Morphologies and properties of polyblends: 1. Blends of poly(methylmethacrylate) and a chlorine-containing polycarbonate

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The morphologies and dynamic mechanical properties of blends of poly(methylmethacrylate) and a chlorine-containing polycarbonate, cast from dichloromethane solutions, have been studied. The results are discussed in terms of a phase diagram which has been determined for the system. It is demonstrated that the blends do not have equilibrium morphologies, which are virtually impossible to attain: nevertheless, their properties and morphologies can be related to the phase diagram and sample histories. Apparently anomolous variations in miscibility with composition are shown to be a consequence of an assymetric phase diagram and preferential solubility of polycarbonate in poly(methylmethacrylate).

Keywords Polycarbonate; poly(methylmethacrylate); blend; morphology; phase diagram; dynamic mechanical properties

INTRODUCTION

Polymer blends in which one component is a block or graft copolymer are being widely investigated[1]. In some studies the blends consist of one homopolymer with a copolymer either added or formed *in situ*. A second major group are blends of two homopolymers with one copolymer. One reason for special interest in the latter group of materials is the possibility of the copolymer acting as an interfacial agent between the phases of immiscible homopolymers, thereby forming stable fine dispersions of one component in the other[2]; or otherwise acting as 'compatibilizers'.

Following our development of a procedure for synthesizing characterizable non-linear block copolymers (essentially graft copolymers)[3] and our investigations of their morphologies in blends with one homopolymer[4], we have recently undertaken an investigation of the physical and mechanical properties of multicomponent polymers in which one component is a block copolymer[5-7]. Part of this programme relates to the influence of copolymer on the morphologies and properties of blends of two homopolymers. For this aspect of the work we have chosen to investigate, in the first instance, blends of a polycarbonate (PCarb) and poly(methylmethacrylate) (PMMA). We have, therefore, developed the synthesis and characterization of PCarb/PMMA non-linear block copolymers[8].

Our investigations of PCarb/PMMA blends have demonstrated that addition of small quantities of copolymer can have marked effects on their morphologies and on their dynamic mechanical properties[8]. All samples used in this work were solvent-cast films and it has become apparent that sample history is a very important factor in determining the properties of the films. To understand the effects of added copolymer it is necessary to establish and use standard conditions for preparing the blends, both in the absence and in the presence of the copolymer. It is also necessary to have some knowledge of the phase diagram relevant to the system under investigation.

In this paper we report the properties of PCarb/PMMA blends cast from dichloromethane solution in the absence of added copolymer, together with the ternary phase diagram for PCarb, PMMA and dichloromethane. The morphologies of the blends, determined by optical microscopy, and their properties are discussed in relation to the phase diagram and the conditions of sample preparation. This paper illustrates some of the consequences encountered in practical systems where equilibrium morphologies are not achieved and, thus, provides essential background information to our investigation of the effects of adding copolymer to the blends; we propose to report the results of that study in a subsequent publication. The mechanical properties of the blends are also discussed in terms of mechanical models using the procedures developed by Takayanagi[9].

EXPERIMENTAL

Materials

The PCarb used in this study was a random copolymer formed by condensation polymerization of an equimolar mixture of bisphenol-A and 1,1,1-trichloro-bis-2-(*p*-hydroxyphenyl)ethane with phosgene. The general synthetic procedure used has been described elsewhere[4]. The PCarb used throughout this study had a number average molecular weight of 49.9 kg mol^{-1}.

PMMA used was a standard material, number-average molecular weight of 48 kg mol^{-1}, prepared by free-radical polymerization and supplied by RAPRA.

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Sample preparation

During our investigations we observed that the details of sample preparation procedures could play an important role in determining the properties of the PCarb/PMMA blends. In order to be able to draw valid comparisons between the properties and morphologies of different blends and to be able to identify the effects of adding copolymer, it was necessary to establish a standard procedure for sample preparation. We therefore adopted a procedure, described below, which provides reproducible data but not equilibrium conditions in bulk polymer.

Films of blends (0.25 mm thick, approximately) were prepared by making dilute solutions of the two polymers in dichloromethane (<4%(w/v) total polymer). The solutions were placed in flat-bottomed Petri dishes (Anumbra), covered and placed in a partially closed container. Solvent was allowed to evaporate slowly at ambient temperatures and, under our standard conditions, at such a rate that a film, dry to the touch, formed in 4–5 days. Residual solvent was removed by storing the films under vacuum at ambient temperature for several days and, subsequently, at 90°C for 24 h. Using this procedure the residual solvent content was sufficiently low that it could not be detected by infra-red spectroscopy. Also, further annealing of PMMA films under vacuum for 24 h at 125°C did not produce any detectable change in the glass-transition temperature (T_g) obtained from dynamic mechanical properties of the films. We have also shown that, when applied to PCarb/polystyrene blends cast from dichloromethane, where separation of the components is virtually complete, our standard procedure results in films whose properties are unchanged by more extensive annealing at high temperatures[7]. Therefore, we conclude that the properties are uninfluenced by residual solvent.

Optical microscopy

The morphologies of the polyblends were determined by optical microscopy using a Leitz polarizing microscope. Small pieces of film were mounted on epoxy-resin supports and sections (2–5 μm) were cut using an LKB Ultratome III, operated manually. In unpolarized light contrast between the phases was extremely poor. However, in cut sections PCarb was seen to be birefringent while PMMA was non-birefringent; this birefringence appeared to be induced by stresses imposed during sectioning and was not observed in uncut films. The difference in birefringence of the two phases provided a convenient means of observing and recording morphologies. A limitation in the use of this technique is that sections from films containing low proportions of PCarb did not always show birefringence, possibly because orientation of PCarb chains was insufficient when small domains were sectioned and, if domain sizes were small compared with film thicknesses, few domains would be cut. Samples containing large proportions of PCarb gave very reproducible results.

