

Phase micro-heterogeneity in bisphenol-A polycarbonate/poly(methyl methacrylate) blends

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The controversial equilibrium phase behaviour in the blend system of poly(methyl methacrylate) and bisphenol-A polycarbonate was re-examined by using differential scanning calorimetry, optical and scanning electron microscopy. This study has shown that the 'transparent' blends of PC/PMMA actually displayed micro-heterogeneity, with domain sizes of ca. 100–300 Å. The micro-heterogeneous domains were so small that the blends exhibited a single glass transition point (T_g) and appeared transparent. Upon heating above the T_g of the matrix components of the blends, the original micro-phase domains suddenly expanded at 180°C, increasing rapidly to about 1–3 µm in size, with increased cloudiness. This present study has also shown that the 'transparent' blends when heated above 240°C also displayed micro-phase separation. Consequently, the phase behaviour in the PC/PMMA blends are re-interpreted from kinetic points of view. Copyright © 1996 Elsevier Science Ltd.

(Keywords: PC/PMMA blends; blend miscibility; heterogeneity)

INTRODUCTION

The issue of miscibility or immiscibility in binary blends of bisphenol-A polycarbonate (PC) with poly(methyl methacrylate) (PMMA) and their true equilibrium phase behaviour have been extensively investigated by many polymer researchers^{1–10}. This equilibrium phase behaviour has long been controversial. Most reports claimed that miscibility with a lower critical solution temperature (*LCST*, located at 160–190°C, depending on the composition) exists in the PC/PMMA blend system. This 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. 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 immiscibility region at 160°C, and then return back to the miscibility state upon further heating above 240°C. At temperatures above the '*LCST*' temperatures, the PC/PMMA blends were thermodynamically immiscible. However, it has also been reported by some investigators upon further increases in the temperatures, the blends could return again to 'miscibility', as judged by the disappearance of the cloudy appearance upon heating. The high temperatures at which the PC/PMMA blends return again to the clear and 'miscible' state have been termed as the '*UCSTs*' and are located on top of the *LCST* curve in

the reported phase diagrams. This phenomenon of a '*UCST* above the *LCST*', if true, is a very unusual and rare case for polymer blends. Debates and studies have therefore since been intensive.

Later, these theories were seriously challenged by other researchers, or in some instances by the original proposing authors themselves. Different theories have been proposed recently in addressing these polymer thermodynamic issues. Paul and coworkers¹² have reported a revised view that solution-cast PC/PMMA blends were actually not thermodynamically miscible and that the previously reported 'miscibility' in solution-cast PC/PMMA blends was just an artifact that was caused by the polymer chains being temporarily trapped into a non-equilibrium, homogeneous state by the solvent preparation procedures.

The origin and existence of the thermodynamic *UCST*, however, has been quite ambiguous among the various investigators, and debates are intense. The *UCST* was originally reported as representing a true 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 the existence of a single T_g for the blends quenched from above the *UCST* temperatures (> 240°C). The view of a thermodynamic origin of the *UCST* in PC/PMMA blends was later questioned. Legras and coworkers¹⁰, and Kyu *et al.*¹¹, and Rabeony *et al.*¹³ all suggested that the *UCST* might be just another artifact, which was a result of chemical interactions between the PC and PMMA occurring at the high temperatures of heating. By using Fourier transform infra-red (FTi.r.) spectroscopy,

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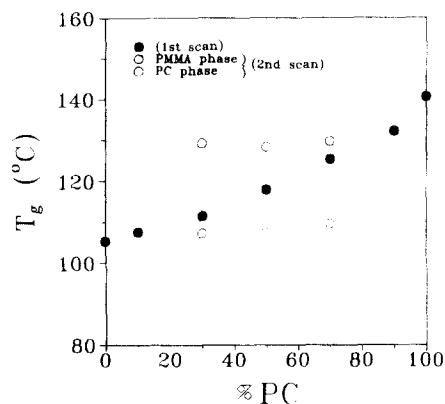


Figure 1 T_g vs. composition for the as-cast PC/PMMA blends (THF, 50°C): filled circles, data from the first d.s.c. scans; open circles, data for the same samples from the second d.s.c. scans

trans-esterification was inferred in the PC/PMMA blends^{11,13}. *Trans*-esterification has also been widely reported in PC/polyester blend systems^{14–18}.

