Interfacial activity of polycarbonate/PMMA graft copolymers in polycarbonate/PMMA blends: effect of copolymer concentration

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This paper discusses the effectiveness of polycarbonate/poly(methyl methacrylate) graft copolymers as emulsifiers in solvent-cast dispersions of poly(methyl methacrylate)/polycarbonate blends. The molecular weight of the copolymer block corresponding to the minor (polycarbonate) phase was distinctly higher than that of the corresponding homopolymer. The results indicate that small amounts ($<5\%$ w/w) of copolymer can act as an effective surfactant, producing fine dispersions and creating significant amounts of interfacial area. Further addition of copolymer into the blend had no effect on the size of dispersed regions or on interfacial area. Dynamic mechanical spectra, microscopy and phase diagrams of the systems provide evidence that additional copolymer causes compositional rearrangement. Although some increased miscibility of the polymer components has been effected by the addition of copolymer in the blend, there is no evidence that the copolymers act primarily as miscibilizers for the blend.

(Keywords: polymer blends; morphology; dynamic mechanical properties; copolymer; interfacial concentration; polycarbonate; poly(methyl methacrylate); compatibilizer)

INTRODUCTION

It has been extensively reported that when a copolymer comprising blocks of polymers A and B is added to a blend of the same immiscible homopolymers (A, B) it is localized at the A–B interface[1] and reduces the interfacial tension in the blend[2], hence aiding dispersion of one polymer in the other[3]. Despite the amount of published data there is no general agreement on the factors which control the interfacial activity of the copolymer and no systematic study of the role of copolymer as an interfacial agent has been made[4]. A number of theories have been developed recently on the micellization of copolymers[5] and, more importantly, on the phase separation in polymer blends in the presence of copolymers[4,6].

In this paper we present data on the interfacial activity of graft copolymers in blends of two homopolymers over a broad range of the copolymer contents. The system studied is a blend of a chlorine-containing polycarbonate and poly(methyl methacrylate) with added polycarbonate/poly(methyl methacrylate) graft copolymers. Eastmond and co-workers have presented investigations on the compatibility of blends of these homopolymers[7] and the effect of added copolymers on the properties of the blend[8]. They have shown that phase separation of the two homopolymers during solvent casting does not normally proceed to equilibrium but that the extent of segregation of the two components is highly dependent on the casting conditions. A qualitative explanation of the morphology of the polyblend with composition was presented in terms of the phase diagrams of the systems. The same authors also reported that small amounts of polycarbonate/poly(methyl methacrylate) graft copolymers produced finer dispersions in blends of the corresponding homopolymers when the molecular weight of the polycarbonate block was greater than that of the corresponding homopolymer.

The present data are the results of a more systematic study of the same system over a wide range of copolymer contents under the specific conditions that the molecular weights of the blocks are greater than those of the corresponding homopolymers. Influence of changes in relative molecular weights of blocks and homopolymers will be discussed separately.

MATERIALS

The poly(methyl methacrylate) (PMMA) homopolymer was supplied by RAPRA ($\bar{M}_n = 48$ kg mol^{-1}). The polycarbonate 'homopolymer' is a random copolymer of bisphenol A and 1,1-trichloro-bis-2-(p-hydroxyphenyl)-ethane prepared by condensation polymerization of an equimolar mixture of the two bisphenols with phosgene as described elsewhere[9]; its molecular weight was determined by gel permeation chromatography (g.p.c.) with THF as carrier solvent and with respect to polystyrene calibration.

Copolymers were prepared by initiating free radical polymerization of methyl methacrylate (MMA) from the trichloromethyl groups on the preformed polycarbonate (prepolymer). Photolysis ($\lambda = 436$ nm) of dimanganese decarbonyl ($Mn_2(CO)_{10}$) initiator leads to the formation of polycarbonate macroradicals through abstraction of a chlorine atom from the pendant trichloromethyl groups[10].

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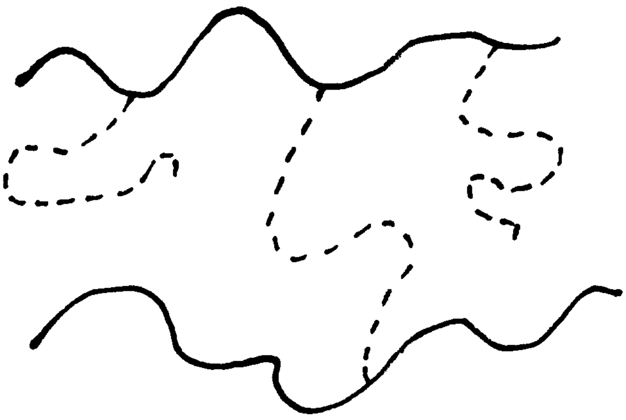

Scheme 1

Reactions were carried out in dilute solutions ($\approx 1.5\%$ w/w) of the prepolymer in methyl methacrylate at 25°C in sealed tubes in a room illuminated with inactive sodium light. Radicals are created randomly from only a small percentage of the trichloromethyl groups on the polycarbonate. The initiation reaction is highly specific and chain transfer to the polymer is negligible at the low concentrations of polycarbonate and methyl methacrylate conversions used. All PMMA chains are, therefore, attached to the polycarbonate prepolymer. The propagating chains undergo termination by combination and disproportionation.

At 25°C, 67% of the propagating chains terminate by disproportionation, forming one graft of PMMA on each polycarbonate chain reacted[10,11]. Combination termination of two propagating chains produces a crosslink between two polycarbonate chains. Because of the multiple functionality of the polycarbonate and the presence of termination by combination the reaction can eventually lead to network formation.

The structure of the copolymers formed and their relation to the polymerization kinetics has been extensively discussed in previous publications[10–13]. Before gelation the reaction mixture contains unreacted polycarbonate and various grafted and crosslinked structures. The critical condition for network formation is one crosslinked unit per weight-average polycarbonate chain. We define the relative crosslinking index, γ_r, which is proportional to the number of crosslinks in the system relative to those necessary for incipient network formation. The crosslinking index was kept below 1 for all our copolymers (typically $\gamma_r = 0.65$). The average structure of our copolymers species can then be depicted as indicated in *Scheme 1*.

PMMA grafts and crosslinks were characterized by g.p.c. after selective degradation of the polycarbonate in the copolymer. A homogeneous degradation procedure based on the reaction of the polycarbonate with triethylamine, introduced by Eastmond and Harvey[13] was used. The molecular weight of the PMMA grafts and crosslinks of our copolymer was 390 kg mol^{-1}. The molecular weight of the polycarbonate used for the blends was 20.2 kg mol^{-1} while that used as prepolymer in the graft copolymer synthesis was 143.8 kg mol^{-1}.

The molecular weights of the homopolymers and copolymers are abbreviated as follows: *MAH*, $\bar{M}_n$ of polycarbonate homopolymer; *MAC*, $\bar{M}_n$ of polycarbonate backbone in the copolymer; *MBH*, $\bar{M}_n$ of poly(methyl methacrylate) homopolymer; and *MBC*, $\bar{M}_n$ of poly(methyl methacrylate) grafts in the copolymer.

TECHNIQUES

The blends were prepared by solvent casting. Films of the blends (0.2 mm thick) were cast from dilute homogeneous solution (4% w/v) in dichloromethane under reproducible conditions. Residual solvent was removed at 115°C under vacuum over one week. The compositions of all blends and copolymers were determined by ultraviolet spectrophotometry and nuclear magnetic resonance (n.m.r.) analysis.