Phase diagram

A three-component phase diagram was constructed for PCarb, PMMA and dichloromethane at 25°C. The method adopted was to prepare separate solutions of the two polymers. Known volumes of the two solutions were added sequentially and carefully to a tube of known transverse area so that no mixing occurred. The tube was sealed and the position of the interface was noted. To facilitate the approach to equilibrium, the solutions were mixed. Subsequent movement of the interface was monitored and when no further movement of the interface could be detected over a period of several hours the new volumes of the phases were calculated. 1 cm^3 of the upper phase was removed and the dissolved polymer was precipitated and weighed. The composition of the isolated polymer was determined by ultraviolet absorption at 230 nm. Solutions of PCarb and of PMMA in dichloromethane were separately shown to obey Beer's Law at 230 nm with extinction coefficients of 5.00×10^4 and $6.95 \times 10^2\,g^{-1}\,cm^2$, respectively. From the overall composition, the composition of the upper phase and the phase volumes, the composition of the lower phase was calculated. In all calculations it was assumed that volumes were additive; i.e. no volume change on mixing; densities of PCarb and PMMA were taken to be 1.30 and 1.20 g cm^{-3} respectively. The calculated final compositions of the two layers are indicated in *Figure 4* as points joined by tie-lines. Inconsistencies in the slopes of the tie-lines indicate some error in the procedure employed, probably because equilibrium conditions were not completely established. Probably the only significant error is in the total polymer contents of the phases and arises because of difficulties encountered in quantitative recovery of polymer from the aliquot of the upper layer; compositions of the phases were determined using samples of the recovered polymer. Additional points on the binodal were determined by slow addition of solvent to heterogeneous mixtures and identifying compositions at which the systems became homogeneous.

Dynamic mechanical properties

Dynamic mechanical properties were determined using a Rheovibron viscoelastometer DDV-IIC (Toyo Baldwin Ltd., Tokyo). Samples (2 × 30 mm, approx.) were cut from the cast films. Measurements were made at an operating frequency of 110 Hz using a heating rate of 1.5°C h^{-1} with the samples in a nitrogen atmosphere.

RESULTS AND DISCUSSION

Dynamic mechanical properties

A series of blends were prepared under the standard conditions outlined above and their dynamic mechanical properties were studied over the temperature range 20° to 230°C. *Figures 1, 2* and *3* summarize the data for blends whose compositions are given in *Table 1* and show, respectively, variations in storage (E') and loss (E'') moduli and $\tan\delta$. Also depicted in these diagrams are corresponding data for the PMMA and PCarb used in preparing the blends.

E' data for PMMA-rich blends, B-1, B-2, show two distinct transitions at temperatures close to those for the α-relaxations, or glass-transition temperatures (T_g's), of the constituents. These data indicate immiscibility of the components and phase separation during casting to give phases of almost pure PMMA and PCarb. This general behaviour is supported by the variations in E'' and $\tan\delta$. Both samples show widely separated major loss peaks for which the temperatures of $\tan\delta_{max}$ are almost identical; their high-temperature loss peaks are almost identical with that for PCarb. Although the E'' data are similar, *Figure 2*, B-2 exhibits a slightly higher temperature for the low-temperature peak than does sample B-1; both peak

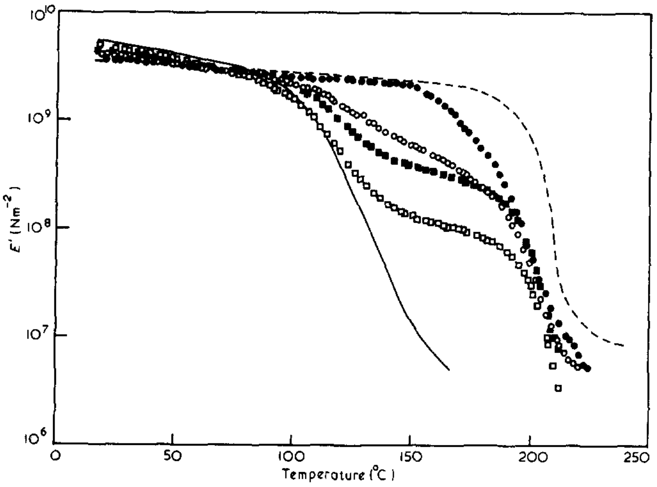

Figure 1 Temperature dependencies of E' for the PCarb/PMMA blends B-1 (□), B-2 (■), B-3 (○), B-4 (●) and for PMMA (——) and PCarb (– – –)

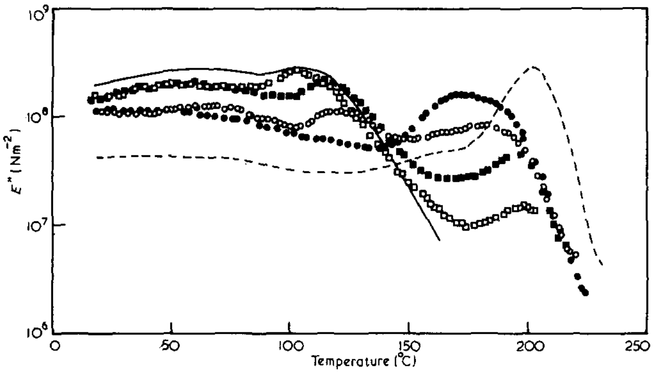

Figure 2 Variations in E'' with temperature for PCarb (– – –), PMMA (——) and blends B-1 (□), B-2 (■), B-3 (○) and B-4 (●)

maxima are located at temperatures close to those for the pure constituents.