The main controversy in interpreting the phase behaviour of blends of PMMA with PC has originated from difference in solvent casting vs. melt blending, or the sensitivity limits of different scanning calorimetry when used to resolve the T_g of the micro-phase domains. In this present study, the PC/PMMA blends in the as-prepared, solvent-cast state before heating, and the morphology of PC/PMMA blends were examined by using optical microscopy and high-resolution scanning electron microscopy. Furthermore, careful experimental schemes were designed in order to observe the detailed morphology of the PC/PMMA blends under various preparative states or post-heating temperatures.

EXPERIMENTAL

Materials and sample preparation

Poly(methyl methacrylate) (*a*-PMMA) with $M_n = 50\,000\text{ g mol}^{-1}$ and $M_w = 90\,000\text{ g mol}^{-1}$ was obtained from a commercial source (Chi-Mei Inc., Taiwan). The Bisphenol-A polycarbonate (PC) used in this work was GE Lexan[®] HF1130, which had an M_w of $23\,000\text{ g mol}^{-1}$. The blend film samples were prepared by solvent casting at two temperatures (25 and 50°C). In addition, two solvents were used, i.e. tetrahydrofuran (THF) and methylene chloride. PMMA and PC were first weighed and then dissolved (with continuous stirring) in one of the two chosen solvents. Subsequently, the resulting polymer solution was then poured into an aluminium mould which was maintained at one of the two chosen temperatures (25 or 50°C). The solvent in the cast samples was removed at room temperature by the use of a circulation oven with an exhaust fan, followed by residual solvent removal in a vacuum oven for 24–48 h at 50–60°C. After this treatment, most of the films were free from solvent. However, as some might still contain trace amounts of solvent (especially the rather tenacious THF), subsequent degassing at 110°C was therefore performed on the THF-cast samples.

Differential scanning calorimetry (d.s.c.)

The glass transition temperatures (T_g s) of the blends were measured with a differential scanning calorimeter

(Perkin-Elmer DSC-7), equipped with a computer for data acquisition/analysis. All T_g measurements were made at a scan rate of $20^\circ\text{C min}^{-1}$, over the range from 25 to 250°C, with the T_g values being taken as the onset of the transition (the change of the specific heat) in d.s.c. thermograms.

Optical and scanning electron microscopy

A polarizing optical microscope (Nikon Optiphot-2) was used. Solutions of the blends were first spread on glass slides to give thin films, and the latter were then dried thoroughly. Heating was then carried out at designated isothermal temperatures for extended times (typically 2 h) in a temperature-controlled oven before they were examined using the optical microscope. Furthermore, the morphology (fracture surface) of the PC/PMMA blends obtained from the various preparation methods and/or heating treatments was examined using a scanning electron microscope (Model JEOL JXA-840). The blend film samples for scanning electron microscopy (SEM) were kept as thick as possible since the fracture surface through the thickness was to be examined. The fractured blend samples were coated with gold by vapour deposition using a vacuum sputterer. Another set of the fractured samples were rapidly etched with acetone before they were sputter-coated and examined using SEM.

RESULTS AND DISCUSSION

The as-cast blend film samples (THF, at 25 or 50°C) before heating were examined first by using optical microscopy at the maximum magnification of 2000. THF-cast blend films at 50°C were visually clear and homogeneous. In addition, no solvent-induced PC crystallization was observed for the 50°C THF-cast blends as the samples were visually clear and d.s.c. scanning of the blends revealed no melting peak for the PC. It was found that casting at 50°C yielded the best quality clear film samples. A visually transparent and seemingly homogeneous blend film was obtained if a casting temperature of 50°C, with THF as the solvent, was used. These clear blends films have been reported to be 'miscible' in the literature, and represent the main objective of re-examination in this report. In this present study, the transparent films were first examined by using d.s.c. and optical or scanning electron microscopy in order to provide a baseline for comparison. The transparent films were then further treated at various temperatures for designated periods of time before they were examined by using the experimental techniques to be described in the following paragraphs.

