components A and C; Su and Fried predict that the compatibilizer would be effective only when the base blend is marginally immiscible ($\chi_{CA} \simeq 0$). The ternary blend of poly(ethyl methacrylate) (PEMA), poly(methyl methacrylate) (PMMA) and poly(vinylidene fluoride) (PVDF), studied by Kwei *et al.*[16], is an example of a symmetric system of type 3 where PVDF acts as a compatibilizer for PEMA and PMMA to produce a single-phase ternary blend over a wide range of composition; two phases are observed at low PVDF concentrations.

Finally, structure type 4 occurs when all three pairs of polymers are miscible. If all three χ_{ij} values are similar in magnitude (symmetric), then a single phase will be obtained. However, varied degrees of phase separation may occur for asymmetric systems owing to a phenomenon similar to that of preferential solvation, termed the $\Delta\chi$ effect[22,24]. Poly(methyl methacrylate) (PMMA)/poly(epichlorohydrin) (PECH)/poly(ethylene oxide) (PEO) is an example of a completely miscible ternary blend reported by Paul *et al.*[13]. *Figure 1* does not deal with asymmetry of the χ_{ij} values, nor the relative molecular weights of each component, both of which are ultimately important in determining the phase diagram. The ternary blend (PS/PC/TMPC) studied herein falls into structure type 3.

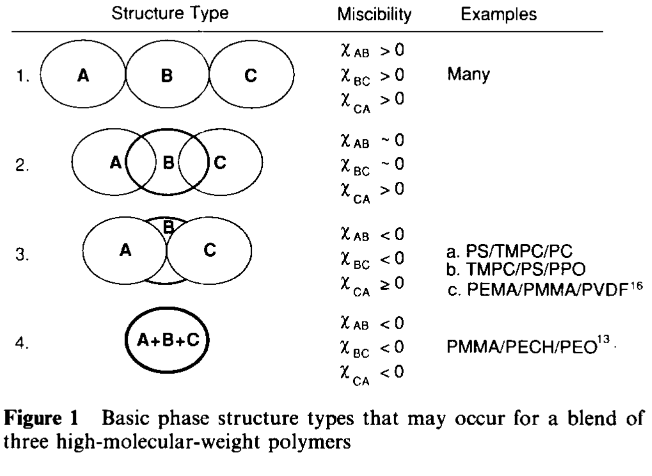

Figure 1 Basic phase structure types that may occur for a blend of three high-molecular-weight polymers

EXPERIMENTAL

Materials

The structures of the polymers used in this study are shown in *Figure 2*. Several polystyrene samples were used; the d.m.s., TEM and most of the d.s.c. data were obtained for samples prepared with a PS of molecular weight $\overline{M}_w = 200\,000$ ($\overline{M}_w/\overline{M}_n = 1.06$) purchased from Pressure Chemical Co., Pittsburgh, PA. D.s.c. data were also obtained for blends prepared using a PS sample with $\overline{M}_w = 20\,400$ ($\overline{M}_w/\overline{M}_n = 1.06$) from Pressure Chemical Co. and a polydisperse Styron 685D from Dow Chemical Co., which has a $\overline{M}_w = 312\,000$ and $\overline{M}_n = 124\,000$ as determined by size exclusion chromatography (s.e.c.) in tetrahydrofuran (THF). Unless otherwise specified, the results and discussion refer to blends prepared with 200 000 molecular weight PS. Bisphenol A polycarbonate (PC) was purchased from Mobay, Pittsburgh, PA. The weight-average molecular weight, measured by light

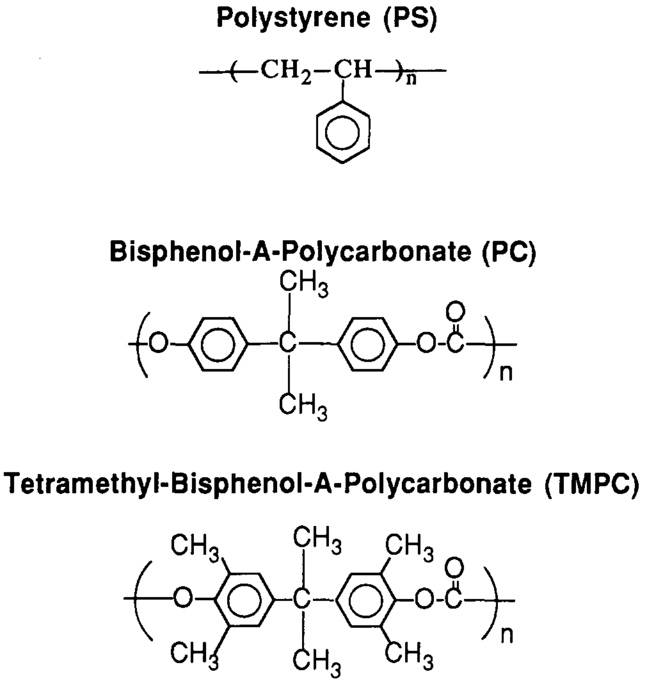

Figure 2 Molecular structures of the polymers studied

scattering in THF, is $\overline{M}_w = 31\,000$. Tetramethyl bisphenol A polycarbonate (TMPC) was generously provided by General Electric Co. and has a $\overline{M}_w = 67\,000$, as determined by light scattering in THF. The polydispersities ($\overline{M}_w/\overline{M}_n$) of PC and TMPC were ~2.6 as determined from s.e.c. in THF (in polystyrene equivalents).