In contrast, data from PCarb-rich samples do not indicate complete separation of the constituents. The E' data for B-3 show one very broad transition, continuous from T_g of PMMA to T_g of PCarb. However, the sample does show maxima in $\tan\delta$ at approximately the same temperatures as observed for B-1 and B-2. Two maxima can also be detected in the E'' data, although these peaks are shifted with respect to those of the separate components. Thus, the data for B-3 might indicate partial miscibility of the PCarb and PMMA with the apparently continuous transition arising from fortuitous overlap of broad relaxation peaks.

Sample B-4 shows even less evidence for immiscibility of PCarb and PMMA. Both the E' and E'' data suggest only one major α-relaxation at a temperature rather lower than that of PCarb and slightly broadened. Such data are readily interpreted in terms of miscibility. However, such a view is inconsistent with the data obtained from the other samples and close inspection of the $\tan\delta$ data for this sample suggests that the relaxation may be more complex than that suggested by the E' and E'' data.

The peaks in *Figures 2* and *3* show systematic trends in the temperatures of the peak maxima with composition and these are summarized in *Table 1*. Other points of note are: (i) for B-1 values of E' in the temperature range 60° to 106°C fall below those for either of the constituent homopolymers. This effect, which occurs to a lesser extent with B-2 and B-3, is presumably not a consequence of residual solvent since all samples were treated identically. A similar effect has also been reported by Dobrescu and Cobzaru[10] in blends of bisphenol-A polycarbonate and PMMA, a system for which some miscibility of the components was reported; (ii) B-1, B-2 and B-3 exhibit narrower relaxation peaks at about 120°C than the major relaxation peak in PMMA.

Phase diagram and morphology

Apparent inconsistencies in polymer–polymer miscibility, identified from the dynamic mechanical data, can be correlated with the phase diagram for the two polymers and the casting solvent, depicted in *Figure 4* and derived by the methods outlined earlier. Since the data points in *Figure 4* were derived by allowing an initially heterogeneous system to approach equilibrium they should give an approximate location of the binodal of the phase diagram. We see that PMMA and PCarb are essentially immiscible in bulk polymer. Of particular note is the assymetric form of the binodal. In moderately concentrated solutions, PCarb has some solubility in solutions of PMMA, but not *vice versa*, except close to the critical point. Although the binodal may not be exact, because true equilibrium was not achieved, the phases on the left-hand side were formed by diffusion of PCarb into PMMA solutions and at least the amounts of PCarb indicated must be miscible in PMMA-rich solutions.

According to the phase diagram, blends of PCarb and PMMA cast from dichloromethane should be heterogeneous and the compositions of the phases, assuming equilibrium conditions are approached, should be pure PCarb and near to pure PMMA; only the volume

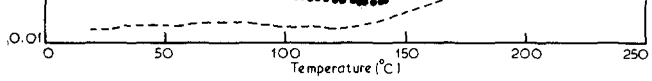

Figure 3 Tanδ as a function of temperature for PMMA (——), PCarb (– – –) and for blends B-1 (□), B-2 (■), B-3 (○) and B-4 (●)

Table 1 Compositions and transition temperatures of polyblends

Sample	Composition %(w/w) PCarb	$T_{E''\max}$ lower	$T_{E''\max}$ upper	$T_{\tan\delta\max}$ lower	$T_{\tan\delta\max}$ upper
PMMA	0	108	–	146	–
B1	18	103	199	125	>210
B2	34	116	197	125	209
B3	59	122	151	132	208
B4	80	170		–	205
B4a	80	138	188	–	204
PCarb	100	–	–	–	214

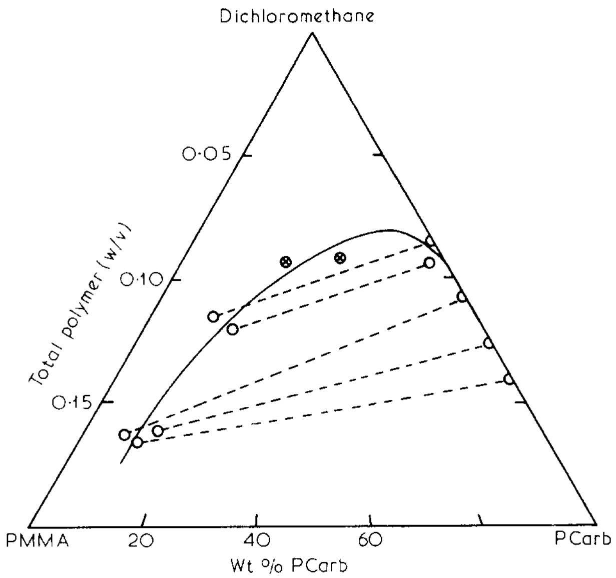

Figure 4 **Ternary phase diagram for dichloromethane, PCarb and PMMA. Points indicated by the same symbol were determined simultaneously. Points (⊗) were determined separately as described in text**

fractions of those phases should vary from sample to sample. This situation was obviously not achieved in our experiments.

Nevertheless, the mechanical property data are understandable in terms of the schematic diagram *Figure 5* which shows the binodal from *Figure 4*. Points A, B, C represent initial solutions used to prepare blends B-1, B-3 and B-4, severally; B-2 is omitted for clarity. As solvent evaporates the compositions follow the lines of constant relative polymer composition (i.e. constant PCarb/PMMA ratio), as indicated, until they cross the binodal. The solutions then become unstable to phase separation by nucleation[11]. Nucleation at the termini of the lines of constant PCarb/PMMA ratio, marked by open circles, produces phases of compositions denoted by the triangles at the ends of the tie lines passing through the termini.

In this study we have not located the spinodal of the phase diagram. However, we know that the spinodal, the line which defines the boundary between metastable homogeneous phases (unstable to nucleation) and totally unstable phases (unstable to phase separation by development of concentration fluctuations), must lie within the heterogeneous region and is coincident with the binodal at the critical point (near the apex of the binodal). By analogy with other phase diagrams, we can reasonably assume that the spinodal gradually deviates from the binodal with increasing polymer content; i.e. the range of compositions over which homogeneous solutions are metastable increases with increasing polymer content. We use full circles to indicate points on the spinodal in the schematic diagram, *Figure 5*. Although the location of these points cannot be exact, this detail does not invalidate the essential features of the following discussion.

