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Utilization of the oligomeric diglycidylether of bisphenol A epoxy in assessing equilibrium phase behaviour of polycarbonate/poly(methyl methacrylate) blends

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The long controversial nature of the equilibrium phase behaviour in the blend system of poly(methyl methacrylate) (PMMA) with bisphenol A polycarbonate (PC) was investigated by dissolving both polymers in an oligomeric epoxy, namely the diglycidylether of bisphenol A (DGEBA). Phase behaviour and morphology changes with temperature were examined by using differential scanning calorimetry (d.s.c.) and optical microscopy. Upon lowering the T_gs of the PC/PMMA blends, thus enhancing the chain mobility by the plasticizing epoxy molecules, phase separation did take place in the blend with an accelerated rate at temperatures as low as 68°C. To our knowledge, this has never been reported previously in the literature. Consequently, the widely reported miscibility and lower critical solution temperature (*LCST*) in PC/PMMA blends have to be carefully reinterpreted. Our results have suggested that the equilibrium behaviour of PC/PMMA blends is actually one of phase separation, with possibly only partial miscibility. In addition, this study has also showed that the single-T_g, transparent blends above 240°C of the reported 'upper critical solution temperature (*UCST*)' are actually not miscible but display microphase domains. A reinterpretation was provided based on these results. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Blends of bisphenol A polycarbonate (PC) and poly-(methyl methacrylate) (PMMA) and their phase behaviour have been extensively investigated by various polymer researchers[1–10]. The nature of their equilibrium phase behaviour has long been controversial. Most workers claimed that miscibility with a lower critical solution temperature (*LCST*) (located at around 160–190°C depending on the composition) exists in the PC/PMMA blend system. That view was later further complicated by a claim that not only a *LCST*, but also a 'rare' upper critical solution temperature (*UCST*) exists in the blend system, which is indicated by an observation of a cloudy-to-transparent appearance of the blends at temperatures above 240°C. Kyu and coworkers[5,6,11] reported the existence of a 'thermodynamic' *UCST* (at 240–250°C depending on the composition) in the blends above the thermodynamic *LCST* temperatures. In other words, when an originally miscible PC/PMMA blend is heated slowly and steadily from room temperature, it will enter an immiscible region at 160°C, and then returns to a miscible region upon further increases in temperature above 240°C.

Above the '*LCST*' temperatures, the PC/PMMA blends were naturally immiscible; however, upon further increases in the temperature, as some investigators have reported, the blends turned 'miscible' again, as judged by the disappearance of the cloudy phases. The high temperatures at which the PC/PMMA blends turn clear and become 'miscible' again have been claimed as representing a *UCST* region, which is located on top of the *LCST* curve in the phase diagram. This, if true, is a very unusual and rare case for polymers. Debates and studies on this topic have therefore been intensive.

These theories were later seriously challenged by other researchers, or in some instances by the original proposers themselves. Different theories have been proposed recently in addressing these polymer thermodynamic issues. Nishimoto et al.[12] have reported a revised view that solution-cast PC/PMMA blends were actually not thermodynamically miscible and that the previously reported 'miscibility' in such blends was just an artifact that was caused by the polymer chains being temporarily trapped in a non-equilibrium, homogeneous state by the solvent preparation procedures that were used.

Evidence for the origin and existence of a thermodynamic *UCST*, however, has been quite ambiguous from the various investigations, and debates on this issue are intense. The *UCST* was originally reported as a true

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thermodynamic phase behaviour by Kyu and Lim[5,6]. The miscibility above the '*UCST*' was judged from the experimental observation of drastic changes of light scattering or transmission intensity, as well as a single T_g for the blends when quenched from above the *UCST* temperatures (>240°C). The sensitivity and reliability of both of the experimental techniques depend on the sizes of the domains. As we shall demonstrate in this report by presenting a direct morphology observation on this blend system, the scattering intensity change, or the single T_g according to differential scanning calorimetry results reported in the literature might lead to an erroneous interpretation.

Furthermore, the view of the thermodynamic origin of the *UCST* in PC/PMMA blends was later revised. Chemical interactions between PC and PMMA has been found to be possible and these were suggested as being responsible for the blend miscibility above the *UCST* temperatures[10,11]. Legras and coworkers[10] and Rabeony *et al.*[13] suggested that the *UCST* might be just another artifact which was a result of chemical interactions between PC and PMMA occurring at the high heating temperatures. By using Fourier transform infrared (*FT*i.r.) spectroscopy *trans*-esterification was inferred in the PC/PMMA blends[11,13]. *Trans*-esterification has also been widely reported in PC/polyester blend systems[14-17]. Legras and coworkers further pointed out that the conditions for occurrence of such reactions could lead to degradation[10].