Morphologies of the films were studied by optical microscopy and transmission electron microscopy (TEM). Relatively thick sections (10–15 μm thick) cut parallel to the film surface were used for the optical microscopy. Microtoming introduced birefringence into the sample[7] and allowed contrast between the phases to be examined under cross-polars. Under these conditions the polycarbonate-rich phase appears bright while the PMMA-rich one is dark.

Ultrathin sections cut parallel to the film surface were used for TEM studies. Sections were stained with ruthenium tetroxide (RuO_4) vapour. It was established that polycarbonate is stained (dark) preferentially.

Phase diagrams of the systems were determined by allowing heterogeneous mixtures in the presence of solvent, of known composition, to separate into two layers and reach equilibrium in sealed glass tubes in a thermostat (28°C). The volumes of the phases were measured. The total polymer concentration of each phase was determined by careful precipitation of a known volume of each phase into petroleum spirits. The relative composition of the two polymers in each phase was determined by n.m.r.

Dynamic mechanical spectra were obtained by using a Rheovibron viscoelastometer (DDV-IIC, Toyo-Baldwin Ltd, Tokyo) on samples (2×30 mm^2) cut from the cast films. Measurements were made at 110 Hz and a heating rate of 1.5°C min^{-1}. The Rheovibron was interfaced to a Research Machines microcomputer for automatic data acquisition and reduction.

RESULTS AND DISCUSSION

Unmodified PMMA/polycarbonate blends

The composition of the system studied in this work was kept at 65/35 w/w PMMA/polycarbonate to allow the stabilizing effect of PMMA grafts on blend morphology to be examined. Previous work[7] has also shown that mechanical relaxations of both components could be resolved at such compositions. It has been established that the morphology of polymer blends is highly dependent on the casting conditions. *Figure 1* demonstrates the different morphologies of a 65/35 w/w PMMA/polycarbonate blend prepared under varying conditions (*Table 1*). The optical micrographs demonstrate clearly the presence of gross incompatibility of the two polymers leading to the formation of two layers. Only when the mixture was shaken during film casting was a one-layer morphology obtained. Unfortunately, this film was very 'cheesy'. The dynamic mechanical spectra of the same systems demonstrate two α-relaxations close to the glass transitions of the two homopolymers (*Figure 2*). As the

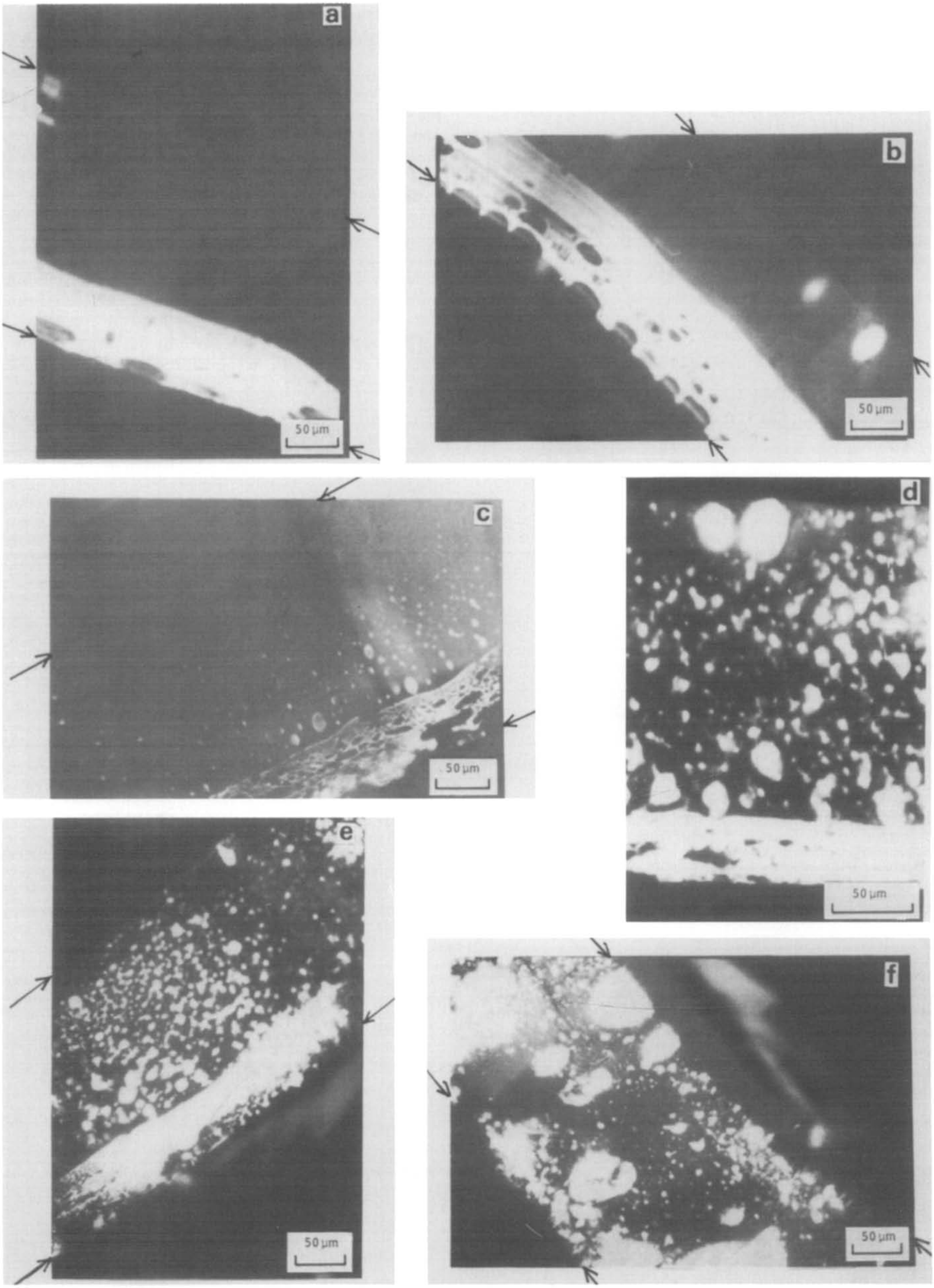

Figure 1 Optical micrographs of cross sections of PMMA/polycarbonate blends (65/35 w/w) cast under varying conditions (see *Table 1*). Arrows indicate the edges of the films. Scale bars represent 50 μm

Table 1 Film preparation conditions for 65/35 w/w poly(methyl methacrylate)/polycarbonate blends

Sample	Casting conditions	*T* (°C)[a]
A	Closed petri dish placed in closed container	25
B	Closed petri dish	25
C	Open petri dish	25
D	Open petri dish	32
E	Open petri dish	40
F	Open petri dish, shaken until touch dry	25