Consider the system corresponding to blend B-1. Phase separation produces a minor phase of virtually pure PCarb and a phase very rich in PMMA. On removal of further solvent only the PMMA-rich phase will adjust its PCarb/PMMA ratio in order to maintain equilibrium composition and follow the binodal. At the high polymer concentrations involved, diffusion will be slow compared with the time scale of sample preparation. Although some adjustment of the PCarb/PMMA ratio may occur, the composition will deviate gradually from the binodal. In principle, secondary nucleation, to form droplets of PCarb solution within the PMMA-rich phase, could occur when the residual matrix phase would become richer in PMMA; this procss may occur to some extent. At some stage the increasing viscosity will restrict translational motion of polymer and the composition will again follow a line of constant PCarb/PMMA ratio. Once the line of constant PCarb/PMMA ratio lies within the metastable region, between the binodal and spinodal, no small-scale concentration fluctuations, which might serve to broaden the α-relaxation in the final film, will develop and, if no further secondary nucleation occurs, a metastable homogeneous phase of PMMA containing a little PCarb will be formed. As drawn, the line of constant PCarb/PMMA ratio will give a PMMA-rich phase containing about 8%(w/w) PCarb.

The implications of this discussion are consistent with the observations that (i) the mechanical property data for B-1 show two relatively narrow transitions, as might be expected from nearly pure homopolymer phases, located at temperatures close to those characteristic of the constituents and (ii) the optical micrograph (*Figure 6*) shows a dispersed phase of PCarb (white) in a matrix phase of PMMA (dark).

Similar considerations apply to the preparation of B-2. Consistent with the predominant morphology observed (*Figure 7a*), initial phase separation will give a dispersion of PCarb solution in a matrix phase; the polymer content of the latter will be about 15%(w/w) PCarb. In this sample phase separation might occur at about 10% total polymer and some modification of the PCarb/PMMA ratio in the PMMA-rich phase might occur before diffusion becomes

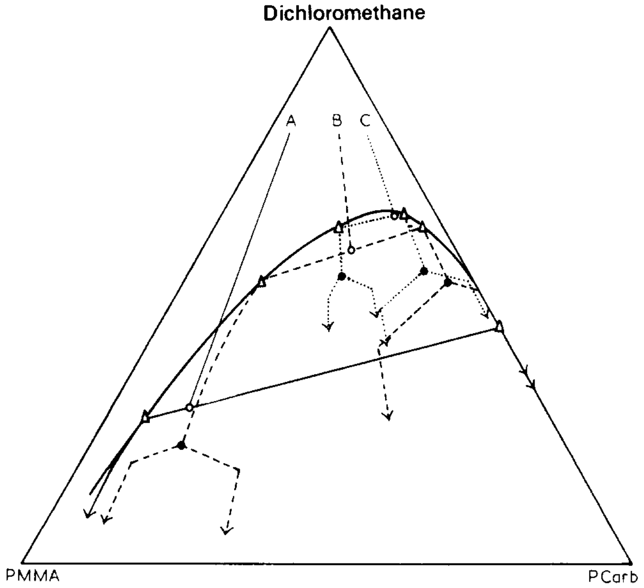

Figure 5 **Schematic phase diagram to illustrate the consequences of casting blends from compositions represented by points A, B, C. Phase separation at points denoted by open circles leads to phases with compositions denoted by triangles. Where appropriate, spinodal decomposition starting at points denoted by full circles leads to ranges of compositions within the limits defined by the associated lines of constant PCarb/PMMA ratios**

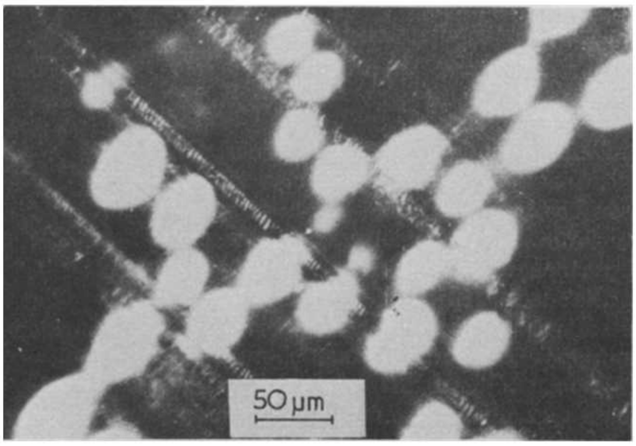

Figure 6 Optical micrograph illustrating the morphology of blend B-1. PCarb appears white, PMMA dark

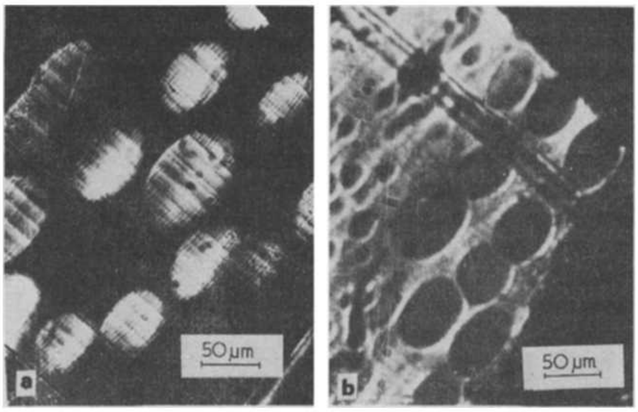

Figure 7 Morphologies of B-2: (a) predominant morphology; (b) reverse morphology observed in some sections

too restricted. Hence the transition temperatures might be close to those of B-1, as observed.