One of the main confusions encountered in studying the phase changes in PC/PMMA blends has been the proximity of the T_g to the so-called '*LCST*' temperatures. The T_g and *LCST* temperatures are so close that a phase separation immediately after the glass transition has led to proposals that the *LCST* is actually not a thermodynamic *LCST* but just an artifact originating from slow phase separation which is then quickened at temperatures above the T_gs of the blend components. It has been demonstrated in our previous report[18] that the diglycidylether of bisphenol A epoxy resin forms miscible blends with either PC or PMMA before or after heating at high temperatures, and detailed T_g-composition behaviour and *FT*i.r. spectroscopic evidence for the binary systems of DGEBA/PC and DGEBA/PMMA have been reported and discussed. There is still a great deal of dispute regarding whether or not PC and PMMA form a truly miscible blend system or simply a temporary homogeneous mixture that phase-separates with slow kinetics. Therefore, since both of the binary pairs of DGEBA/PC and DGEBA/PMMA are miscible, it can be argued that a ternary blend system formed by dissolving PC and PMMA into a common solvent, DGEBA, should also be miscible.

By using the oligomeric epoxy to lower the glass transition temperatures of both PMMA and PC, the kinetic process of phase separation, whether this is actually unstable or immiscible thermodynamically, can be enhanced. In the as-prepared state before heating, the DGEBA-plasticized blends would have relatively low T_gs, and observations of the phase changes in the PC/PMMA blends might be attempted within a reasonable experimental time-scale at relatively low temperatures. This will help to clarify the conflicting proposals in the literature on the phase behaviour and origin of the *LCST* and/or *UCST* in the PC/PMMA blends.

EXPERIMENTAL

Materials and sample preparation

The epoxy resin used in this study was the diglycidyl ether of bisphenol A (DGEBA) (Epikote-828, Shell Corp., USA). The bisphenol A polycarbonate (PC) employed was GE Lexan[R] HF1130 ($M_w = 23\,000$ g mol^{-1}). Poly(methyl methacrylate) (a-PMMA) was obtained from a commercial source (CM-205, Chi-Mei Inc., Taiwan), ($M_n = 50\,000$ g mol^{-1}; $M_w = 90\,000$ g mol^{-1}). Ternary blends were prepared from these components, exercising particular care not to induce any chemical changes during the blending step. PMMA and PC were weighed respectively and dissolved in tetrahydrofuran (THF) solvent and the resulting polymer solution was then mixed with a predetermined quantity of the epoxy resin at room temperature. The solvent in the mixture was vaporized at room temperature by using a circulation oven with an exhaust fan, followed by residual solvent removal in a vacuum oven for 24 h at 60°C. Room-temperature or slightly above-room-temperature solution blending was chosen to cast ternary epoxy/PC/PMMA blend samples for experimental characterization. It was found that film casting at ~50°C yielded the best quality of film samples. A visually transparent film was obtained at the end of this step.

Differential scanning calorimetry

The glass transition temperatures of the blends were measured with a power-compensated type of differential scanning calorimeter (Perkin-Elmer DSC-7, equipped with an intracooler and a computer for data acquisition/analysis). All T_g measurements were made at a scan rate of 20°C min^{-1} over the range from −25 to 200°C, and the T_g values were taken as the onset of the transition (the change of the specific heat) in the heat-flow curves.

Optical microscopy

A Nikon polarizing microscope (Optiphot-2, POL) equipped with UFX-DX automatic exposure was used. The blend samples were first spread as thin films on glass slides, and then heated at designated isothermal temperatures for extended times in a temperature-controlled oven before they were examined using the microscope. For dynamic heating, the samples were heated on a hot plate, and then periodically removed from the plate and placed on the observation stage of the microscope for examination and photographic recording of the phase changes.