While the films cast with THF at 50°C were transparent and seemingly homogeneous, those cast at 25°C with THF (or using solvents other than THF) were found to be visually cloudy. THF-cast blend films at 25°C were visibly opaque, thus indicating phase separation and/or solvent-induced PC crystallinity. Preliminary d.s.c. analysis showed that PC/PMMA blends cast with THF at 25°C did in fact reveal PC crystals with a distinct T_m of 225°C. The PC crystals might be partially responsible for the opacity in the 25°C THF-cast blends. Blends were also dissolved in methylene chloride and cast at two temperatures, i.e. 25 and 50°C. Methylene chloride casting of the blend films at either 25°C or 50°C yielded opaque, non-homogeneous films,

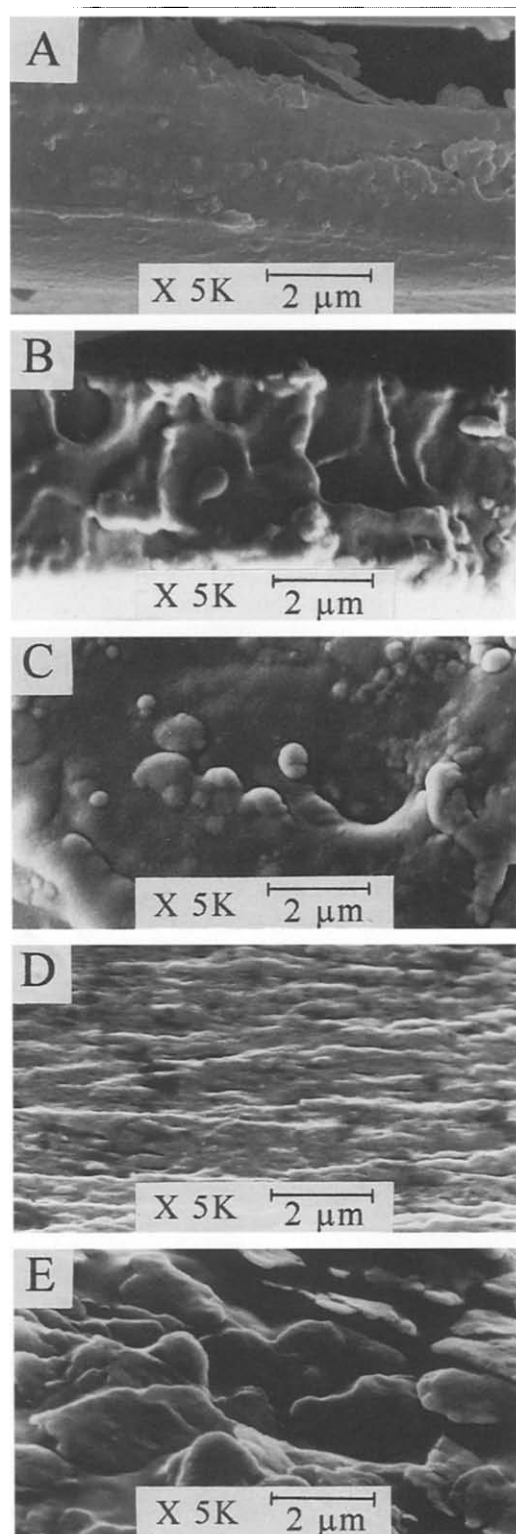


Figure 2 Scanning electron micrographs (cross-sections) of THF-cast PC/PMMA blend samples of various compositions: (A) 10/90; (B) 30/70; (C) 50/50; (D) 70/30; (E) 90/10

and optical microscopy examination of these blend films also revealed large grossly separated domains. However, preliminary d.s.c analysis showed that there was no solvent-induced PC crystallization for the methylene chloride-cast blend films at either temperature. Consequently, it can be postulated that the opaqueness in the methylene chloride-cast blends was most likely to be solely due to phase separation.

Glass transition behaviour of cast blends

First as a screening analysis, T_g characterization was performed on the transparent blend samples that had been cast from THF at 50°C. *Figure 1* (filled-circle data) showed a T_g vs. composition plot for the as-cast PC/PMMA blends (THF, 50°C). The T_g values were taken as the onset of the transition in the d.s.c thermograms, which all exhibited a single glass transition temperature. Furthermore, fitting of the experimental T_g data by using the Gordon–Taylor equation¹⁹ yielded a parameter k of 0.50. On the same figure, the open-circle data represent the T_g values obtained from a second d.s.c scanning of the same blend samples after heating to 240°C and then quenching. However, these results revealed that the original single T_g was no longer observed. Instead two T_g s were clearly observed in the d.s.c thermograms for each of the re-scanned samples; these results are consistent with the reports in the literature^{1–10}.