[a] *T*, film casting temperature

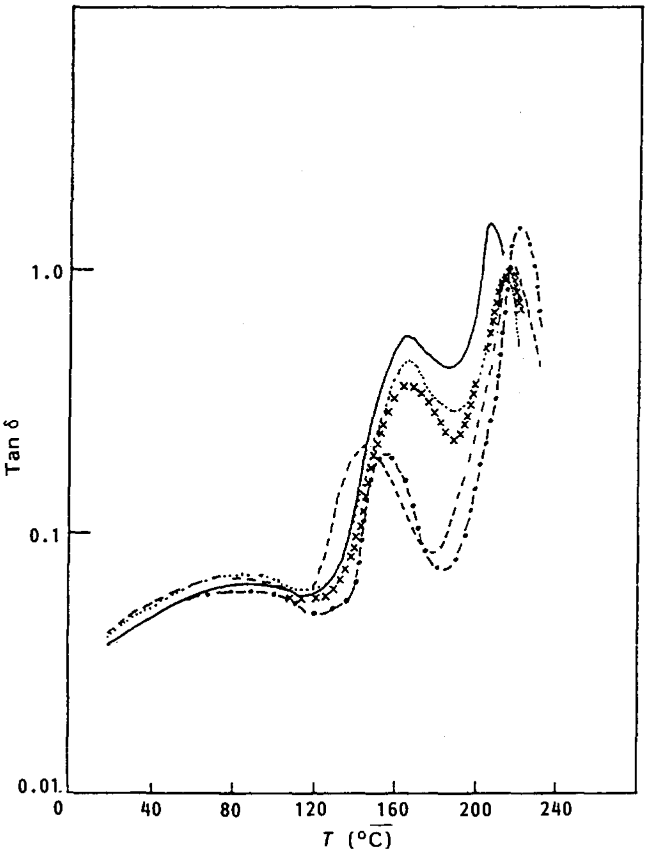

Figure 2 Effect of film casting procedure on dynamic mechanical properties of 65/35 w/w PMMA/polycarbonate blends: — — —, sample A; —·—, sample B; × × × ×, sample C; ·····, sample D; ——, sample E. Casting procedures are given in *Table 1*

polycarbonate-rich phase is more completely dispersed the maximum in the logarithmic decrement from the PMMA-rich phase increases and the glass transition temperatures of the two phases approach each other; the latter indicates mixing of the two components at higher rates of solvent evaporation and is consistent with earlier observations[7].

As an initial polycarbonate dispersion was considered necessary as a reference morphology for the comparison with the copolymer modified systems, casting procedure E was adopted in this work.

Blends containing copolymers

In agreement with previous studies, addition of copolymer was found to produce finer dispersions as shown by optical microscopy. The size of the dispersed phases depends on the block molecular weights. If the molecular weights of the copolymer blocks are distinctly greater than those of the corresponding homopolymer it is possible to achieve blends which appear homogeneous when examined under the optical microscope (*Figure 3*). Optical micrographs in *Figure 3* confirm that addition of copolymer to the blend leads to the disappearance of the 'coalesced' lower polycarbonate-rich layer in the films. The morphology on this scale is much more uniform than in the absence of copolymer (cf. *Figure 1*) and consists of a dispersion of relatively uniform polycarbonate-rich domains in a PMMA-rich matrix at resolutions of ≈1 μm. Addition of >5% copolymer gives optically 'homogeneous' materials although TEM reveals heterogeneities on a sub-micrometre scale (*Figure 4*). The influence of copolymer molecular weights on morphology

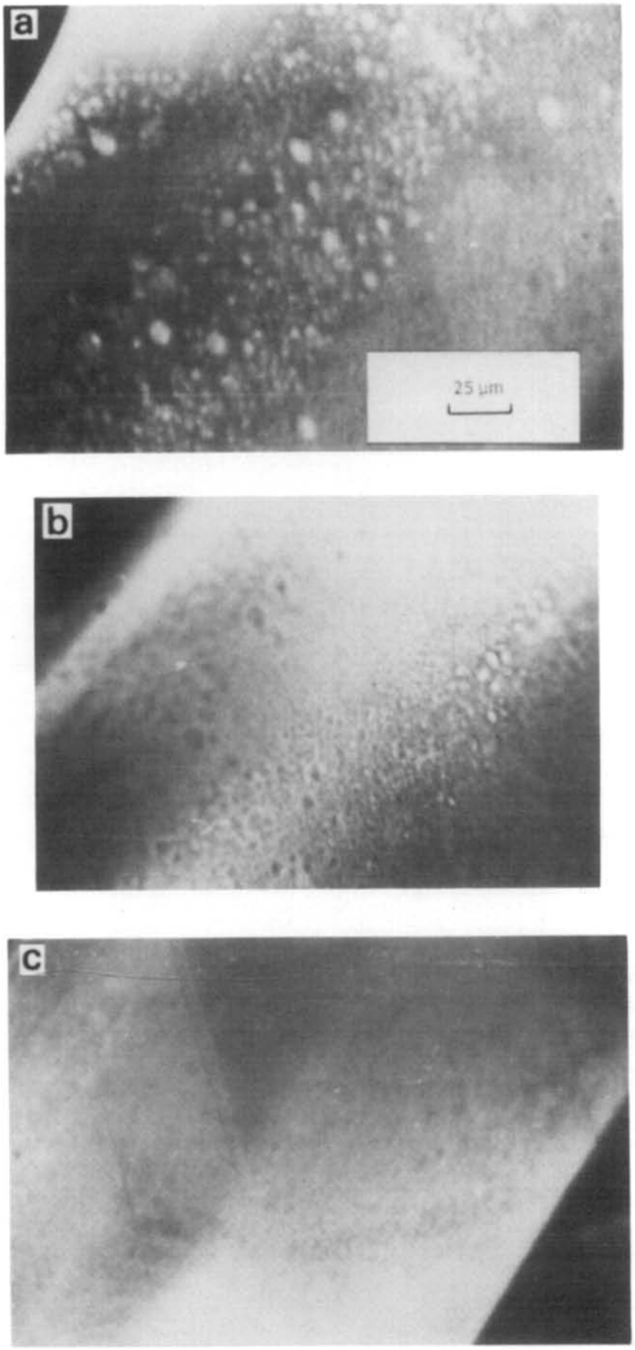

Figure 3 Optical micrographs of cross sections of PMMA/polycarbonate blends (65/35 w/w) containing (a) 2, (b) 5 and (c) 10% w/w copolymer