RESULTS AND DISCUSSION

Homogeneity in as-prepared ternary blends

Ternary blends of various compositions were prepared by THF-solution casting, and the as-cast films of blend samples before heating were examined first by using optical microscopy at the maximum magnification of 2000. The microscopic observation showed that the as-cast ternary blends were homogeneous, with no discernible phase domains. In addition, T_g characterization was performed on these samples. *Figure 1* shows that the d.s.c. thermograms of DGEBA/PC/PMMA blends (10 different compositions) all exhibit a single glass transition temperature. The d.s.c. thermograms shown are the second heating scans after quenching from 250°C. The

brief heating prior to scanning was for sample uniformization and elimination of PC crystallinity. A relatively sharp, single T_g is obvious in each of the d.s.c. thermograms of the ternary blends. *Table 1* lists the T_g values obtained for these blends. In addition, a comparison is made in the table by showing the difference between the experimental T_g data and the calculated T_g values according to the linear dependence on composition: $T_g = \omega_1 T_{g1} + \omega_2 T_{g2} + \omega_3 T_{g3}$, where ω_i is the weight fraction of the ith component. It was not expected that the T_g vs. composition curve would show a linear relationship; however, the linearity was used only as a standard to measure how great was the deviation of the blend T_g. The data show that the T_g values of all of the blends exhibited an almost constant,

DGEBA/PC/PMMA Ternary Blends

Figure 1 D.s.c. thermograms ($20°C$ min^{-1}) of ternary DGEBA/PC/PMMA blends over a wide composition range, all showing a single T_g

negative deviation from the linearity relationship, with the deviation being between 30 to $40°C$ depending on the blend composition. We will show later that the blends showing a single T_g were actually phase-separated systems with rather small phase domains.

Indeed, it has been argued that the single T_g in the d.s.c. thermograms alone does not necessarily indicate homogeneity or miscibility in the ternary mixtures[19,20]. That argument is true since the phase domains might be quite small and beyond the detection sensitivity of d.s.c. However, homogeneity in these ternary mixtures before heating was also proven by direct optical microscopy observation. At the maximum magnification, no recognizable phase domains larger than $0.05 \mu m$ or so were detected in these mixtures. The actual phase-domain sizes might be even smaller than this, which was beyond the resolution limits of optical microscopy. The co-solvent, i.e. DGEBA, did enhance the homogeneity in the ternary blends before heating. The microscopy and thermal analysis results taken together showed that the as-cast ternary blends were indeed homogenous, regardless of their true thermodynamic state.

Phase separation in ternary blends upon heating

Introducing a common solvent into PC and PMMA apparently reduced significantly the phase-domain sizes in the ternary blends, to the extent that they can be regarded as being homogeneous. However, questions still remained as to whether or not these 'homogeneous' ternary mixtures were truly thermodynamically miscible. Alternatively, were the polymer chains temporarily locked, for example, in a chain-entanglement conformation due to the presence of the cosolvent? Experiments were performed to determine at what temperatures these blends might exhibit phase separation. Phase separation, and the temperature at which it occurs, is usually observed by measuring the temperatures at which the blends turn cloudy when the latter are heated at finite, slow rates. This method may yield a misleading interpretation if the phase-separation process is inherently or kinetically so slow that it does not take place during the heating time-scale. For example, a phase-separation process at below the blend's T_g would be very slow.
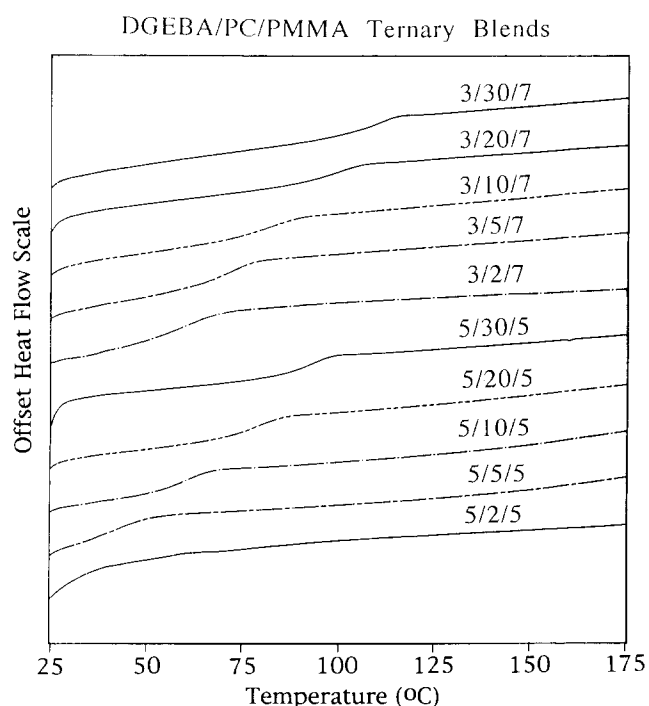
The present blend system was plasticized by the