For B-3 and B-4 the situations are a little different because their mechanical properties indicate partial miscibility of the constituents. Their properties, however, must be consistent with the phase diagram and the processes which occur during sample preparation. We propose the following mechanism for preparation of B-3, the arguments for which are based on a knowledge of the location of the binodal and other necessary characteristics of the phase diagram. Casting from point B phase separation will give a dispersed PMMA-rich phase, containing some PCarb, in a matrix PCarb solution phase, containing a low concentration of PMMA; the point at which phase separation would occur is possibly more dilute in total polymer than indicated in the schematic diagram *Figure 5*. The PMMA-rich phase, relatively dilute in total polymer, may adjust its composition through diffusion, not necessarily along the binodal but, say, along the line from the triangle to the full circle, indicating a gradual deviation from the binodal as a result of the increasing viscosity as solvent is removed. During this process secondary nucleation, to form PCarb-rich droplets within the dispersed PMMA phase, could occur to give regions of similar composition to those formed during casting of B-1 and B-2. The variations in E' and E'' with temperature would then be expected to show two transitions at the T_g's of the constituents, which they do not. We assume, therefore, that secondary nucleation does not occur to any serious extent but that the phase remains homogeneous and its composition follows the line indicated through the metastable region of the phase diagram until the spinodal, represented in the schematic by the full circle, is reached. As further solvent is removed local fluctuations in the PCarb/PMMA ratio will arise and develop through spinodal decomposition[11]. This process is indicated by the two lines emerging from the full circle. Assuming spinodal decomposition does not proceed to completion, a spread of local compositions will develop which will ultimately be frozen in; the range of such compositions is indicated by the two lines of constant PCarb/PMMA ratio terminating in arrows. Similarly, the composition of the PCarb-rich phase formed on initial phase separation, will follow the line joining the triangle and full circle, assuming no secondary nucleation occurs. When the composition crosses the spinodal at, say, about 10% total polymer, spinodal decomposition will generate concentration fluctuations to give a continuous range of compositions, possibly from 60 to 100% PCarb.

The above mechanism is consistent with the occurrence of two glass transitions, seen in the E'' and $\tan\delta$ data, the relaxation peaks of which are broader than those in blends B-1 and B-2. The main feature of these data is the very broad upper transition, extending from 150° to 230°C, approximately, consistent with a very broad range of compositions in the PCarb-rich phase, as a result of incomplete spinodal decomposition. Similarly, the lower temperature transition is shifted to a slightly higher temperature and is also broader than the corresponding transition in B-2, indicative of inclusion of more PCarb in the PMMA-rich phase and some local variation in composition.

In addition, the proposed mechanism is consistent with the predominant morphology of B-3 (*Figure 8a*). The large, dark, dispersed PMMA-rich regions, which we believe result from initial phase separation, show no evidence of PCarb inclusions formed by secondary nucleation but could contain variations in composition which are not apparent; as mentioned in a previous section, it is difficult to observe contrast at low PCarb contents. *Figure 8a* also shows a PCarb continuum containing dark inclusions. From the overall composition (59% PCarb) and from the height of the low-temperature

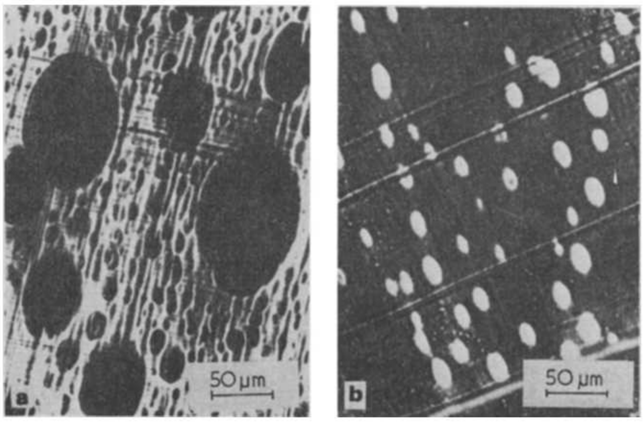

Figure 8 Morphologies of B-3: (a) predominant morphology; (b) reverse morphology observed in some sections

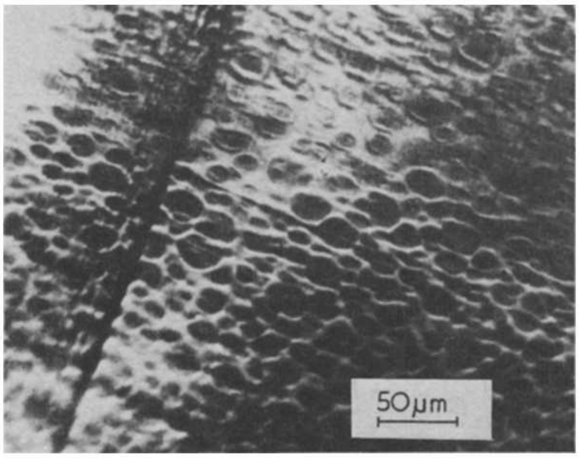

Figure 9 Morphology of blend B-4

α-relaxation peak, these inclusions cannot be PMMA. We suggest that these regions arise from spinodal decomposition which has progressed to an extent sufficient to allow contrast in the micrograph to be apparent and to give a variety of compositions rich in PCarb which, in turn, give rise to the broad relaxation peak observed.

We believe that the mechanism, as outlined above is a conceptually correct description of the processes involved during sample preparation under our standard conditions. The detailed composition ranges existing within each phase will depend, of course, on the exact location of the spinodal, on the translational diffusion coefficients of the constituents and the rate of solvent removal.