Micro-heterogeneity in clear cast blends

The above T_g results demonstrated that the clear PC/PMMA blend films (THF, 50°C) showed only one T_g . In addition, the originally clear blends (50°C, THF) turned opaque and exhibited two T_g s upon a second d.s.c scanning after quenching from above 180°C. However, are the optically clear and seemingly homogeneous blends (THF, 50°C) really miscible, thermodynamically? It may well be that the phase domain sizes might be simply beyond the detection or resolution limits of the optical microscopy or thermal analysis and techniques.

To probe this further, electron microscopy was performed. First, the fracture surfaces of the THF-cast (50°C), transparent PC/PMMA blends with a single T_g were examined by using SEM. *Figure 2* shows scanning electron micrographs of THF-cast PC/PMMA blend samples of various compositions. The micrographs show that there are some tiny segregated particulate domains (0.3–0.5 μm) scattering across the fracture surfaces (cross-sections) of the blends at all compositions. The single T_g in the THF-cast blends might be simply explained by the fact that the PMMA domain sizes are so small that they appear ‘homogeneous’ as far as the sensitivity limit of d.s.c. is concerned. The SEM results, however, did not show these blends as being homogeneous, since SEM did reveal micro- (but observable) heterogeneity of ultra-small domains in these clear PC/PMMA blends cast with THF at 50°C.

To enhance the contrast in the phase domains, delicate manipulation was carried out in order to prove more conclusively that this was indeed a phase-separated morphology. Since the PMMA domain could supposedly be dissolved in acetone and the PC phase domain could not, the fracture surface of the blends was quickly immersed in acetone in order to etch out the PMMA domain. *Figure 3* (micrographs A–E) shows the acetone-etched surface of the same blend samples of various compositions. The phase contrast is now more obvious. From top to bottom, the micrographs show that the PMMA component (the etched domain) forms the continuous phase, with PC forming the discrete phase, for the PMMA-rich blends. Similarly, the PC component forms the continuous phase, with the PMMA component forming the discrete phase (etched to craters), for the PC-rich blends.