The desired compositions of binary or ternary blends of PS, PC and TMPC were prepared in dichloromethane at levels of 5–10 wt% solids. The polymer solution was either poured into a petri dish and the solvent allowed to evaporate at room temperature for one day, or knife-coated onto a glass plate. The results were found to be independent of preparation method. Samples were further dried at 80°C for two days under vacuum.

Measurements

The glass transition behaviour for each sample was obtained using either a Perkin-Elmer DSC II, or a Dupont 990 thermal analyser. A sample weight of 8–12 mg and a heating rate of 20°C min^{-1} were used. The T_g is defined as the onset in the change in heat capacity with temperature.

Dynamic mechanical measurements (d.m.s.) were obtained using a Rheovibron DDV-II dynamic tensile tester (Toyo Measuring Instruments Ltd, Japan) automated by Imass Inc. The data were obtained at frequencies of 1.1, 11.0 and 110.0 Hz, using a heating rate of 1.5°C min^{-1}. The 11 Hz data are plotted.

Optical microscopy (OM) was performed using an Olympus BH-2 microscope equipped with a phase-contrast optical stage. Transmission electron microscopy (TEM) was performed on thin (< 1000 Å), microtomed sections (embedded in epoxy resin) using a JEOL TEM 100CX-II (JEOL Ltd, Tokyo, Japan) transmission electron microscope. The samples were stained with RuO_4, which is preferentially absorbed by the polystyrene.

RESULTS AND DISCUSSION

Morphology

D.s.c. and TEM measurements were performed on the binary blends of PS/PC, PS/TMPC and PC/TMPC to establish the reference states. For the PS/PC blends, two glass transitions are observed at each composition, corresponding to the values of T_g of the individual polymeric components; the polymers are immiscible. TEM reveals 1–10 μm diameter PS spherical domains dispersed in a PC background for the 50/50 wt% mixture. Both the PS/TMPC and PC/TMPC binary blends exhibit a single T_g for all compositions studied. No phase separation is observed by TEM for the 50/50 mixtures. Marin and Monge[19] have reported that, in the composition range of 75/25 PC/TMPC, the two polymers are not miscible. This difference in miscibility may be due to sample preparation. The samples prepared for this work were made by solution casting the films, and may be more homogeneous prior to coating than the samples prepared by Marin and Monge, which were made by mechanical mixing using a Brabender instrument. *Figure 3* shows T_g *versus* composition for the miscible binary blends of PS/TMPC and PC/TMPC. It has been shown[25] that the Gordon–Taylor (GT) equation, using $k = 2$ ($\Delta\alpha_{PS}/\Delta\alpha_{TMPC}$), provides the best fit to the composition dependence of T_g for the PS/TMPC blend. In the PC/TMPC blend, the T_g varies linearly with increasing composition of TMPC and $k = 1$ is obtained from a GT fit. The d.s.c. data for a few compositions of the PS/PC/TMPC ternary blend are shown in *Figure 4* and tabulated in *Table 1*. All compositions show two glass transitions with the exception of the blends that were very rich in TMPC, where only one T_g is observed. *Figure 5* shows that the T_g of the high-T_g phase increases linearly with TMPC content, behaving like the binary TMPC/PC blend, although the data fall slightly below the GT equation for the binary blend. The T_g of the low-T_g phase is only moderately increased by the addition of TMPC up to 70%. The data fall well below the GT equation for the binary PS/TMPC blend. The results seem to indicate that TMPC has more affinity for PC than for PS, consistent with the observations of Marin and Monge[19]. Although the d.s.c. data shown in *Figure 5* qualitatively imply the presence of two distinct phases, one consisting of PS and TMPC (PS-rich

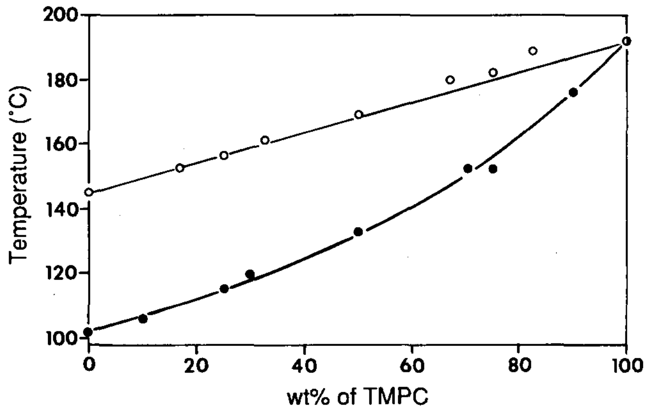

Figure 3 Composition dependence of the glass transition temperature for the binary blends of (●) PS/TMPC and (○) PC/TMPC. The full curves represent fits to the Gordon–Taylor equation with $k = 2$ for PS/TMPC and $k = 1$ for PC/TMPC

Table 1 D.m.s. and d.s.c. results for selected PS/PC/TMPC ternary blends

PS/PC/TMPC (wt%)	D.m.s. peak temperature (°C)						D.s.c.
	Tan δ			E''			
	110 Hz	11 Hz	1.1 Hz	110 Hz	11 Hz	1.1 Hz	T_g (°C)
100/0/0	130	124	119	120	115	109	102
0/100/0	167	162	155	158	154	150	145
0/0/100	215	211	205	211	203	196	192
33/33/33	151,185	143,178	137,175	145,174	139,169	134,161	113,160
50/25/25	160	148	138	140	135	127	109,155
25/50/25	146,180	138,174	134,169	143,170	135,167	132,153	107,153
25/25/50	181	175	167	167	161	152	113,166
5/5/90	208	206	201	202	194	189	187