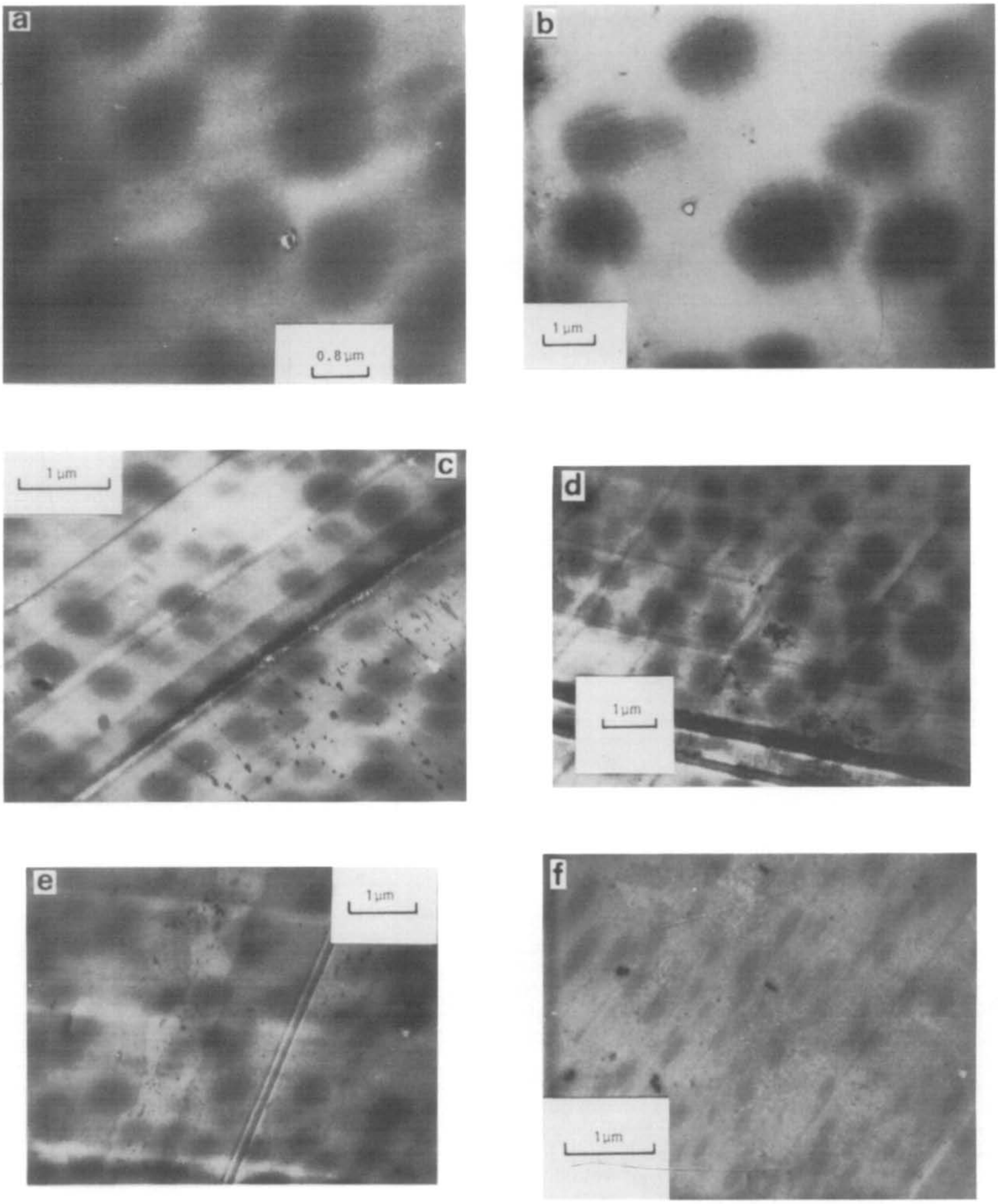

Figure 4 Transmission electron micrographs of PMMA/polycarbonate blends (65/35 w/w) containing (a) 1, (b) 2, (c) 5, (d) 10, (e) 20 and (f) 30% w/w copolymer

and properties will be presented elsewhere. In this paper we only consider the variation of the copolymer concentration in one system where addition of copolymer will yield optically homogeneous materials.

The morphologies of copolymer-modified blends are characterized by polycarbonate-rich domains (dark) dispersed in a PMMA-rich matrix as shown by TEM (*Figure 4*). It is apparent from the transmission electron micrographs that the size of the polycarbonate-rich dispersed phases is not uniform. We believe that this partly reflects the presence of a whole distribution of local compositions created during solvent evaporation. Furthermore, there is no reason *per se* why the domains in blends should have a uniform size as would be expected for pure block copolymers with narrow molecular weight distribution where molecular constraints lead to regularity in morphology.

The average diameter of the polycarbonate-rich domains decreases with the addition of the initial 2–5% w/w copolymer. Thereafter, it remains constant up to rather high copolymer contents (*Figure 5*). This behaviour is further seen in a more detailed representation of the blend

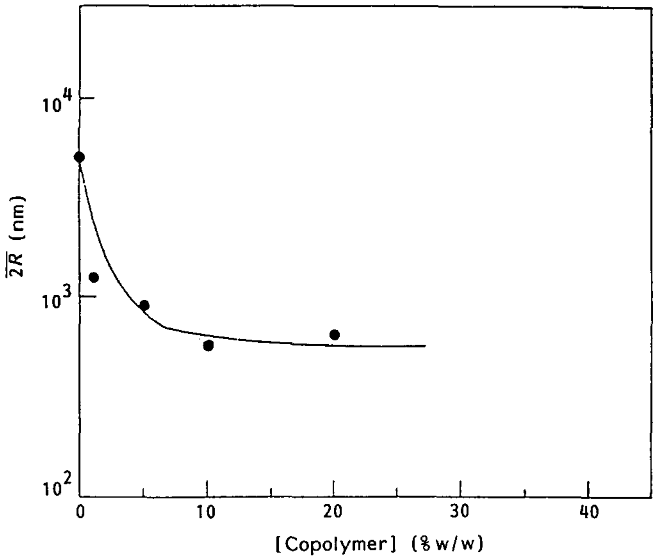

Figure 5 Variation of the average diameter of polycarbonate-rich domains with varying added copolymer content in PMMA/polycarbonate (65/35 w/w) blends

morphology by the distribution of particle sizes given in *Figure 6*. The average interfacial area per unit total volume ($\langle SV \rangle$) and per unit volume of dispersed phases ($\langle S_D \rangle$) can be calculated with standard stereological equations which are independent of the system's specific geometry[14].

$\langle SV \rangle$ is easily calculated from

$$\langle SV \rangle = 2NL \qquad (1)$$

where NL is the ratio of the number of intersections made by a set of sampling lines with the boundaries of the polycarbonate-rich domains to the total length of the sampling lines LL. Slight modification of equation (1) can provide the interfacial area per unit volume of dispersed phase ($\langle S_D \rangle$):

$$\langle S_D \rangle = 2NL(LL/DD) \qquad (2)$$

where DD is the sum of the lengths of the sampling lines traversing the polycarbonate-rich domains. A 1 cm^2 grid was used with about 10 sampling lines per micrograph. Data from up to four micrographs of different sections were used in the calculations.

Figure 7 depicts the variation of the average interfacial concentration with increasing copolymer concentration. Again, it is evident that incorporation of only a small percentage of copolymer into the blend leads to a dramatic increase in the interfacial area. Further addition of copolymer into the system does not create more interfacial area.

Paul[1] derived an equation for the average surface area occupied by block copolymer molecules assuming that all the copolymer is located at the interface and that the blocks of the copolymer completely penetrate their corresponding phases at the interface:

$$a = 3\phi_A M / NRW \qquad (3)$$

where ϕ_A is the volume fraction of polymer A dispersed as spherical domains of radius R, M is the molecular weight of the copolymer, N is Avogadro's number and W is the weight of copolymer added to the blend as a percentage (assuming unit density). Although we have not got an AB block copolymer we assumed for the