Table 1 T_g values of ternary DGEBA/PC/PMMA blends[a]

Compositions (DGEBA/PC/PMMA)	Experimental T_g (°C)	Calculated T_g (°C)	Deviation from linearity (°C)
5/30/5	87	119.3	32
5/20/5	75	111.4	36
5/10/5	52	93.7	42
5/5/5	37	76.6	40
5/2/5	20	59.5	40
10/5/5	11	54	43
10/10/5	31	72	41
3/30/7	105	125.0	20
3/20/7	90	118.0	28
3/10/7	75	105.2	30
3/5/7	63	91.6	29
3/2/7	50	78.4	28

[a] T_g of DGEBA $= -20°C$; T_g of PC $= 150°C$; T_g of PMMA $= 105°C$

oligomeric epoxy; thus phase separation, if occurring, would be relatively easy to observe over reasonable time-scales. To evaluate the kinetic effects, two sets of experiments for observing phase separation were performed. One set of samples were heated at finite, slow rates (1–3°C min⁻¹) on a temperature-controlled hot plate, and withdrawn from the hot plate at a designated temperature and then quenched to room temperature to 'freeze' the phase domains. These withdrawn samples were then carefully examined by using a polarizing microscope to record heating-induced changes in the phase morphology. Another set of samples were heated in an oven at a constant low temperature (68–80°C) for extended periods of time (120–150 h) before examination using the same microscopy technique.

Figure 2 shows the temperatures at which the originally homogeneous blends turned to a phase-separated morphology after a dynamic heating scan (ca. 1–3°C min⁻¹). Usage of 'cloud points' was avoided in constructing the phase-separation curves. It was found that the definition of cloud points by intensity changes in light scattering or by the unaided eye could result in erroneous interpretations since what appeared transparent to the naked eye could exhibit distinct phase-separated domains when examined using optical microscopy. Three compositions of the ternary DGEBA/PC/PMMA blends were tested: (5/5/5), (10/5/5) and (10/10/5). These blends were carefully examined before heating by using the microscope, and a homogeneous phase was observed for all of these compositions. The samples (on glass slides) were then heated slowly on a hot plate, and withdrawn from the hot plate at designated temperature intervals for immediate microscopy examination. The (10/5/5) composition possessed the lowest T_g among the three; thus phase separation occurred at the lowest

temperature of about 100°C. Phase separation of the other two compositions (5/5/5 and 10/10/5) occurred at slightly higher temperatures of about 140 and 130°C, respectively.

At these temperatures, phase separation was readily apparent, judging from the blends turning visually cloudy and from the microscopy observations revealing a grossly separated morphology. Note that all of these temperatures are significantly lower than the cloud points reported in the literature for the PC/PMMA blends, thus indicating that plasticization of PC and PMMA by DGEBA significantly accelerated the kinetic process of phase separation. They remained cloudy once these temperatures were exceeded, and never became homogeneous again upon lowering the temperature.

Additionally, in order to examine the reversibility of this phase behaviour, these blend compositions were heated at 190°C for 12 h to induce a phase-separated morphology before they were heated again slowly on the hot plate for microscopic observation of any further phase changes. *Figure 3* shows that all of these originally phase-separated blends remained unchanged in their phase morphology upon a second heating from room temperature to about 300°C. This suggests that phase separation, once it has taken place, is irreversible in the blends.

Furthermore, in order to investigate whether or not the transition from a homogeneous to a phase-separated morphology for these blends was a thermodynamic *LCST* phenomenon, further experiments were performed to observe phase separation. Three compositions of originally homogeneous ternary blends were heated for 150 h at 68°C, a temperature which is well below the cloud point temperatures (as shown in *Figure 2*). Another set of samples of the same three compositions were heated at 80°C for 120 h. The samples after the
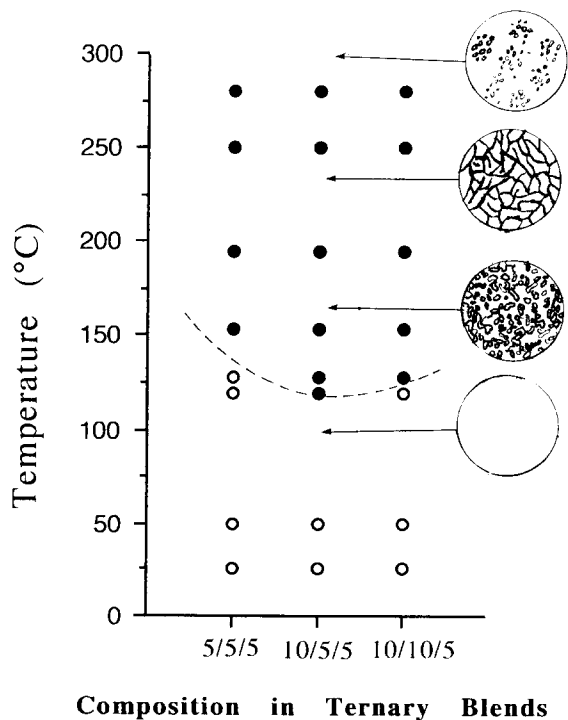