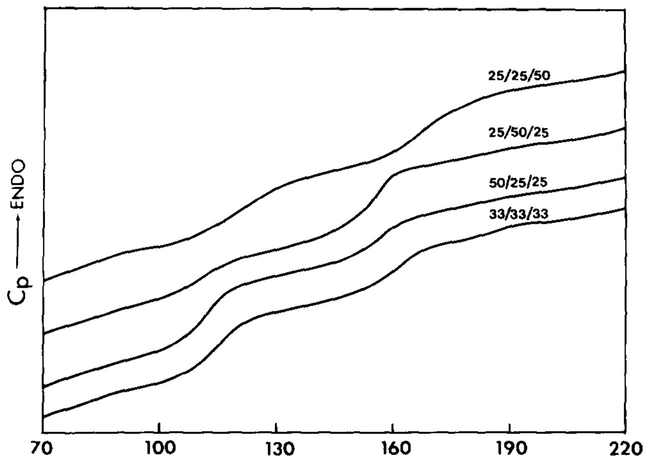

Figure 4 Selected d.s.c. traces for ternary blends of PS/PC/TMPC of various compositions

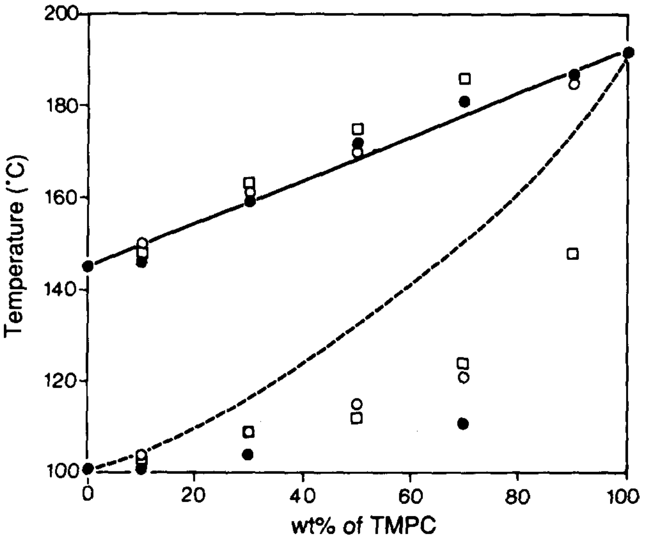

Figure 5 Composite plot of all d.s.c. data for the ternary blend of PS/PC/TMPC prepared with 200000 molecular weight PS, where the ratio of PS/PC in the ternary blends is (●) 1/3, (○) 1/1, (□) 3/1. The broken curve is the Gordon–Taylor equation for the binary blends as described in *Figure 3*

phase) and the other of PC and TMPC (PC-rich phase), the morphology of these ternary blends is far more complex. Each phase must comprise a mixture of all three polymers in order to compute values of T_g as a function of composition that equal those obtained experimentally. This will be discussed in further detail below. One must also consider that, as with binary blends, errors may be induced in the interpretation of the calorimetric responses obtained for ternary blends if two phases have compositions leading to similar values of T_g.

A combination of optical and transmission electron microscopy was used to elucidate the morphology of these blends. Optical microscopy provides an overall view of the phase structure; the presence of distinct domains that are on the order of 10–500 μm and that vary in size, shape and continuity depending on composition are observed. The use of optical microscopy in conjunction with the microtoming also ensures that the sections cut for TEM sample each macroscopic phase. The thin sections (for TEM) were stained with RuO_4, which darkens the PS-rich phases. The contrast thus provided permits differentiation between PS-rich and PC-rich phases; the presence or absence of TMPC, or of minor quantities of the third component, in each of these phases cannot be discerned. The following compositions of PS/PC/TMPC were studied: 5/5/90, 25/25/50, 25/50/25, 50/25/25 and 33/33/33.

No phase separation is observed for the 5/5/90 blend, for which only one glass transition was obtained by d.s.c. The morphologies of the 33/33/33, 50/25/25 and 25/50/25 blends are alike. These show a combination of PS-rich (dark) spherical domains dispersed in an extended PC-rich (light) phase, and PC-rich (light) spherical domains dispersed in an extended PS-rich (dark) phase. A low-magnification micrograph of the 50/25/25 blend is shown in *Figure 6a*. The entire thickness of the film is seen, sandwiched between epoxy resin. The extended PS-rich and PC-rich phases seem to be co-continuous; however, it was not possible to resolve the issue by TEM. The ultrathin sections that are required for TEM are small and do not sample very much of the film in question. This, combined with the large dimensions of the phase-separated domains observed for these samples, restricts what conclusions can be drawn about the global morphology of the sample. The phase continuity cannot be determined for most of the samples studied by TEM without examining an infinite number of sections. Information on the phase continuity could be obtained by OM for thinner samples than the ones prepared herein, using the appropriate staining. Some information on the phase continuity was obtained qualitatively for a few of the thinner samples (~25 μm thick); however, further work was not pursued since the exact morphology of