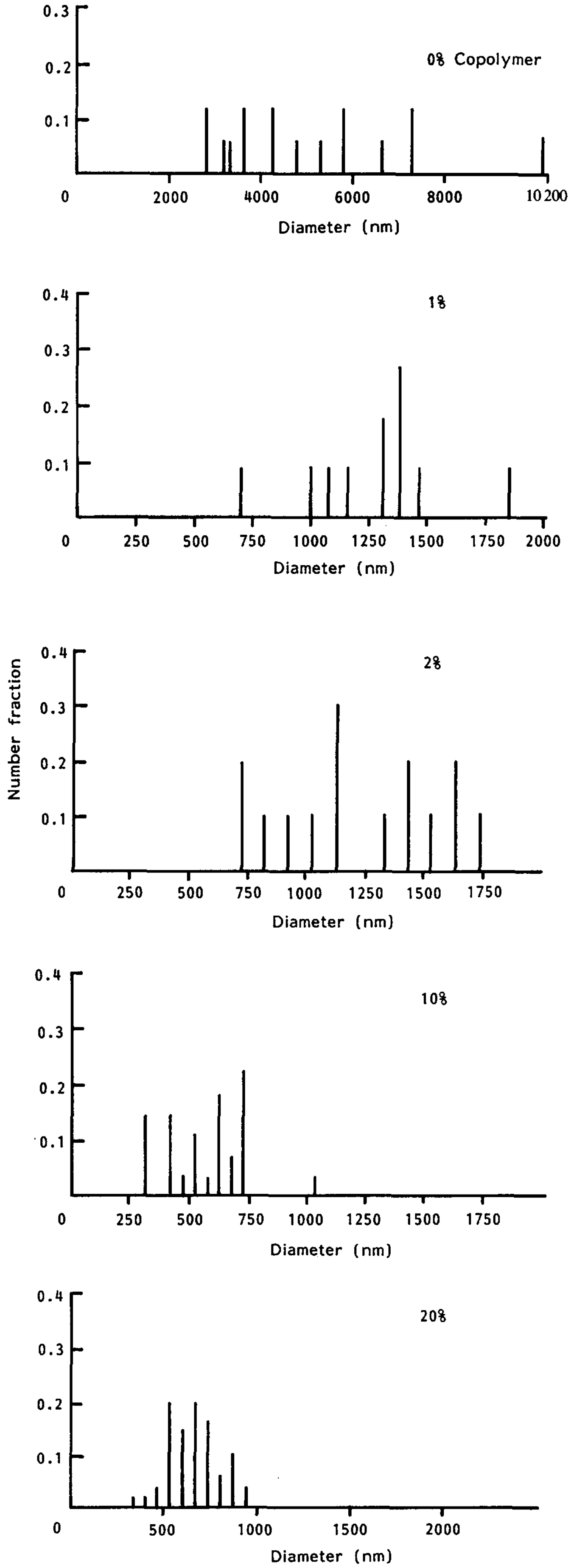

Figure 6 Histograms of the relative frequency of polycarbonate-rich domain diameter for PMMA/polycarbonate blends (65/35 w/w) with varying copolymer content

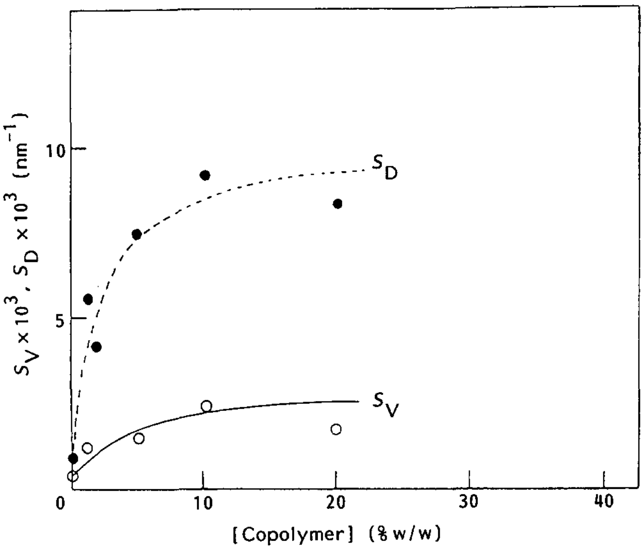

Figure 7 Effect of copolymer concentration (% w/w) on the interfacial area per unit total volume, S_v (○) and per unit volume of dispersed phase, S_D (●)

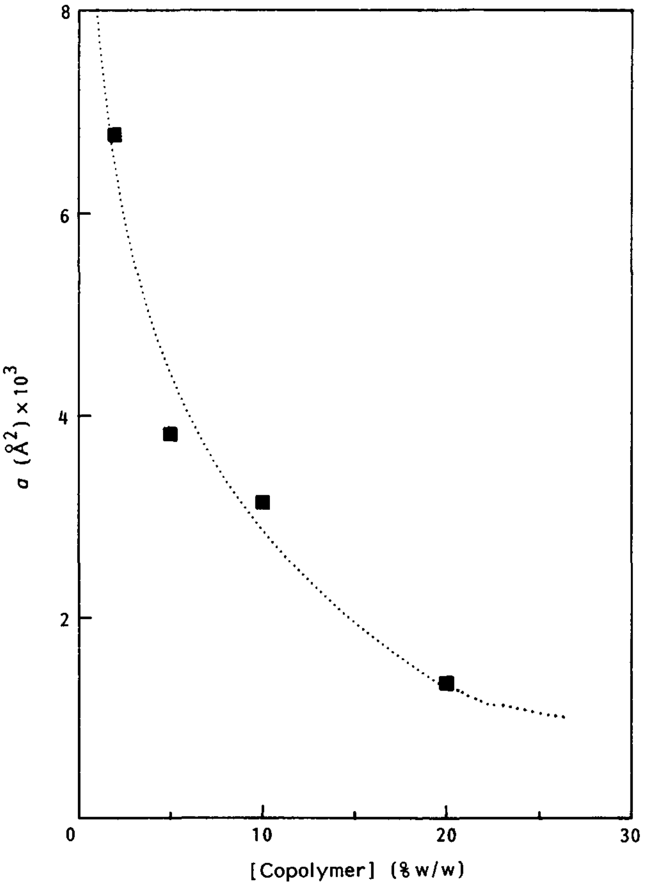

Figure 8 Variation of area occupied by a single copolymer at the interphase with added copolymer concentration as calculated by equation (3)

purpose of the calculation that

$$M = MAC + MBC$$

where MAC and MBC were defined earlier. The data are summarized in *Figure 8* and *Table 2*. Values calculated from the electron micrographs are significantly greater than those reported in the literature for other systems[1,15] (*Table 2*). We suggest that this difference is due to structural features of our copolymer species affecting their conformation at the interface and also the presence of limited mutual solubility of the two components at high polymer concentration in the casting solvent. Complex species such as those we have used would be expected to occupy a greater interfacial area per molecule than simpler species reported in the literature. Moreover, the presence of a limited solubility between the components in our system would tend to favour a more extended conformation of the copolymer molecules at the interface, leading to an increase in α. As we have shown in *Figure 7* the total surface area present reaches a plateau value beyond which it is unaffected by additional copolymer. The experimental decrease in area occupied per molecule with copolymer content shown in *Figure 7* is a simple consequence of this fact and the assumption that all copolymer is located at the interface. It is more likely that as copolymer content is increased, a level is reached at which it saturates the system. Any additional copolymer will either form micelles or a separate copolymer-rich phase. We have not observed the presence of such a phase but micelles or small aggregates of copolymer could well exist undetected at the resolution provided by our techniques.

Thus we suggest that the plateau in phase size corresponds to a levelling out in the amount of copolymer at the interface.

Dynamic mechanical behaviour

While polymer blends (65/35 w/w PMMA/polycarbonate) with less efficient copolymer as interfacial agents show multiple α transitions[8] in systems with very fine dispersions, there is no evidence for multiple relaxations in the tan δ data for samples used in the current study. The effect of the increasing copolymer content on the dynamic mechanical behaviour of the blend is summarized in *Figure 9*. A single α-relaxation is observed for all systems at temperatures between the glass transitions of the two homopolymers. Initially the T_g, defined as the temperature at which tan δ is a maximum, shifts to higher temperatures with the addition of up to 5% w/w in the blends and then becomes independent of copolymer content (*Figure 10*). The simple inverse rule of mixtures[16] predicts polycarbonate contents between 20 and 44% w/w in the PMMA-rich matrix; above 170°C moduli were too low to be measured with the Rheovibron. The assignment of the observed relaxation to any phase in the blend requires confirmation that there is no relaxation at temperatures above 170°C and close

Table 2 Variation of interfacial area (Å²) occupied by a single copolymer as calculated by equation (3), with copolymer content in the blend

W (%)	$10^{-3}\alpha$ (Å^2)
1	6.780
2	3.820
5	3.140
10	1.567
20	1.350
20[a]	0.195
10[b]	0.026

[a] AB diblock copolymer; $\phi_A = 0.20$, $R = 1.0\,\mu$m, $W = 20\%$, $M = 10^5$ g mol^{-1} (Reference 15)

[b] PS-b-PIP-b-PMMA; $\phi_A = 0.20$, $R = 0.5\,\mu$m, $W = 10\%$, $M = 1.3 \times 10^5$ g mol^{-1} (Reference 15)