Similar arguments can be applied to B-4. Starting from point C, phase separation gives droplets of a PMMA-rich phase in a matrix PCarb-rich phase; in both phases the polymer content will be more than 50%(w/w) PCarb. Assuming again that secondary nucleation is insignificant, the PCarb/PMMA ratios in both phases will remain constant until the spinodal, represented by full circles, is crossed. As further solvent is removed concentration fluctuations will develop to produce a range of compositions within, say, the pairs of lines of constant PCarb/PMMA ratio arising from the full circles. Thus, the final polymer could contain a wide range of local compositions, all rich in PCarb. No relaxation from a PMMA-rich phase is expected, only a broad transition at higher temperatures, as observed. The small shoulder in the tan δ data (*Figure 3*) is consistent with formation of a minor phase relatively rich in PMMA on initial phase separation. *Figure 9* shows the morphology of B-4 as seen in the polarizing microscope. Because PCarb appears white under these conditions and the sample contains 80% PCarb, the dark regions must contain relatively large proportions of PCarb but insufficient to give rise to birefringence under the sectioning procedures used. In addition, contrast between light and dark regions is relatively poor and consistent with comparatively small differences in composition. The volume fraction of the dispersed phase also appears too large to be formed on initial phase separation. We therefore suggest that the morphology observed arises by spinodal decomposition of the major PCarb-rich phase.

The above discussion allows us to reconcile the mechanical property data of the blends, with the relevant phase diagram and with the observed morphologies. We see that observations are consistent with failure to establish equilibrium morphologies, thus illustrating the importance of kinetic factors in controlling morphologies and properties of polyblends. We have previously demonstrated the importance of kinetic factors in controlling the morphologies of copolymer blends[4]. It is to be expected that, at the high polymer concentrations involved, the transfer of polymer between phases through diffusion will be too slow to maintain equilibrium compositions. A novel element in the above arguments is the assumption that secondary nucleation does not occur to any appreciable extent. This is probably a reasonable assumption in view of the high viscosities involved and the probable lack of sufficient adventitious impurities to act as nucleation sites.

To establish the importance of kinetic factors in the present context, we recast B-4 from homogeneous solution. The rate of solvent removal was reduced, by further restricting the aperture available for loss by evaporation, so that it took three weeks instead of five days to produce a film dry to the touch. *Figure 10* summarizes the mechanical property data for the slowly cast sample, B-4a, and compares them with data obtained from B-4 prepared under standard conditions. Clearly, the slowly cast film exhibits greater separation of the constituents and there is evidence for an almost pure PMMA component. Thus, some secondary nucleation or large-scale diffusion must have taken place during the longer time scale of this experiment. While this result clearly demonstrates the importance of kinetic factors it also illustrates the problems in attempting to achieve equilibrium conditions in cast films and, probably, in any other sample, so that the detailed properties inevitably reflect their history. Hence, the necessity for adopting a set of standard conditions for sample preparation to be used in studying effects of added copolymer on the properties of polyblends is apparent.

It is interesting to note how the preceding discussions resolve an apparent contradiction. We can now understand how the detailed properties and

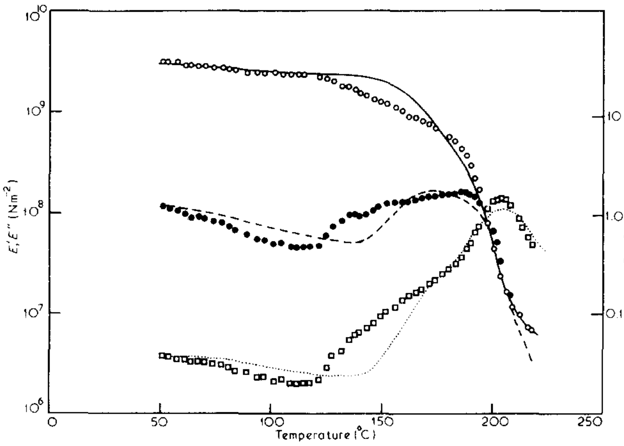

Figure 10 Variations in mechanical properties with temperature for blend B-4 cast under standard conditions (E' ——, E'' – – –, tanδ ···) and under very slow casting conditions (E' ○, E'' ●, tanδ □)

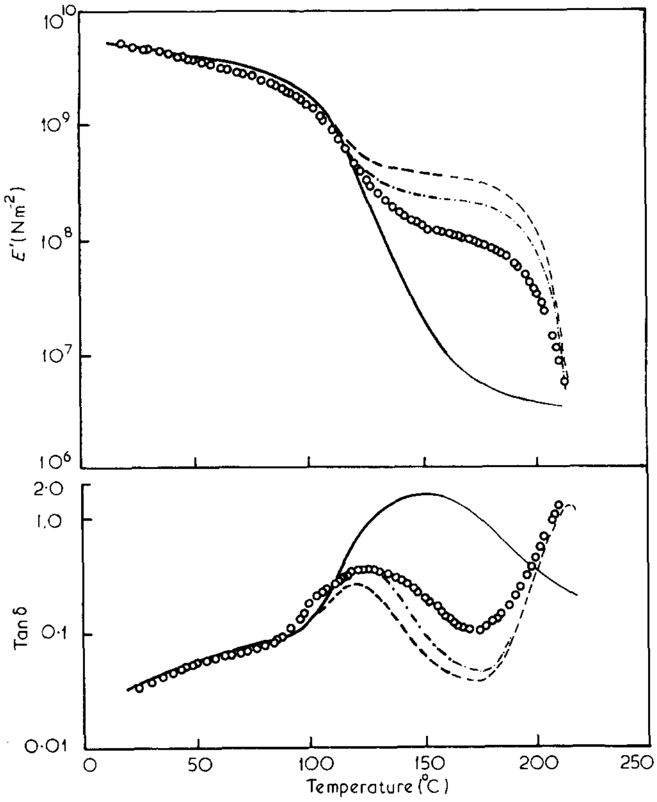

Figure 11 Variations in E' and tanδ with temperature for blend B-1 (○). Calculated curves for spherical dispersions of PCarb in PMMA (A, ——), PCarb/PMMA laminate (B, – – –) and spherical dispersion of PMMA in PCarb (C, ·–·–·). Portions of calculated curves based on extrapolated PMMA data are indicated by thin lines

morphologies of the blends are consistent with greater solubility of PCarb in PMMA solutions than *vice versa* although, in isolation, the properties of B-4 might have been interpreted in terms of significant solubility of PMMA in PCarb in bulk polymer.