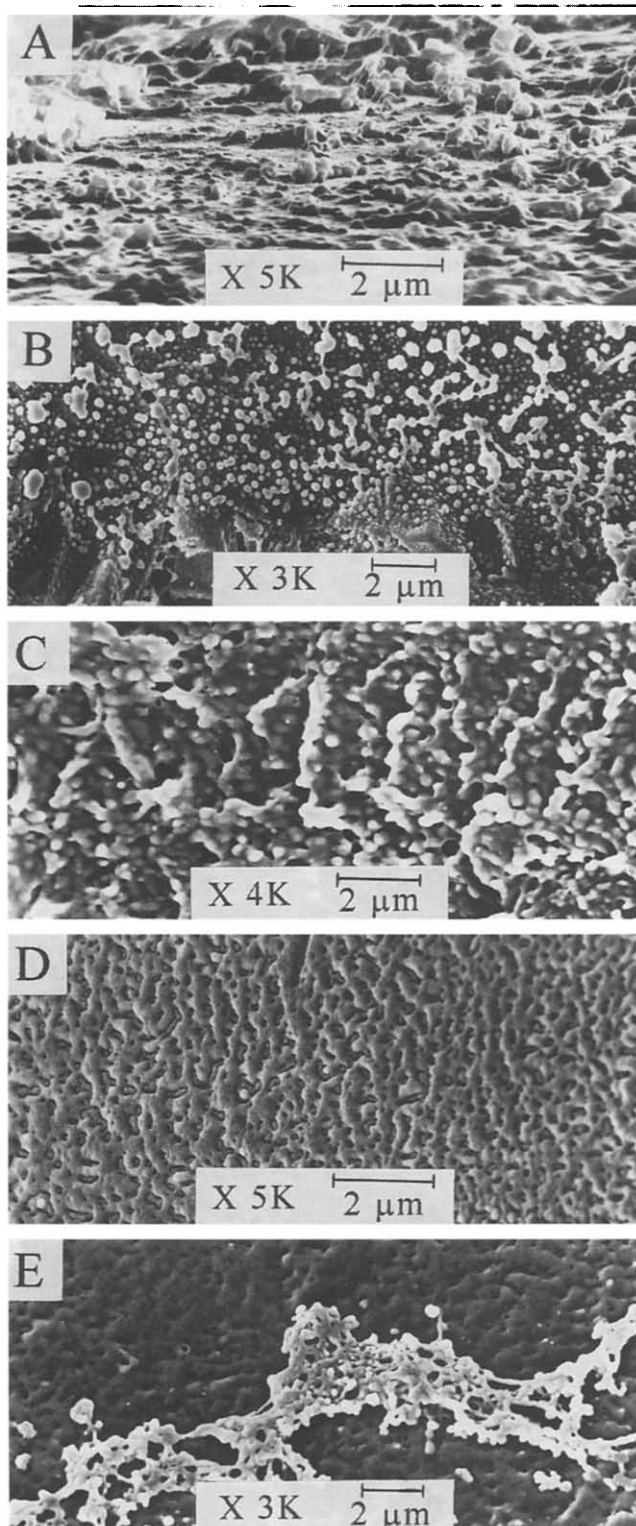


Figure 3 Scanning electron micrographs (cross-sections, acetone-etched) of THF-cast PC/PMMA blend samples of various compositions: (A) 10/90; (B) 30/70; (C) 50/50; (D) 70/30; (E) 90/10

Our SEM results have demonstrated that the as-cast transparent blends with a single T_g were actually phase separated, only with micro-phase domains that might be beyond the detection limits of optical light techniques or thermal analysis. Indeed, it has been argued that a single T_g in the d.s.c. thermograms alone does not necessarily indicate phase homogeneity or miscibility in the blends^{20,21}. This argument is valid since the phase

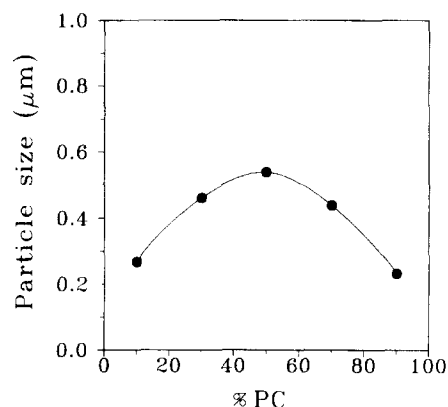


Figure 4 Average domain size as a function of the composition of PC/PMMA blends cast from THF solution at 50°C

domains might be quite small and beyond the detection sensitivity of d.s.c. Interestingly, the domain sizes seem to be dependent on the composition, but the irregular shapes of the domains made it difficult to estimate these sizes. However, an averaging method was used to obtain a fair estimate. *Figure 4* shows the average domain size as a function of the blend composition, which gives a maximum average size of $\sim 0.5 \mu\text{m}$ at a composition of 50/50. This is consistent with the d.s.c. results, and generally shows a maximum glass transition breadth for the PC/PMMA (50/50) blend composition.

In order to observe the effect of temperature on changes in the phase morphology, the clear blend film of PC/PMMA (50/50) was then heated at various heating/cooling rates between 100 and 180°C, and examined again using SEM. *Figure 5* shows scanning electron micrographs of the fracture surface of a PC/PMMA blend (50/50) sample (after being heated to 180°C). Prior to the heating treatment, the blend, although clear, actually displayed a morphology with a micro-heterogeneity of $0.5 \mu\text{m}$. Upon heating to 180°C, the originally clear blend film turned visually opaque, and the micrograph revealed much larger and grossly separated domains of $\sim 3\text{--}5 \mu\text{m}$, i.e. the phenomenon of phase separation persisted and progressed to a greater extent, with the domain sizes now expanding significantly from $0.5 \mu\text{m}$ to $\sim 3\text{--}5 \mu\text{m}$ at temperatures above 180°C. This, however, should not be regarded as a phenomenon whereby the originally homogeneous blend 'phase-decomposed' to form grossly separated domains, but rather that the originally existing micro-heterogeneous domains in the blend simply expanded in size when the polymer chains gained enough mobility. The process of expansion of the domain sizes can be greatly accelerated by heating above the glass transition temperature of the continuous phase of the blends.