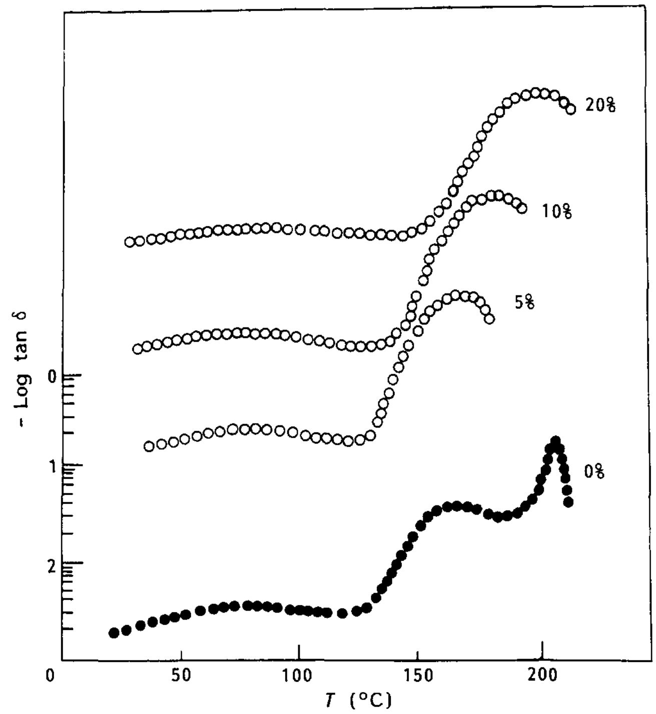

Figure 9 Logarithmic decrement curves for PMMA/polycarbonate blends (65/35 w/w) containing 0, 5, 10 and 20% w/w added copolymer

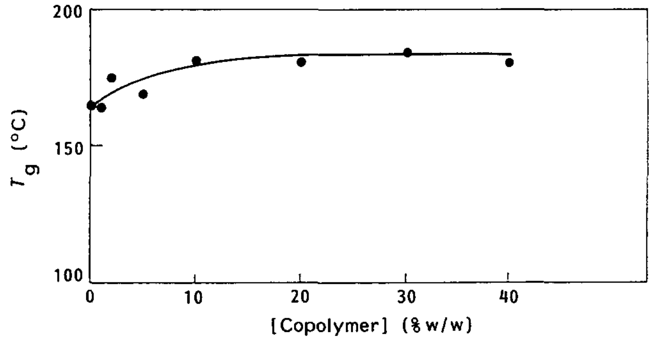

Figure 10 Variation of $T_g(\tan\delta)_{\max}$ of PMMA/polycarbonate blends (65/35 w/w) with added copolymer concentration

to the T_g of the polycarbonate homopolymer, recorded at 220°C. We, therefore, tested supported specimens containing 20% w/w added copolymer. Obviously, in this case the recorded properties are those of the composite rather than the polymer alone.

Whatman GF/A glass fibre filter paper proved to be the most suitable for the relatively high temperatures involved ($\approx$230°C) and complied with the substrate requirements[17]. The $\tan\delta$ curves for the two homopolymers, the unmodified blend and the same blend containing 20% w/w copolymer are compared in *Figure 11*. The essential features of all curves are identical to those recorded for similar unsupported specimens.

The data demonstrates clearly that there is no additional relaxation at temperatures between 170 and 260°C. We, therefore, conclude that the relaxation of *Figure 9* is the only α-relaxation and, since the systems are clearly phase separated, that relaxation must be a composite one comprising the relaxations from both phases observable by electron microscopy. Values of $T_{\tan\delta,\max}$ are, therefore, apparent T_gs, the values of which are dependent on the composition, volume fractions of the individual phases and the morphology of the system.

Phase diagrams of blends containing copolymers

Figure 12 presents the phase diagrams of PMMA/polycarbonate/dichloromethane blends with and without copolymer at 25°C. The phase diagram of the unmodified blend is characterized by a slight asymmetry, indicating preferential solubility of polycarbonate into the PMMA-

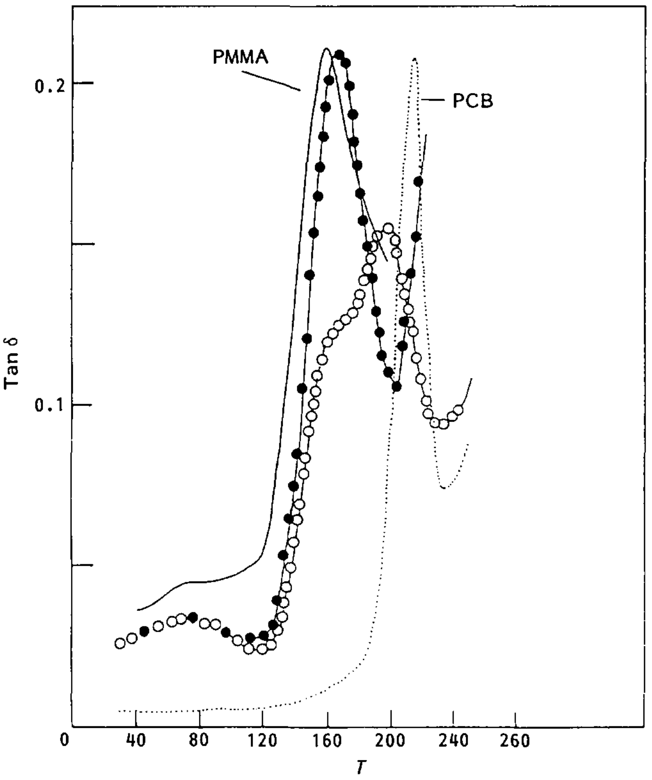

Figure 11 Dynamic mechanical spectra of PMMA (——), polycarbonate homopolymer (·····), PMMA/polycarbonate blend (65/35 w/w) (○) and the same system with 20% w/w added copolymer (●), using supported specimens

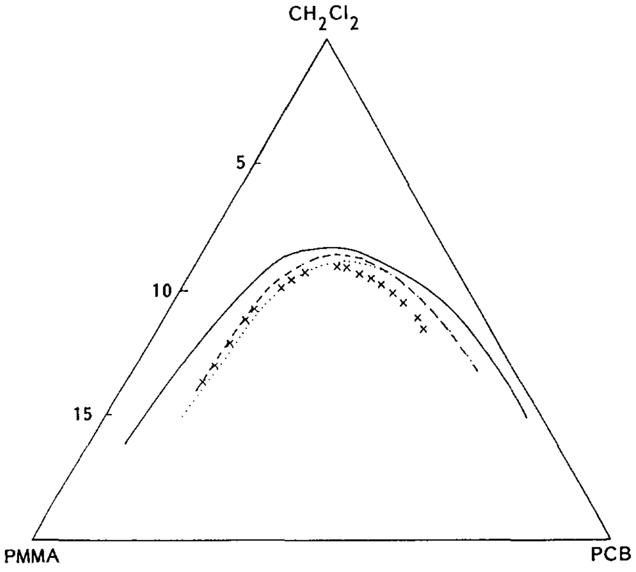

Figure 12 Effect of added copolymer concentration on the experimentally determined phase diagram of PMMA/polycarbonate blends (65/35 w/w): ——, 0%; × × ×, 13%; — — —, 9%; ·····, 4.8%