Mechanical model calculations

The dynamic mechanical properties of heterogeneous polyblends may be predicted from the properties of their components using mechanical equivalent models, e.g. the Takayanagi models[9]. According to these models the complex modulus E^* of a composite consisting of a dispersion of polymer 2 in a matrix of polymer 1 is given by

$$E^* = \left[\frac{\varphi}{(1-\lambda)E_1^* + \lambda E_2^*} + \frac{1-\varphi}{E_2^*}\right]^{-1}$$

where E_i^* is the complex modulus of species i. λ and φ are parameters, positive and less than unity, which relate to the composite morphology; the product $\lambda\varphi = v_2$, the volume fraction of species 2. E^* may be decomposed into its real E' and imaginary E'' components and expressed in terms of E_i' and E_i''.

To calculate the variations in properties of a blend with temperature we must base the calculations on the temperature variations of the properties of the PCarb and PMMA. Calculation assumes that the properties of each component in the composite are identical to those of the components separately. That is, there are no modifications in properties on incorporating a component into, say, a blend. Thus, the calculated moduli of the composite material are direct combinations of the properties of the components and must fall within the limits set by those components. Examination of the experimental data and the discussions of the previous sections show that strict use of mechanical models is not possible in the present context. For example, the low values of E' for blend B-1 at about 100°C are not predictable. This effect may have its origin in the limited miscibility of PCarb in PMMA; a similar effect has also been observed in bisphenol-A polycarbonate/PMMA blends[10]. We have seen that, in general, separation of PCarb and PMMA is incomplete and even in B-1 and B-2 there may be some PCarb in the PMMA phases. In cases where there definitely are mixed phases we do not know the compositions of those phases or how to combine the properties of the constituents to simulate the properties of the mixed regions in order to incorporate them into the calculations.

Nevertheless, it is instructive to compare experimental and calculated properties for some blends, especially for those which show well-defined T_g's close to those of the constituent polymers. For this purpose we have used the simple Takayanagi models assuming phases of pure PCarb and PMMA. For PMMA homopolymer the experimentally determined properties were extrapolated smoothly to temperatures higher than those at which measurements on PMMA could be made (164°C); any errors in this extrapolation do not affect the validity of the subsequent discussion.

Figure 11 shows the variations in E' and tan δ for B-1 determined experimentally and calculated on the basis of several models. Curves A present data calculated assuming a spherical dispersion of PCarb in PMMA ($\lambda = 0.500$, $\varphi = 0.335$), consistent with the morphology in *Figure 6*. Obviously, there are large discrepancies between the experimental and calculated results, Specifically, the calculated values of E' at temperatures between the T_g's of the constituents are about an order of magnitude too low. There are also discrepancies between experimental and calculated values and tan δ and all discrepancies are in the sense that experimentally PCarb has a greater influence on the properties than allowed by the model assumed.

The observed morphology is not the equilibrium morphology which should be a laminate formed by coalescence of the droplets of the dispersed phase. We have calculated the properties for this morphology, curves B, using the Takayanagi parallel model ($\lambda = 0.168$, $\varphi = 1.00$) and the results are in rather better agreement with experiment in that the moduli above 100°C are only a factor of three too high and the model predicts a high value of tan δ at T_g of PCarb and a low value of tan δ between the two T_g's, as observed.

The high experimental values of E' can only be explained in terms of some connectivity of PCarb in the direction parallel to the film surface. To illustrate this we calculated the variations in E' and tan δ with temperature for a model assuming a dispersion of PMMA spheres in PCarb, curves C ($\lambda = 0.899$, $\varphi = 0.925$). Although the model is inconsistent with the observed morphology, the discrepancies between experimental and calculated data are less and could be reduced by changing the values of λ and φ.

We performed similar calculations for B-2 (see *Figure 12*). Again, assuming a PCarb dispersion in PMMA

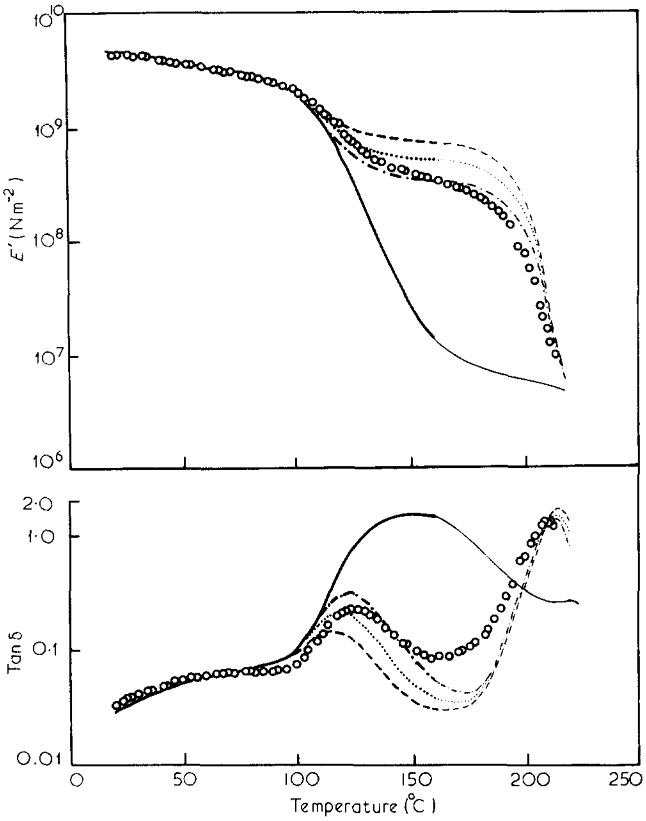

Figure 12 **Variations in E' and tanδ with temperature for blend B-2 (O). Calculated curves for spherical PCarb dispersions in PMMA (A, ——), PCarb/PMMA laminate (B, – – –), spherical dispersions of PMMA in PCarb (C, ···) and for PMMA dispersions with reduced PCarb connectivity (D, ·–·–·)**