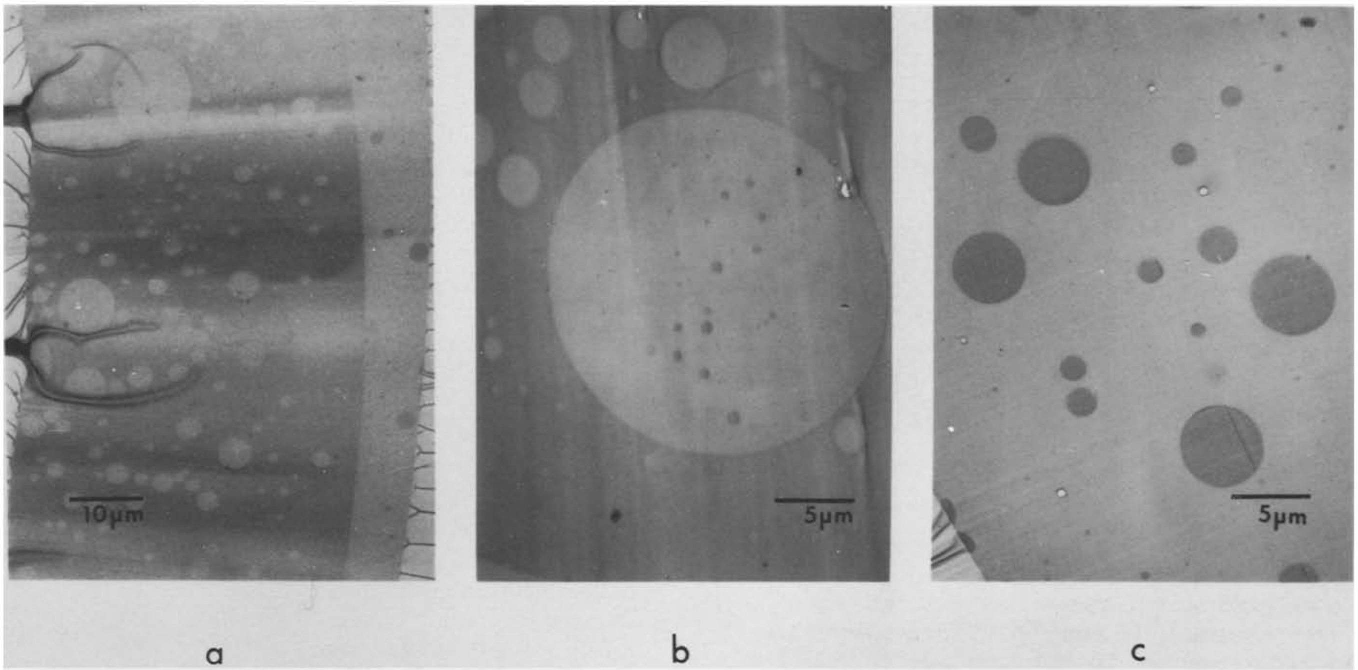

Figure 6 TEM of a PS/PC/TMPC blend of weight composition 50/25/25: (a) the entire thickness of the film; (b) PS-rich domains (dark) dispersed in PC-rich domain (light), which is in turn dispersed in a PS-rich background; (c) PS-rich domains (dark) in a PC-rich background

these high-T_g samples will depend on the sample preparation (solvent, rate of vitrification and therefore sample thickness). *Figures 6b* and *6c* show higher magnifications of each of the extended PS-rich and PC-rich phases, respectively. Most of the dispersed domains are on the order of 1–5 μm in diameter. There are also some submicrometre-size PC-rich domains, and some larger ($>10\,\mu$m) PC-rich domains in which submicrometre-size PS-rich domains are dispersed. Subtle differences in the size and number of the dispersed domains occur for various compositions. *Figure* 7 shows the presence of submicrometre PS-rich domains in addition to the micrometre-size domains dispersed in the PC-rich phase in the 33/33/33 blend. The PC-rich domains dispersed in the PS-rich phase seem to be more uniform in size.

The morphology of the 25/25/50 blend is different from those previously discussed. Both OM and TEM show that the PC-rich phase is continuous and that the PS-rich phase is dispersed, although these PS-rich domains are still on the order of 100 μm in diameter. Within some of these there exist other submicrometre PC-rich domains. Smaller ($\sim$1–5 μm) PS-rich domains are also present in the continuous PC-rich phase; these are shown in *Figure 8*. An important observation is that the dimensions of the 'extended' PS-rich phase are reduced by the addition of an excess of TMPC.

Since the exact dimension of the domain in the phase-separated blend depends on the method of preparation and sample history, the phase dimensions reported herein are particular to the blends prepared under the specified conditions and may be different for other preparation conditions.

Although substantial phase separation has occurred in the ternary blends, all these films were optically transparent. The indices of refraction of the three polymers, in particular PS and PC, are reasonably close: 1.59 for PS, 1.58 for PC and 1.55 for TMPC. These were measured using an Abbé refractometer with a mercuric iodide/potassium iodide wetting solution. Since TMPC mixes with each of the other polymers, the refractive indices of each phase will be closely matched.