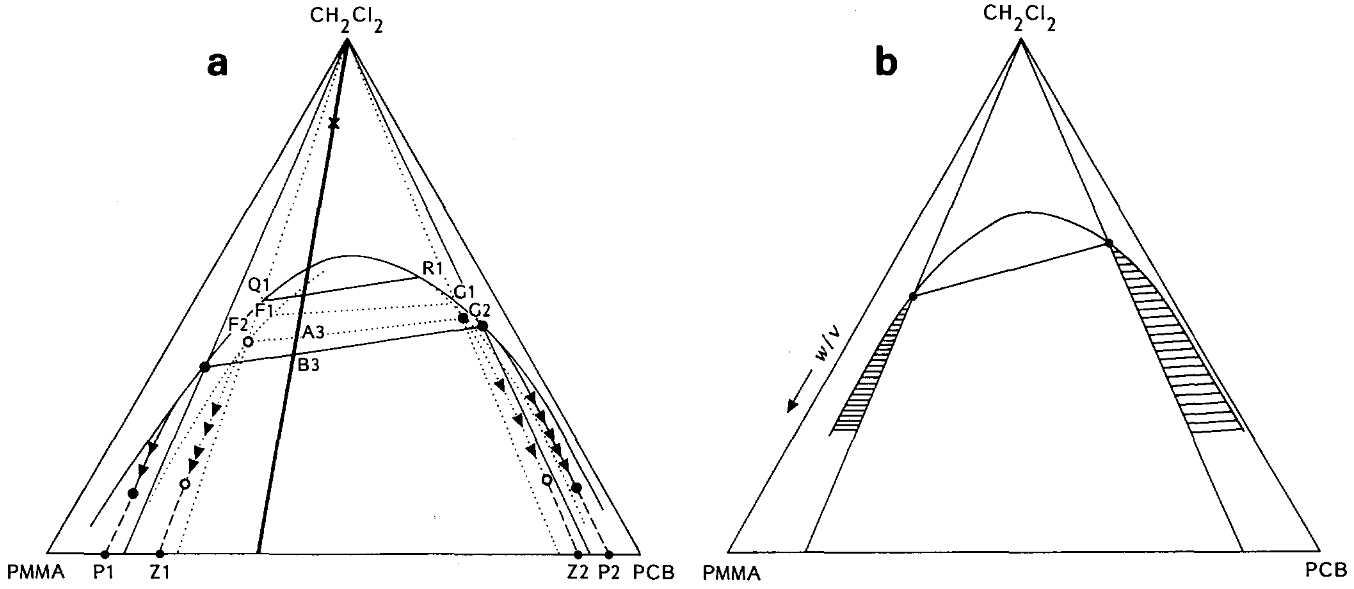

Figure 13 (a) Phase separation during solvent evaporation for PMMA/polycarbonate blends (65/35 w/w) with and without added copolymer. ——, Unmodified blend behaviour; ·····, copolymer modified system; ▬, isopleht of original composition; ⤳⤳⤳, deviation of phase decomposition from equilibrium binodal decomposition due to increasing viscosity as solvent is removed. (b) Schematic representation of the limits of compositions available through limited polymer diffusion during solvent evaporation

rich phase at moderately concentrated systems. The system remains homogeneous for all blend compositions at total polymer concentrations $\lesssim 7.5\%$ w/v. The phase diagram of the copolymer modified blends showed noticeable scatter in the data because of difficulties in sampling the individual phases. The problem of attaining true equilibrium is expected to become more significant in these systems as the interfacial activity of the copolymer delays segregation of the two phases. The binodals were each constructed from four tie lines. Solutions were allowed to approach equilibrium in sealed tubes for two months.

Addition of copolymer to the blends appears to show some compatibilizing effect at all copolymer concentrations and, in particular, at higher copolymer contents. The binodals recorded suggest slightly different effects on the miscibility of the two components at moderately concentrated solutions.

Increased solubilization of polycarbonate chains in the PMMA-rich phase is achieved with the very first addition of copolymer in the system and it does not change thereafter. On the other hand, dissolution of PMMA chains in the polycarbonate-rich phase is shown to increase with increasing copolymer concentration.

Although the recorded behaviour may, to some extent, reflect the effect of the copolymer on the kinetics of phase separation, it can provide qualitative information on the phase separation of the components during film formation. *Figure 13a* compares the phase separation process for a blend containing 9% w/w with that of the unmodified blend.

Following our previous arguments[7], a solvent-cast blend of homopolymers is expected to produce phases with final composition of, say P_1 and P_2 through initial equilibrium phase separation and a subsequent departure from equilibrium as solvent is completely removed. The initial phase separation in dilute solution may give equilibrium compositions to the two phases (Q_1, R_1). Equilibrium may persist while the diffusion required can occur within the time scale applicable to the removal of solvent. As the viscosity increases this possibility decreases and compositions then deviate from the equilibrium and finish at, say, P_1 and P_2. The shaded area of *Figure 13b* represents the limits of compositions available through limited polymer diffusion during solvent evaporation.

Phase separation in the presence of copolymer would occur by the same process. Two phases F_1 and G_1 would be formed as the system crosses the binodal. Further solvent evaporation leads to compositional rearrangement of the two phases to create phases F_2 and G_2. Comparison of the composition of the two phases between the modified and the unmodified systems shows that increased mixing of the two components occurs in the former system.

Consider, for the sake of argument, that deviations from the equilibrium phase separation begin at A_3 for the modified system and at B_3 for the unmodified blend. We believe it is reasonable to expect the system containing copolymer to deviate first from equilibrium due to the presence of the rather bulky copolymer molecules, increasing the overall viscosity and stabilizing the dispersed phases. The procedures described earlier would lead to formation of phases with final compositions P_1, P_2 and Z_1, Z_2 for the original and modified blends, respectively, with increasing mixing occurring in the latter system. If Z_1, Z_2 are sufficiently close, this mechanism would be consistent with the inability to resolve the α-relaxations in the dynamic mechanical spectra of the blends containing copolymer. This behaviour can be understood in part by the changes in the slope of the binodals with increasing copolymer contents (*Figure 12*). In addition, an increased copolymer concentration would not be expected to shift the T_g of the PMMA-rich phase markedly since the increased copolymer concentration ($>4\%$) does not alter the binodal at this side. Simultaneously increasing amounts of copolymer alter slightly the shape of the binodal on the polycarbonate-rich side, reflecting an increased incorporation of PMMA chains into that phase. This effect will shift the relaxation of this phase towards that of the PMMA-rich matrix.

GENERAL DISCUSSION

Before attempting to interpret the interfacial behaviour of the graft copolymer in the blends we review briefly the thermodynamics relating to interface formation.

In a completely phase-separated, amorphous binary blend of polymers A and B nearly all chains adopt random-coil conformations and the interfacial area and A, B contacts are minimized. Generation of additional interface, through the creation of finer dispersions, inevitably increases the number of A, B contacts and produces an unfavourable enthalpic contribution to the free energy of the system. In addition, more chains are brought into the neighbourhood of interface.

The entropy of those chains is reduced with respect to random coil conformations since they are effectively constrained to one side of the interface and there is a so-called turning-back contribution to the entropy which opposes an increase in interfacial area[18].

The interfaces are not infinitely narrow but have a thickness associated with the concentration profiles of the A and B components where they interpenetrate to some extent. The interfacial thickness is determined by a balance of enthalpic and entropic factors; for the high molecular weight polymers the enthalpic component dominates.

The equilibrium situation for a blend of homopolymer is that which, within the confines of the experimental system, leads to minimum interfacial area. The other component in the system is the copolymer which, if segregated from the homopolymer, will adopt a microphase-separated morphology determined by its composition and will adopt a low-surface area morphology, moderated to some extent by molecular constraints required to produce uniform density; factors determining morphology and chain conformations, and their contribution to the free energy of the system, have been considered by others. Within the limitations of having a pure copolymer phase, the morphology adopted (at equilibrium) is the minimum-energy structure. A microphase-separated structure has a high surface area per unit volume.