Figure 2   Phase curves of ternary blends of DGEBA/PC/PMMA after dynamic heating at 1–3°C min⁻¹: open circles indicate homogeneity; filled circles indicate phase separation
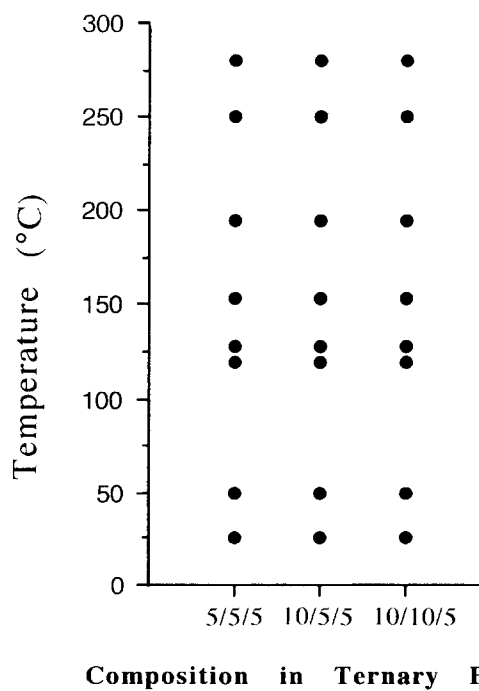

Figure 3   Phase curves (reheating at a rate of 1–3°C min⁻¹) of ternary blends of DGEBA/PC/PMMA that had been treated at 190°C for 12 h; filled circles indicate phase separation

heating treatment were examined immediately using optical microscopy. To our complete surprise, at these relatively low isothermal temperatures, the blends eventually exhibited a distinct phase-separated morphology, which was normally only observed at much higher temperatures (120–125°C for the ternary blends, or 150–180°C for the binary PC/PMMA blends) after dynamic heating scans. *Figure 4* shows that all of the three compositions, i.e. (10/5/5), (10/10/5) and (5/5/5), exhibited a phase-separated morphology with phase domains of ~1–3 μm after extended times (150 h) at 68°C. The third composition (5/5/5), with its T_g being the highest (35°C) among the three, yielded the slightest extent of phase separation, with its phase-separated domains being visible, but small and harder to detect. At the slightly higher heating temperature of 80°C for 120 h, all three compositions, including the (5/5/5) blend, exhibited much more distinct phase-separation phenomenon. Their micrographs were similar to the set of samples heated at 68°C, and are not shown here. Since these micrographs showing phase-separated domains were taken after the blends were cooled back down to room temperature, the results indicated that all three ternary blend compositions did not return to their original homogeneous state, but instead remained phase-separated upon lowering the temperature from 68 or 80°C to room
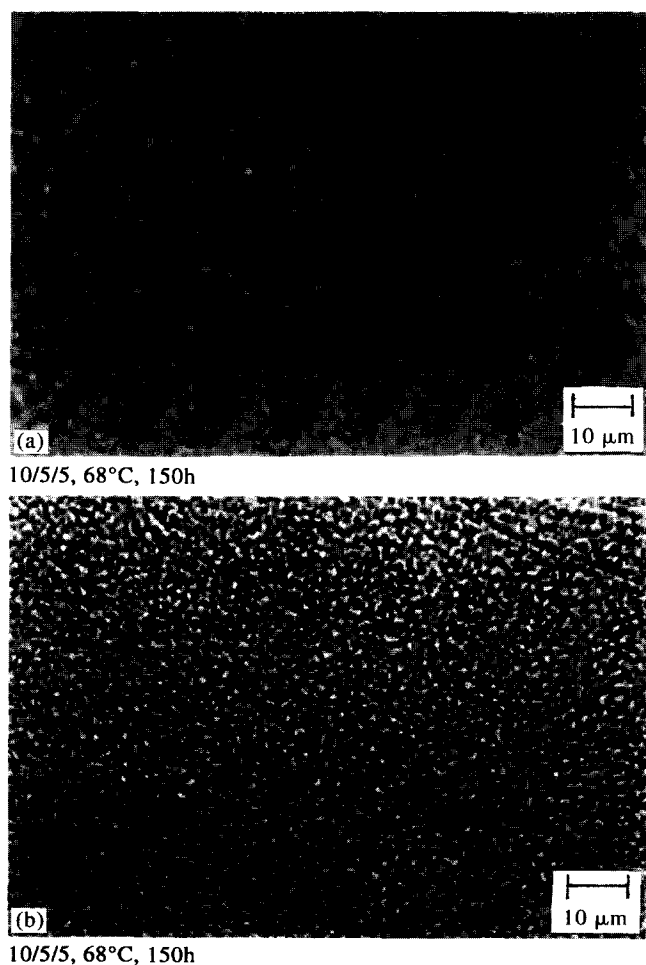
temperature. These results suggest that PMMA and PC may not be thermodynamically miscible.