Figure 6 shows the cloud-point curves constructed by observing the transparency–cloudiness transition of blends which have been heated isothermally for 2 h at a specific temperature. This procedure was adopted in order to avoid the time-lag effect of dynamic heating. The lower curve in the figure indicates the temperatures at which the blends turned from 'transparent' to 'cloudy', while the upper curve indicates the higher temperatures at which the blends turned from 'cloudy' to 'transparent'. It must be emphasized that the definition of a cloud point by either intensity changes in light

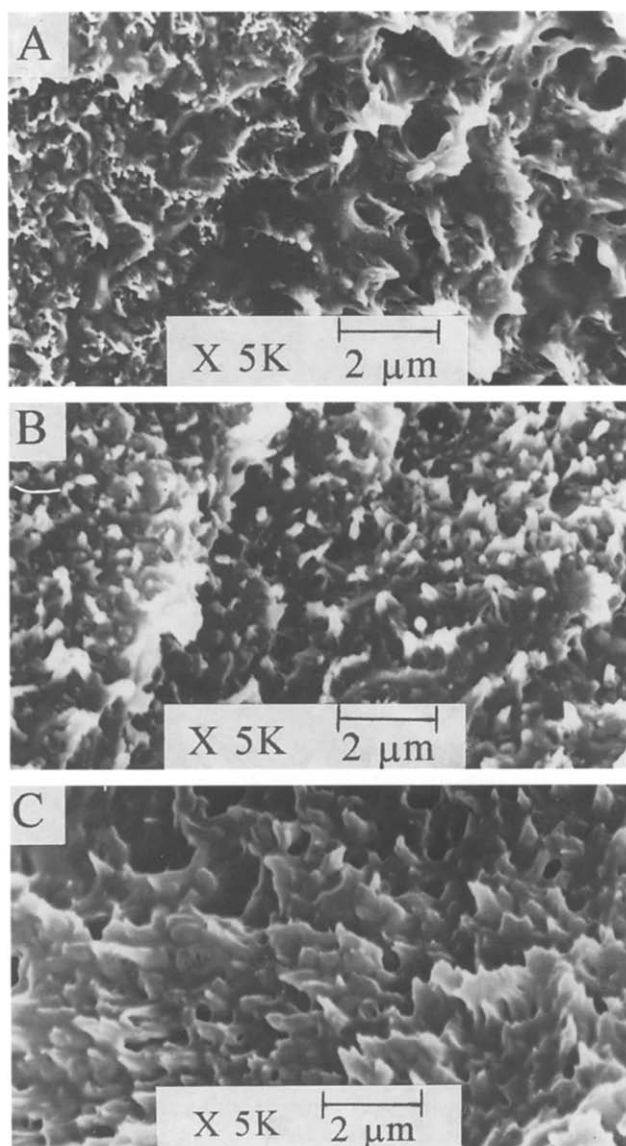


Figure 5 Scanning electron micrographs (cross-sections) of the THF-cast PC/PMMA (50/50) blend post-heated to 180°C: (A) heated and cooled between 100 and 180°C at 0.1°C min⁻¹; (B) heated between 100 and 180°C at 500°C min⁻¹, then cooled from 180 to 100°C at 0.1°C min⁻¹; (C) heated and cooled between 100 and 180°C at 500°C min⁻¹

scattering measurements or by the naked eye might result in an erroneous interpretation since what appears to be transparent to the eyes can actually exhibit distinct phase-separated domains when examined using an optical or electron microscope. Therefore, the transition to blend cloudiness in constructing these plots was determined not only by visual inspection, but was also judged by a determination of the domain sizes using the optical microscope. This was carried out by the 'onset' from transparent to cloudy being judged by an exact microscopy criterion in which the phase domain sizes reached 1 μm. As expected, the shapes of the curves are similar to those well reported in the literature¹⁻¹⁰. However, the temperature locations of the curves differ slightly from the literature values due to the more exact and specific criterion of the 'transparent-cloudy transition' used in this study.