We have previously demonstrated that in mixtures of graft copolymer with one homopolymer the equilibrium situation approximates to a total segregation of AB copolymer and homopolymer[19]. In these mixtures chains of component B, not present as homopolymer, must be under severe conformational constraints and these constraints and their consequent effect on the A-chains to which they are attached are probably minimized by segregation of the copolymer.

In contrast, work in several laboratories, including our own, has clearly shown that addition of block and graft copolymer to a binary blend causes a massive increase in interfacial area between the homopolymers and loss of the copolymer phase. The increase in interfacial area between the homopolymer phases is counterbalanced by a loss of interface and other constraints on both components in the copolymer.

The obvious conclusion from experiment[3,8] supported by calculation[6] is that the copolymer acts as an interfacial agent and becomes located at the interface between the homopolymer phases. Theory and experiment support the conclusion that copolymers in which the block copolymer molecular weights are greater than those of the corresponding homopolymers are most efficient as interfacial agents; we have reported preliminary data, relevant to this system, supporting this view in the past[8] and will report additional data separately. Here we are concerned with copolymer content under conditions that the copolymer is an efficient interfacial agent and with the influence of copolymer content on the nature of the blend.

We have already noted that addition of very little copolymer markedly increases the interfacial area in the blend and produces a more uniform and finer dispersion. These effects are quite acceptable in a system where phase separation occurs from a homogeneous medium in which the phases, once formed, are protected from coalescing by the copolymer at the interface, which reduces the interfacial energy and therefore reduces the driving force for coalescence. The massive increase in interfacial area produced by a little copolymer is consistent with having an interface dilute in copolymer; it is already established that at interfaces where a high concentration of copolymer chains or grafts are located those chains are immiscible with homopolymer[20,21]. The system prefers to create interface rather than have a 'concentrated' interface. The surprising observation, therefore, is that addition of larger amounts of copolymer ($>5\%$) does not increase the interfacial area further and produce still finer dispersions. The obvious question is: Where is the additional copolymer located?

Obviously, addition of copolymer cannot remove the unfavourable interaction between the components which causes phase separation between the homopolymers. The phase diagrams with added copolymer also show that such copolymer has little influence on the thermodynamics of the system and, at first sight, addition of copolymer might only be seen to increase interfacial area, having little effect on phase composition. Because we were unable to find a separate copolymer phase, we assume that, in the presence of larger quantities of copolymer, the copolymer is distributed throughout the sample on the molecular level or as micelles which were undetected.

Although the optical microscopy and dynamic mechanical loss peaks might seem to indicate homogeneity, electron microscopy confirms that the blends, even in the presence of high concentrations of copolymer, are heterogeneous with phases each containing both components. The constant interfacial area attained at finite levels of copolymer suggests it may be present as micelles or microdomains of size below the detection limits of our technique. We know, from work on simple blends, that the polycarbonate used in this study and PMMA are mutually immiscible. It is also known, from work with graft copolymers of the type used in this study and other block and graft copolymers, that total segregation of the consistent block in bulk copolymer is possible, with the possibility that the high molecular weight blocks in the copolymer might dissolve added like homopolymer. In principle, therefore, there is no reason why separation of the components cannot proceed to total segregation with the appearance of loss peaks characteristic of the individual constituents.

We must presume that the added copolymer interferes

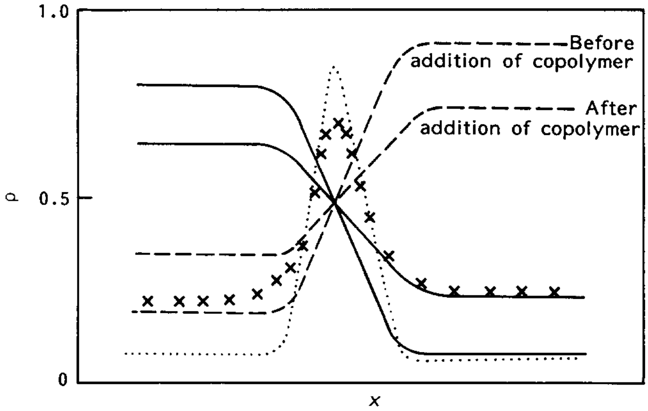

Figure 14 Density profile of PMMA/polycarbonate blend (65/35 w/w): ——, PMMA-rich phase; — — —, polycarbonate-rich phase; · · · · ·, copolymer at low copolymer contents in the blend (< 5% w/w); × × × × ×, copolymer at higher copolymer contents in the blend (> 5% w/w)

with the processes of segregation to produce, even at modest copolymer content, phases of similar composition (similar enough to give overlapping loss peaks in dynamic mechanical spectroscopy) with little further effect on adding considerable proportions of copolymer. The additional questions which arise, therefore, are: Why is equilibrium not approached in the presence of copolymer? Why does the interfacial area not increase further in the presence of large amounts of copolymer?

These questions are relevant to the system in the presence of solvent since, once the morphology is established there will be little opportunity for reorganization of the phase compositions. Previously we noted that the extent to which phase separation occurred in solvent-cast blends, even in the absence of copolymer, depends markedly on the details of sample preparation and this observation has been reinforced in the present study.

Rapid solvent removal in blends of intermediate composition can give overlapping relaxation peaks, attributed to incomplete segregation of the components on initial phase separation and a lack of achieving equilibrium on complete solvent removal. Slower solvent removal or subsequent thermal treatment allows more complete segregation of the components and closer approach to equilibrium. We adopt a similar reasoning to explain our current observations.

In the absence or presence of copolymer, initial phase separation by, say, nucleation and growth, to give phases of equilibrium composition (dilute in total polymer), or by spinodal decomposition will give homogeneous phases, one PMMA-rich and one polycarbonate-rich (the compositions joined by a tie line), with comparatively little difference in relative contents of the two polymers (*Figure 13a*).

In the absence of copolymer, as further solvent is removed, equilibrium may be approached by diffusion of polymers across the interface and unstabilized phases may be coalescing.

Phase separation will probably produce phases with similar compositions, irrespective of copolymer content. Thus, in the presence of little copolymer, the phases will consist largely of the homopolymers but as the copolymer content increases approximately the same composition will be achieved by replacing the homopolymer by copolymer. This is depicted in the density profile of *Figure 14*.

Once the phases have been formed there will be small concentration gradients at the interface between phases which contain solvent, PMMA and polycarbonate in slightly different proportions. Both theory and experiment tell us that copolymer molecules will be preferentially located at the interface. Theory also says that homopolymer will tend to be excluded from the interface[20,21]. Thus, as further solvent is removed, the position of equilibrium will change and equilibrium will require diffusion of homopolymer across the interface to make the compositions of the phases more different, progressing towards pure PMMA and pure polycarbonate in the complete absence of solvent. Such diffusion may occur very slowly but, we suggest, does not occur to any significant extent on the time scale for our sample preparation conditions. This picture of significant concentrations of copolymer in each phase is consistent with the overall lack of contrast between the phases, in the presence of copolymer, compared with that in the absence of copolymer. What is perhaps surprising is that segregation of the components to give a fine texture within each of the phases, corresponding to microphase separation of the high molecular weight components in copolymer, is not apparent. However, the dimensions of the phases are small and, according to theory, even at equilibrium, high molecular weight copolymer extends some distance from the interface and, in this case, the domain size may be comparable with those dimensions.

Although the final morphology will be established in the presence of solvent, the phase dimensions are not much larger than radii of gyration of the larger chains in the domains and situations are being created where perturbations from normal chain conformations in well separated systems might be starting to play a role.

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