Is it a temporarily trapped homogeneity?

Upon stirring and then freshly casting from a low-viscosity THF solution, the PC and PMMA polymer chains in the blends, due to certain degrees of interaction, might become easily entangled (trapped). This can result in the formation of a blend of apparent homogeneity. In this study, we purposefully introduced DGEBA to enhance the chain mobility of both of these polymer chains. These carefully designed experiments demonstrated that the polymer chains could easily reach their thermodynamic state of phase separation at temperatures as low as 68°C, without having to be heated to temperatures above the T_gs of the component polymers (105 and 150°C for PMMA and PC, respectively). This observation significantly helps to clarify the origin of the 'LCST' cloud points for the PC/PMMA blends as amply reported in the literature (generally 140–190°C). The cloud points observed in the PC/PMMA blends are highly kinetically dependent and may simply be the temperatures at which the polymer chains possess sufficient mobility to regain their original thermodynamic states. In order to physically illustrate these discussed points, *Figure 5* depicts a schematic diagram showing that the polymer chains in the blends can go from a temporarily trapped 'homogeneous' state to one displaying an equilibrium phase-separated morphology, a change which can be drastically accelerated with enhanced chain mobility. Nishimoto et al.[12] pointed out that low-mobility systems which phase-separate slowly may be trapped into a non-equilibrium, homogeneous state, and that the widely reported cloud point curves at 140–190°C for PC/PMMA blends may be just artifacts of very slow phase separation. Our present study shows that given enough time, phase separation
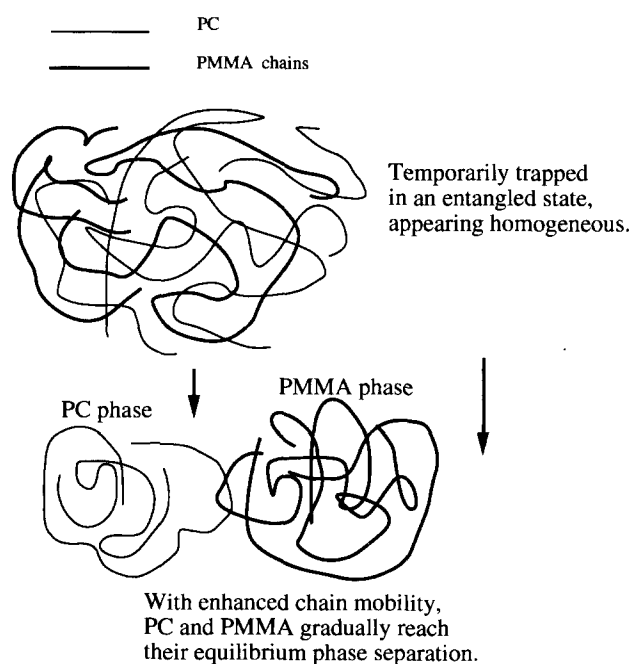

(a)

10 μm

10/5/5, 68°C, 150h

(b)

10 μm

10/5/5, 68°C, 150h

Figure 4 Optical micrographs (×800) obtained for DGEBA/PC/PMMA blends after treatment at 68°C for 150 h: (a) (10/5/5); (b) (10/10/5) blend compositions

———— PC

———— PMMA chains

Temporarily trapped in an entangled state, appearing homogeneous.