Although these two curves have been discussed with reference to the 'LCST' and 'UCST' in many reports in

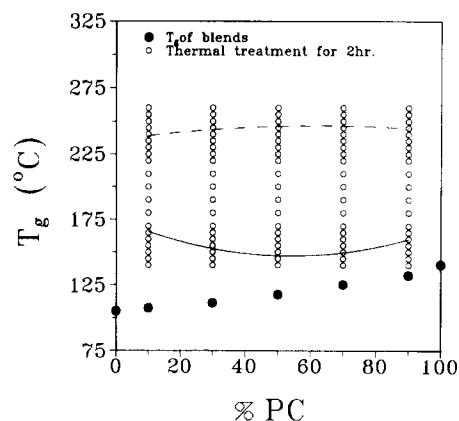


Figure 6 Cloud-point curves for the PC/PMMA blends constructed from optical microscopy data obtained by annealing samples at closely spaced isothermal temperatures for 2 h

the literature, we feel that these might have been erroneously labelled. According to the above experimental morphology results, the 50°C-cast PC/PMMA blends are actually not miscible but simply display micro-heterogeneity. The phase domains are simply so small that they are almost transparent to visible light or light scattering, especially when samples are prepared as thin films, but they are actually not miscible in the thermodynamic sense. If these visually clear blends with one apparent T_g are actually *not* thermodynamically miscible to begin with, does it make any sense to propose an LCST or UCST is present or not in the PC/PMMA blends?

Interestingly, the convex-shaped curve of the composition-dependent domain sizes in the clear PC/PMMA blend films is roughly the mirror image of the concave curve of cloud points vs. composition. This can be explained by kinetic considerations. The transparent blends with a predominant component (PC or PMMA) as the continuous phase tend to have relatively smaller discrete domain sizes (0.1–0.3 μm), while the blends with compositions near 50/50 tend to have relatively larger domain sizes (0.4–0.5 μm). To reach the cloud point, the discrete domain sizes have to grow to a certain level, say 1.0 μm. Naturally, the temperature driving force has to be larger for the blends with smaller domain sizes and vice versa. The cloud-point curve thus assumes a concave shape when plotted with the composition as the x-axis. One example is worth mentioning here in order to stress the possible kinetic effects. By using an oligomeric epoxy as a co-solvent for PC and PMMA for lowering the blend's T_g and enhancing the segmental mobility of the polymer chains, one of our recently published papers²² has demonstrated that at isothermal temperatures as low as 68°C, the epoxy-solubilized PC/PMMA blends can exhibit a distinct phase-separated morphology. This is in distinct contrast to those systems normally reported at 180°C or above. Furthermore, it remains to be explained whether or not the cloudy-transparent transition of the blends when heated above 240°C could be properly called an 'UCST'. This means that there is serious doubt as to whether or not the upper cloud-point curve in Figure 6 is really a true UCST, since the UCST transition should mean that the blends above 240°C are truly miscible and not just an observable change in light transmission or scattering intensity.

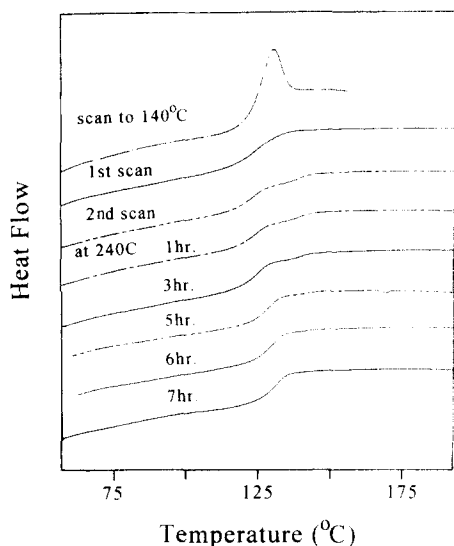


Figure 7 D.s.c. thermograms of PC/PMMA blend samples (50/50 composition, THF-cast at 50°C) post-heated at 240°C for various periods of time from 0–7 h