(curves A) ($\lambda = 0.605$, $\varphi = 0.565$) discrepancies between experiment and theory at about 140°C are excessive. The simple parallel model (curves B), assuming a laminate ($\lambda = 0.342$, $\varphi = 1.00$), is in closer agreement with experiment and better agreement can be achieved by assuming the reversed morphology of a dispersion of PMMA spheres in a matrix of the minor PCarb component, curves C ($\lambda = 0.794$, $\varphi = 0.827$).

However, surprisingly good agreement for B-2 can be achieved by retaining the reversed morphology and modifying the values of λ and φ in such a way as to decrease the amount of PCarb which has connectivity in the stress direction, i.e. parallel to the film surface, curves D ($\lambda = 0.877$, $\varphi = 0.750$). Although the predominant morphology is a dispersion of PCarb in PMMA, examination of many sections showed that the reverse morphology could be found in some places close to the bottom surface (during casting) of the film, *Figure 7b*. These regions probably formed by PCarb droplets coalescing and entrapping some PMMA solution. Such a layer with a PCarb matrix may provide the necessary connectivity of PCarb to produce high moduli at intermediate temperatures. Although we did not observe the reverse morphology in B-1 we cannot entirely exclude its presence, since only small regions of the film were sectioned and examined in detail, and the high moduli of that film at temperatures between 120° and 200°C could have the same origin.

It is of interest to note that the calculated variations in tanδ with temperature for B-1, B-2, for models with PCarb connectivity, show relatively narrow loss peaks at about 100°C, even though PMMA is the major component. The temperatures for tan δ_{max} are dependent on the λ and φ values assumed but are comparable with the experimentally observed values. Therefore, although some PCarb may be trapped in the PMMA phase, and may be responsible for the detailed shapes of the relaxation peaks, it is not necessary to assume this to explain the observed modifications in temperatures for tan δ_{max}.

Obviously, the complex morphologies observed are outside the scope of the simple Takayanagi models. However, a more complex but realistic model would be a parallel model of components A,B of which one is a dispersion of polymer 1 in 2 and the other of 2 in 1. This model could be used to calculate mechanical properties of polyblends and it could undoubtedly give satisfactory results. We have not performed these calculations because there are too many variables of which we have no knowledge, e.g. the relative volumes of the phases with different matrices and the volume fractions of the dispersed regions in either of those phases.

We have also calculated the properties of B-3 and B-4 using the Takayanagi models. The breadths of the transitions in the samples, as a result of incomplete separation of the components, precludes the determination of any information of practical value. Although no real evidence could be obtained for the existence of regions with a reversed morphology in these samples, examination of sections in the polarising microscope revealed their existence in B-3 (see *Figure 8b*).

CONCLUSIONS

Our studies of blends of PMMA with a chlorine-containing polycarbonate have enabled us to understand how the properties of solvent-cast films vary with overall composition and with detailed aspects of sample preparation.

A ternary phase diagram for PMMA, PCarb and dichloromethane was constructed from which it is seen that, in moderately concentrated polymer solutions, PCarb is more soluble in PMMA solution than *vice versa*. From the form of this phase diagram, and by taking into account kinetic factors relating to diffusion of polymer molecules in viscous systems generated during solvent-casting, a variety of morphologies may be predicted.

Assuming non-equilibrium separation of PMMA and PCarb in bulk polymer and by using both nucleation and growth processes and spinodal decomposition processes for separation of components, it is possible to predict morphologies and properties of the blends consistent with experimental observations. Thus, by combining the assymetric phase diagram with non-equilibrium morphologies, the apparently anomolous miscibilities indicated by mechanical property data can be understood.

In one case, it was demonstrated that by modifying the kinetics of solvent casting the properties of a blend could be modified in a predictable manner.

Although not strictly applicable to systems in which phase separation does not yield pure components, the application of mechanical model calculations was useful in identifying the origin of high moduli in PMMA-rich blends at high temperatures in terms of the connectivity of the minor PCarb component; in some cases direct morphological evidence for such connectivity was obtained.

The results of this paper confirm that the morphologies and properties of polyblends are very dependent on sample preparation conditions. Consequently, we cannot state the definitive properties of a polyblend. In order to study effects such as the influence of copolymer on the morphologies and properties of polyblends, therefore, it is essential to establish and use standard conditions for sample preparation. The results of this paper will be used as background for examining the effects of PCarb/PMMA copolymers on these blends.

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Note added in proof

It has recently come to the authors' attention that a report on the properties of bisphenol-A polycarbonate/PMMA blends (Z. Garlund, *Polym. Prepr.* 1982, **23(1)**, 258) contradicts the conclusions expressed in ref.10. Dobrescu and Cobzaru[10] conclude that bisphenol-A polycarbonate and PMMA are partially miscible while Garlund states that they are immiscible over the whole composition range. These conclusions are inconsistent with equilibrium conditions existing in both studies. The disagreement probably represents another example of sample histories rather than equilibrium morphologies controlling sample properties which reinforces the conclusions of this paper.

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