PC phase   PMMA phase

With enhanced chain mobility, PC and PMMA gradually reach their equilibrium phase separation.

Figure 5 Schematic diagram showing PC and PMMA in cast blends going from a temporarily entangled state of homogeneity to an equilibrium disentanglement and phase-separated morphology

could occur at temperatures as low as 68°C. This critical experimental finding has provided stronger evidence for such a view.

Furthermore, it still remained to be explained whether or not the cloudy–transparent transition of the blends when heated above 240°C could be properly called a '*UCST*'. *Figure 6* shows the optical microscopy results of a ternary blend (5/5/5 composition) being heated from room temperature to above 240°C. The sample was first transformed from a homogeneous to a cloudy appearance, and then back to a visually transparent blend. Phase-morphology changes were recorded at several closely-spaced temperature intervals; however, for brevity, only four representative micrographs (a–d, from bottom to top) are shown, which depict the phase morphology over four temperature ranges. At
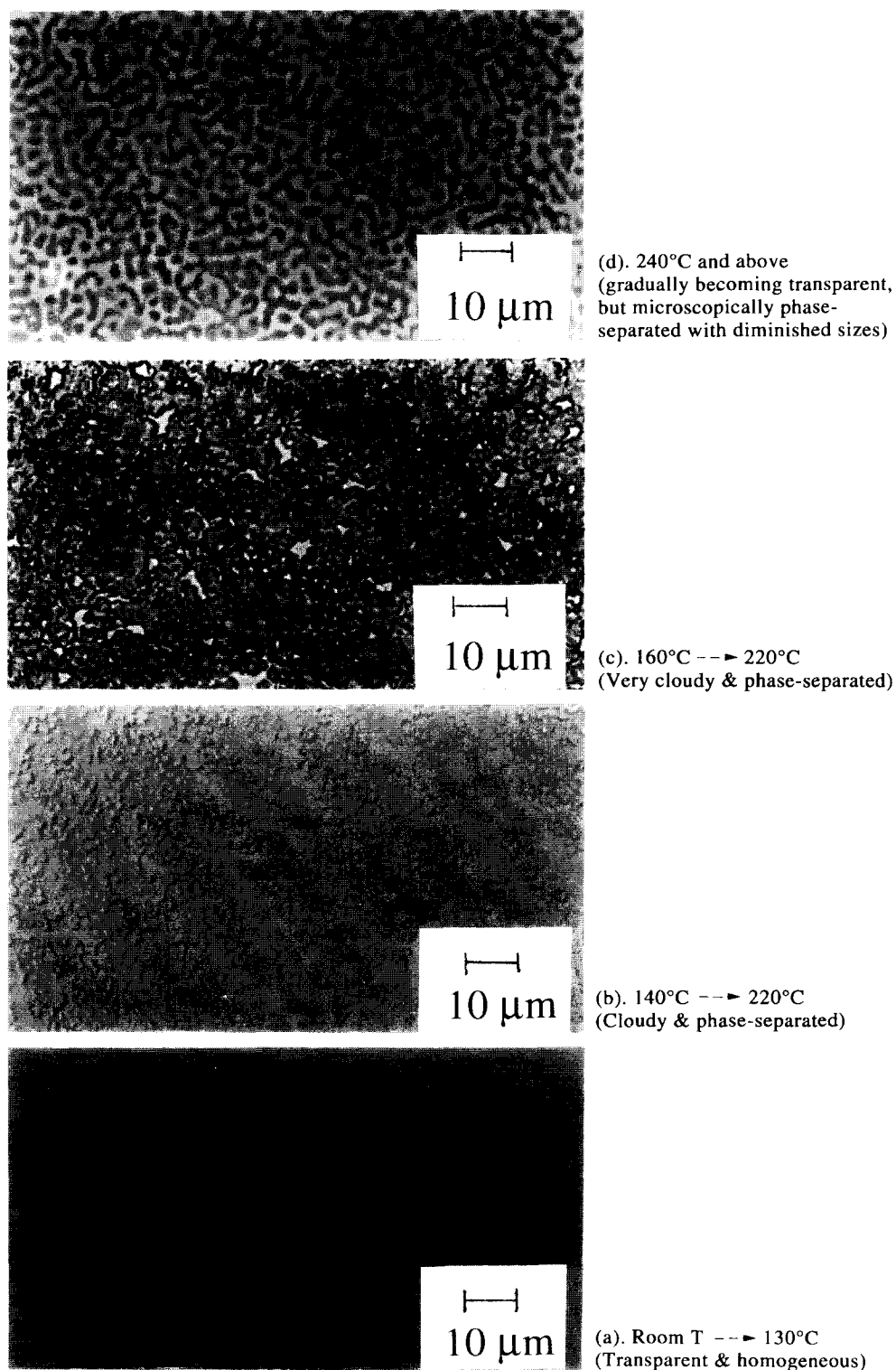