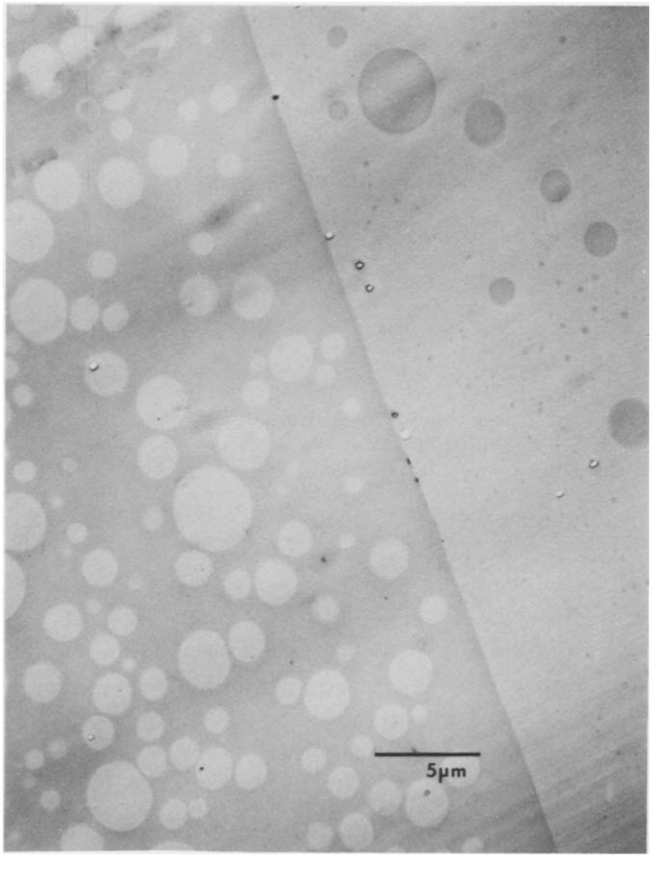

Figure 7 TEM of a PS/PC/TMPC blend of weight composition 33/33/33

The d.m.s. results for the three individual polymers are shown in *Figure 9*. The glass transition temperatures for these materials are distinct and the d.m.s. peaks are well

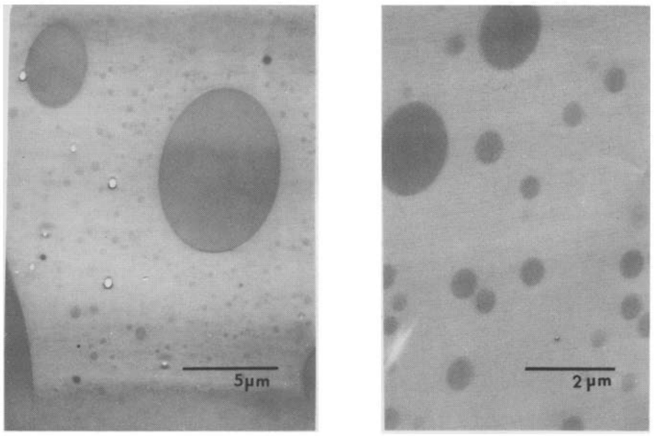

Figure 8 TEM of a PS/PC/TMPC blend of weight composition 25/25/50

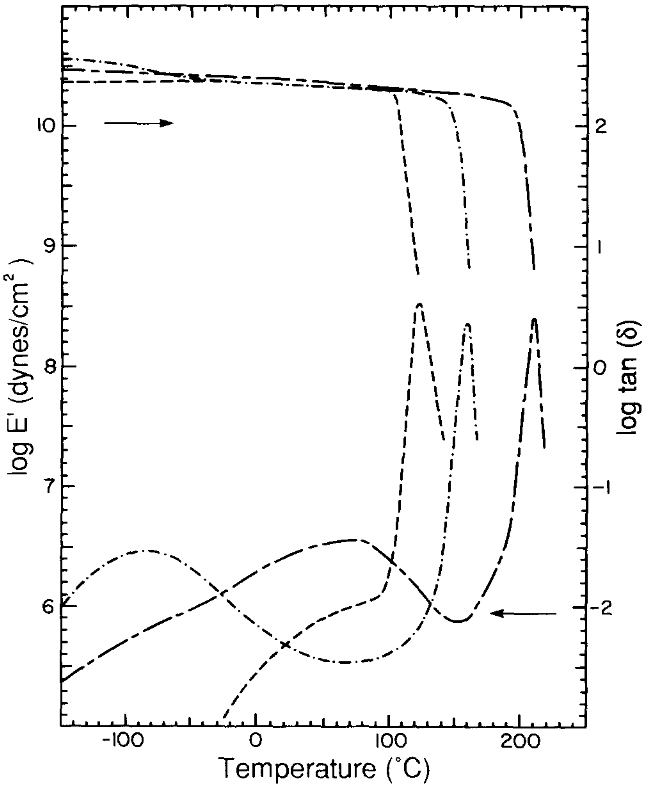

Figure 9 D.m.s. results, at 11 Hz, for (---) PS, (-·-) PC and (———) TMPC

resolved. Therefore there should not be any difficulty in sensing shifts in T_g upon blending resulting from intimate mixing of the components.

Since the samples used in these d.m.s. experiments are self-supporting films under tension, results can only be obtained for as long as the sample retains its mechanical integrity. When a material contains two or more components, such as in the present ternary blends, one phase will be continuous and the other will be dispersed, or the two phases may be co-continuous. This is of course a simplified view of the picture. Once the continuous phase reaches its T_g and enters the flow regime of viscoelasticity, the sample loses its mechanical integrity and further data cannot be obtained. Therefore, the glass transition of the dispersed phase (if it occurs at a higher temperature) will not be observed. This is distinct from the d.s.c. results where all glass transitions are observed experimentally. Thus, the d.m.s. experiment is expected to provide valuable information on the nature of the phase continuity in these ternary blends.

Figure 10 shows the d.m.s. curves for several compositions of the PS/PC/TMPC blends. The d.m.s. values for T_g, based on both tan δ and E'', are tabulated in *Table 1*. In general, the results follow the expected trend. Only one T_g is obtained for the 5/5/90 blend. This may indicate a miscible system; however, the amount of PS and PC in the blend may be insufficient for phase separation to be observed by this technique. One phase was observed by TEM, which is supporting evidence.

Samples PS/PC/TMPC 33/33/33 and 25/50/25 show the presence of two intermediate values of T_g, which correspond to a PS/TMPC-rich phase and a PC/TMPC-rich phase, as were observed by TEM. Minor quantities of the third component may be present in each phase. The lower T_g values are closer to the GT curve of the binary blend than were the d.s.c. results; however, many fewer samples were examined by d.m.s. For both these blends the PC/TMPC-rich phase is most probably the continuous or dominant phase; however, co-continuity of phases may also exist.

Only a single relaxation peak was observed for the PS/PC/TMPC 50/25/25 blend by d.m.s. However, the TEM results revealed the presence of two distinct phases. We can therefore postulate that the observed loss peak corresponds to the lower T_g and the PS/TMPC-rich phase. The peak temperature obtained from the tan δ (or E'') data is slightly higher than would be expected.

The d.m.s. results obtained for the PS/PC/TMPC 25/25/50 blend also reveal only a single loss peak. The temperatures obtained from both the tan δ and the E'' data are intermediate between the calculated GT values

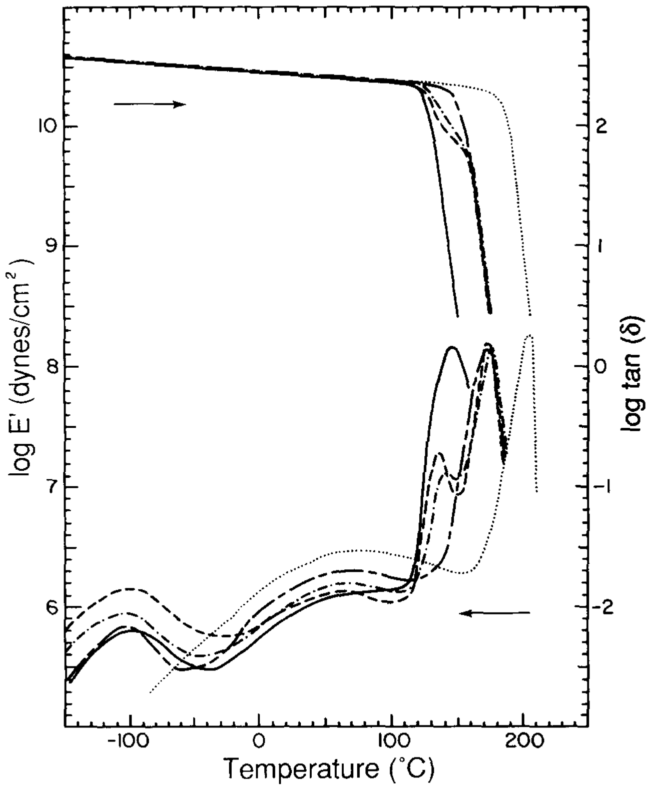

Figure 10 D.m.s. results, at 11 Hz, for selected ternary blends of PS/PC/TMPC: (-·-·-) 33/33/33, (---) 25/50/25, (———) 25/25/50, (——) 50/25/25 and (··········) 5/5/90

for the binary blends. This is similar to the results discussed for sample 50/25/25, although the effect is more pronounced. These results would appear to contradict the OM/TEM results, which indicated that the PC-rich phase was continuous. A caveat thus arises when considering samples in which the size of the phase-separated domains is large relative to the sample dimensions. The films that were used for d.m.s. measurements are typically 40–70 μm thick. Since the PS domains for the 25/25/50 blend can be as large as 100 μm, thus exceeding the thickness of the sample, the continuity of the PC-rich phase may be interrupted and the sample may fail in the tensile mode before the T_g associated with this phase is observed. Therefore, the conclusions drawn above from the d.m.s. data about phase continuity apply to relatively thin samples ($\leqslant 70$ μm) and may be different for samples of much larger dimensions.

To demonstrate that the samples were in equilibrium states, the d.m.s. results were obtained on sample 33/33/33 after it had been annealed at 150°C for 90 min. The experiment was repeated after further annealing at 180°C for 3 h. The d.m.s. curves obtained in both cases were identical to those shown in *Figure 10*.

The beta transitions for the PC and TMPC are very distinct. It is interesting to note that the shape of these transitions and their peak temperatures are not affected by the apparent molecular mixing of the components. The peak heights change in proportion to the composition of the blends. This behaviour has been observed for binary blends of PC and TMPC by Fisher *et al.*[26].

Phase diagram

In order to compare the experimental data with theoretical predictions, one must have a knowledge of the χ_{ij} values for each of the binary pairs in the system. The pertinent interaction parameters were obtained from the literature. $\chi_{PS/PC}$ values were taken from the published data of Kim and Burns[9]; these were obtained from d.s.c. measurements. The $\chi_{dPS/TMPC}$ and $\chi_{dPC/TMPC}$ values[25,27] were obtained by SANS.