(d). 240°C and above
(gradually becoming transparent, but microscopically phase-separated with diminished sizes)

(c). 160°C − − ▶ 220°C
(Very cloudy & phase-separated)

(b). 140°C − − ▶ 220°C
(Cloudy & phase-separated)

(a). Room T − − ▶ 130°C
(Transparent & homogeneous)

Figure 6 Optical micrographs (×800) obtained for DGEBA/PC/PMMA blends on being heated from ambient temperature to above 240°C, showing changes in phase morphology, as well as phase separation with diminished domain sizes at temperatures above 240°C

temperatures above 240°C, the blend might appear visually or optically transparent, but microscopic examination showed that a distinct phase-separated morphology was obvious, only with the phase-domain sizes being significantly depressed. A $UCST$ transition should mean that the blends above 240°C are truly miscible, but we have proved that the 'visually transparent' blends after heating to 240°C or so actually displayed phase domains of about 0.2–0.5 μm in size. Accordingly, the blends heated to 240°C could not be classified as 'miscible'. Thus, a significant change in light transmission or scattering intensity might easily lead to an erroneous interpretation of the transformation of the blends from immiscibility into 'miscibility'. Consequently, results obtained from light scattering techniques, such as those reported by Kyu et al.[11], should be carefully interpreted. Changes in light scattering intensity cannot always be interpreted as corresponding changes from single phase to phase separation or vice versa. It was a fact that the blends turned from cloudy to transparent at high temperatures. However, our microscopy observation of the 'transparent' samples at temperatures above 240–250°C unambiguously revealed a phase-separated morphology, only with diminished, but still microscopically discernible, domain sizes. In other words, the phase behaviour at temperatures above 240°C is not a thermodynamic miscibility and the $UCST$ transition in PC/PMMA blends might have been mislabelled.

CONCLUSIONS

This present study has provided an innovative way of examining the long controversial issue of the so-called '$LCST$' in PC/PMMA blends. Equilibrium phase behaviour and the origin of the $LCST$ in the widely reported, but highly controversial, blend system of poly(methyl methacrylate) (PMMA) with bisphenol A polycarbonate (PC) were investigated by using a novel approach. An oligomeric epoxy was used to plasticize the molecular chains of PC and PMMA by blending all three components into a ternary system. The phase changes of the originally homogeneous ternary DGEBA/PC/PMMA blends were examined at various temperatures. Our study has shown that, given enough time, phase separation in the PC/PMMA system could occur at temperatures as low as 68°C, instead of the normally reported 140–190°C, with no reversibility of the phase behaviour upon lowering the temperature. Thus, the transparent–cloudy transition in PC/PMMA blends, should be more appropriately regarded as the approach to an equilibrium phase-separated state, rather than a thermodynamic $LCST$ phenomenon.

PC and PMMA might have a borderline partial miscibility toward each other due to certain degrees of polar interaction and reasonably matched solubility parameters. Thus, their molecular chains can become easily entangled, especially when they are co-dissolved and mixed in a common (good) solvent, which results in the polymer chains being temporarily trapped into a non-equilibrium homogeneous state with an entangled conformation. This entanglement conformation can be altered when the polymer chain segments gain enough mobility and shift from the temporarily entangled state with an apparent homogeneity to eventually give segregated chains upon reaching their equilibrium state.

Incidentally, our study has also helped clarify the controversy in the recently reported rare '$UCST$' phenomenon in PC/PMMA blends. Our microscopy results did not support the view that the blends above the '$UCST$' curves were homogeneous. The blends above 240°C might appear transparent to light transmission or scattering; however, these visually transparent blends actually exhibited a distinct phase-separated morphology, only with greatly diminished domain sizes in comparison to those in the visually cloudy blends below 240°C.

ACKNOWLEDGEMENTS

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