The d.s.c. data for all of the PS/PC/TMPC blends are shown in the ternary phase diagram in *Figure 11*. The full circles correspond to compositions exhibiting only one value of T_g. The open circles correspond to those compositions where two glass transitions were observed. The miscibility window is extremely small and occurs only when TMPC is present in excess of ~90 wt%. The theoretical curve for the spinodal for this ternary system is generated using equation (2). Values for y_i are estimated using the ratio of weight-average molecular weight of polymer to the molecular weight of the repeat unit, i.e. the degree of polymerization of the polymer. The application of this equation assumes that the binary interaction parameters are concentration-independent. The χ_{ij} values obtained for these binary blends are somewhat concentration-dependent[9,25,27], particularly those obtained from SANS. Also, the χ_{ij} that one obtains from SANS is not exactly equivalent to the Flory–Huggins interaction parameter, but is related to it through the concentration derivatives of the free energy[28]. These experimental values of χ_{ij} will nonetheless be used in calculating the spinodal. The segmental χ_{ij} values taken from the SANS and d.s.c. data are those near the midpoint of the composition range for each of the binary blends. These are 0.026, −0.034 and −0.029 for PS/PC, PC/TMPC and PS/TMPC, respectively. The $\chi_{PS/PC}$ value obtained from ref. 9 was recalculated using the average volume of the PS and PC repeat units as the volume of the reference lattice cell for consistency with the SANS calculations[25,27]. The calculated spinodal curve is compared with the d.s.c. data in *Figure 11*. A single phase is predicted only at very high TMPC compositions, as was observed experimentally. The effect of varying $\chi_{PS/TMPC}$ through the range of values obtained by SANS as a function of composition is shown in *Figure 12*. Although the exact position of the spinodal does change somewhat, the effect is not that significant. The value of $\chi_{dPS/TMPC}$ obtained by SANS is less negative at high TMPC compositions. This would have the effect of increasing the immiscible region of the phase diagram for compositions rich in TMPC and is consistent with the observation of phase-separated blends at high TMPC content where single-phase compositions are predicted from the phase diagram in *Figure 11*.

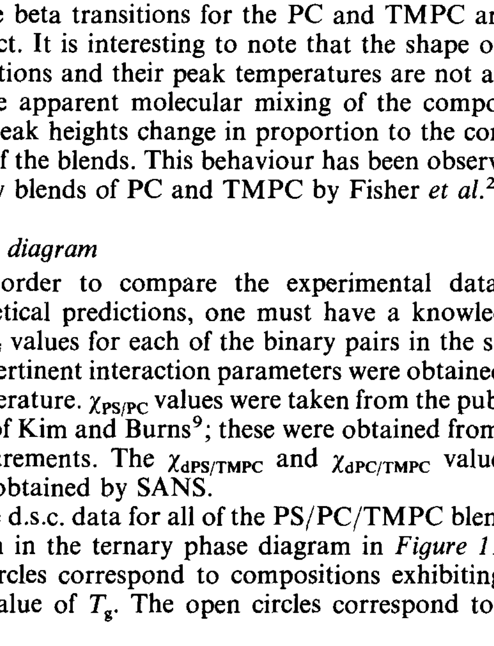

Figure 11 D.s.c. data for all of the ternary blends of PS/PC/TMPC. The open circles represent compositions where two glass transitions are observed and the full circles represent compositions where a single T_g is observed. The full curve is the spinoidal calculated using equation (2), with $\chi_{PS/TMPC} = -0.029$, $\chi_{PC/TMPC} = -0.034$, $\chi_{PS/PC} = 0.026$, $y_{PS} = 1923$, $y_{PC} = 122$ and $y_{TMPC} = 216$

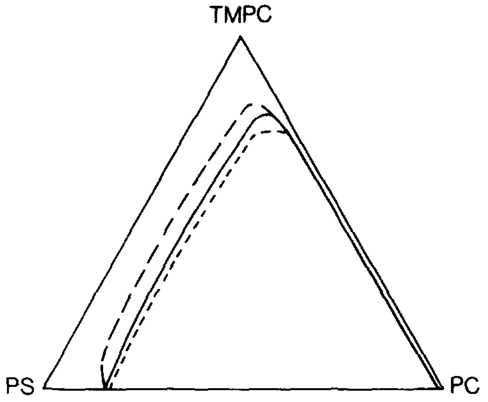

Figure 12 Effect of varying $\chi_{PS/TMPC}$ on the spinodal for the ternary blend: (————) $\chi = -0.0164$, (———) $\chi = -0.0288$ and (----) $\chi = -0.0412$. Values for y_i and other χ values as in *Figure 11*

A more dramatic effect is observed when the molecular weights of the components are changed. This is illustrated in *Figure 13*. The PC and TMPC have similar values of y_i, ~100 and 200, respectively. The PS, however, has a much higher molecular weight, resulting in a y_i value close to 2000. When all three y_i values used in the calculation are identical, and equal to 200, the spinodal

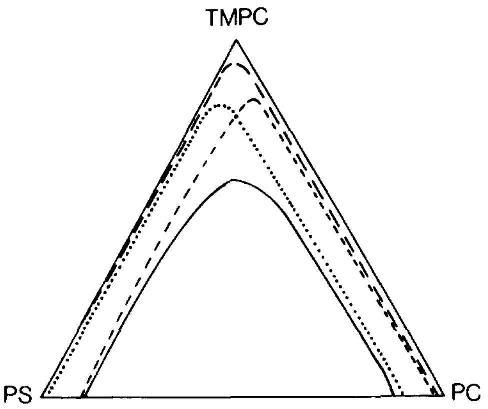

Figure 13 Effect of varying the degree of polymerization on the spinodal for the ternary blend: (———) for $y_{PS} = y_{PC} = y_{TMPC} = 200$ (the same curve is obtained using $y_{PS} = y_{PC} = 200$ and $y_{TMPC} = 2000$); (————) for $y_{PS} = y_{PC} = y_{TMPC} = 2000$; (··········) for $y_{PS} = y_{TMPC} = 200$ and $y_{PC} = 2000$; (---) for $y_{PS} = 2000$ and $y_{PC} = y_{TMPC} = 200$. Values for χ_{ij} as in *Figure 11*

curve is symmetric and the miscible region is much larger than that observed for the present system. Increasing all three y_i values to 2000 decreases the miscible region substantially. The effect of increasing only one of the molecular weights (either PC or PS), similar to the present ternary system, induces asymmetry to the spinodal and decreases the miscible region. It is interesting to note that increasing y_i for TMPC alone has no influence on the location of the spinodal.

Experimentally, it is observed that decreasing the molecular weight of PS affects the location of the lower T_g without significantly altering the value of the higher T_g. A blend of PS/PC/TMPC 15/15/70, prepared using PS ($\overline{M}_w = 20400$), shows two transitions, at 140 and 181°C, compared to 121 and 180°C observed for a blend of the same composition prepared using PS ($\overline{M}_w = 200000$). Polydispersity in the molecular weight of PS (using the Styron 685D sample) also increased the value of the lower T_g without altering the higher T_g; this is most probably due to the low-molecular-weight fraction of the PS sample.

From the calculated phase diagrams shown in *Figures 11–13*, one sees that, for any composition in the unstable region, the blend will separate into two phases. Each of these will consist of a mixture of all three polymers in different proportions. This is consistent with the interpretation given for the d.s.c., d.m.s. and TEM data. Changes in the molecular weight of the PS or PC will alter the phase diagram, thus altering the compositions of the phases formed upon phase separation. This results in changes in the observed T_g values. The phase diagram shown in *Figure 13*, for all y_i values equal to 200, predicts that the blend of PS/PC/TMPC 15/15/70, prepared with the PS ($\overline{M}_w = 20400$) would be single-phase. However, polydispersities in the molecular weights of PC and TMPC, which influence the exact location of the spinodal and critical point, as well as the tie-lines, have not been considered in these calculations, nor were they considered in the computation of χ_{ij} values from SANS data[25,27].

Although the calculated spinodal compares relatively well with the experimental data, one must keep in mind that it is not clear that the spinodal has a precise experimental meaning[27]. The data should preferably be compared with the binodal curve; however, this is far more difficult to calculate. Also, spinodals provide a qualitatively similar phase diagram to binodals.

CONCLUSIONS

The ternary blend discussed in this work represents one in which two of the binary blends form single-phase, miscible systems. These are the PS/TMPC and PC/TMPC blends. The other binary blend, PS/PC, does not form a miscible system. The concept that the addition of a third polymer, such as TMPC, to an immiscible blend may solubilize these components, similar to the effect of adding a common solvent, has been frequently discussed. The phase behaviour of the ternary system, however, is strongly dependent on the asymmetry of the binary interaction parameters χ_{ij} and the molecular weights of the polymers.

Values for χ_{ij} are used to calculate the spinodal curve for the ternary blend according to the equation used by Tompa[21]. The χ_{ij} values used for PS/PC, PS/TMPC and PC/TMPC are 0.026, −0.029 and −0.034, respectively. The miscibility region for this system is found experimentally to be quite small. The d.s.c. data also suggest that TMPC is more miscible with PC than with PS. However, this is mainly the result of asymmetry in a form not treated by Su and Fried[23], the molecular weights. The value of y_i for PS is 10 times greater than those for PC and TMPC. This has an effect on the relative miscibility of TMPC with each of the other polymers, as the critical χ for phase decomposition is much smaller for PS/TMPC than for PC/TMPC. Differences in monomer volumes and molecular-weight polydispersity may also affect the results; the theory assumes a common reference lattice volume and monodispersity.

The thermal and mechanical data show the presence of two glass transitions for most of the compositions in the ternary blend. A closer look at their morphology, by optical and transmission electron microscopy, reveals the presence of extended phase regions, each of which contains smaller domains, which are on the order of 0.1–10 μm. Based on these data and the predicted phase diagram it is inferred that each phase contains all three polymers, although in different proportions. One phase will be rich in PC and TMPC, but will have a minute amount of PS dissolved within it; the other phase will be rich in PS and TMPC, but will also contain a minor amount of PC. Owing to the asymmetry in molecular weights, the phase diagram (*Figure 11*) predicts that more PC will be dissolved in the PS/TMPC-rich phase than PS in the PC/TMPC-rich phase; this is also evidenced by the d.s.c. results (*Figure 5*).

Although the present ternary blends are phase-separated, the complexity of the morphology and the mixing of the three polymers within each phase could provide reinforcement to the interfacial regions and result in improved physical properties. A preliminary investigation of the ternary blend of PS, TMPC and poly(phenylene oxide) indicates that its phase behaviour is similar to that observed for the PS/PC/TMPC system.

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