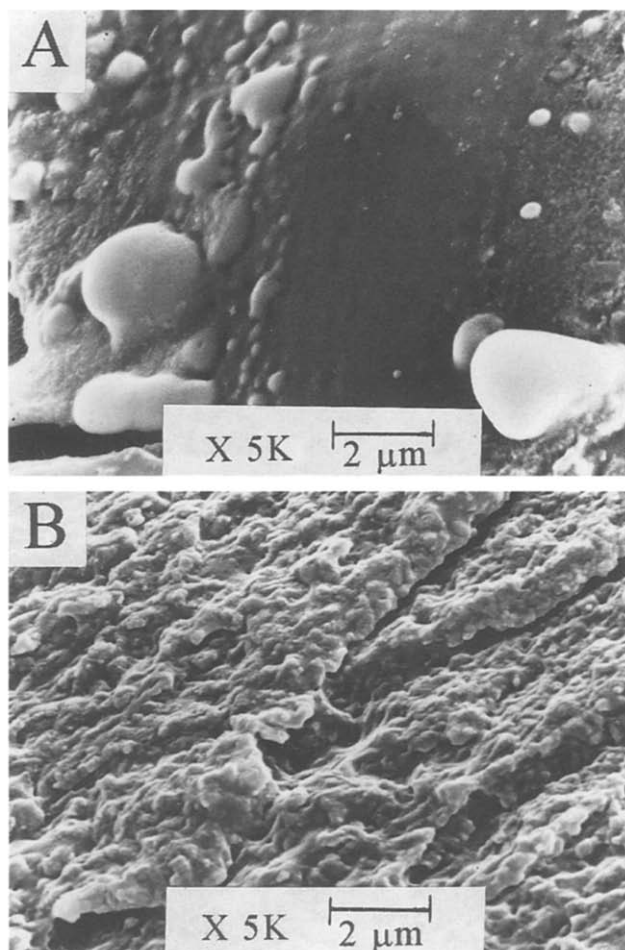


Figure 8 Scanning electron micrographs (cross-sections) of the THF-cast PC/PMMA (50/50) blend post-heated at 240°C for 7h: (A) annealed at 240°C for 7h; (B) heated/cooled between 100 and 240°C at 0.1°C min⁻¹

Figure 7 shows the d.s.c. thermograms of the PC/PMMA blend of 50/50 composition (THF, cast at 50°C) subjected to annealing at 240°C for various lengths of time (0–7 h),

as indicated in the graph. Prior to the thermal treatment, the transparent blend exhibited a single T_g . However, after annealing at 240°C for 1–3 h, two T_g s were observed in the heated blend samples. Interestingly, after heating for longer than 6 h, the multiple- T_g behaviour was reversed and only one T_g was observed. Does this mean that the blends after extended annealing at 240°C (above the upper cloud-point curve, i.e. in the transparent region) might eventually transform into a single-phase system?

The SEM micrographs in Figure 8 show that the 50/50 blend sample which has been heated for 7 h at 240°C is still phase-separated although the phase morphology is significantly less heterogeneous than the blends heated at 180°C (between the lower and upper cloud-point curves, i.e. within the cloudy region). Again, the single T_g of the blends heated to 240°C does not correspond to a homogeneous single-phase morphology, but only suggests a morphology of more reduced domain sizes. Certainly, chemical interactions^{10,11} between PC and PMMA might have been responsible for the greatly suppressed domain sizes. Contrary to reports in the literature^{10,11} that blend miscibility is achieved at temperatures above the upper cloud-point curve, our results suggest that this is still a phase-separated morphology, only of depressed domain sizes, and clearly not a homogeneous state. Therefore, 'UCST' may not be an appropriate term for describing the cloudy-to-transparent transition.

Effects of film thickness and casting temperature on domain sizes

Although casting with THF at 50°C yielded the most transparent blend films, the extent of micro-heterogeneity in the cast blends was found to depend on the film thickness. Figure 9 shows scanning electron micrographs of the THF-cast blend sample of 50/50 composition (at 50°C) with various thicknesses, ranging from 10 to greater than 40 μm. The figure appears to show that the extent of micro-heterogeneity increases with the film thickness. This is difficult to explain thermodynamically, since the solvent (THF) and temperature (50°C) are the same for all of the blend preparations. This fact suggests that the blend morphology might be influenced by the kinetic rate of solvent evaporation. Faster rates of evaporation in the thin films resulted in a greater extent of chain entanglements, and thus lower extents of heterogeneity.

The same kinetic argument also applies to the temperature effect. Figure 10 shows T_g vs. composition plots for the as-cast PC/PMMA blends (THF, 25°C). It should be noted here that the T_g s of the blends with high PC contents were masked by the presence of PC crystals. While re-scanning after quenching from a first scan to 250°C was the only way to melt the PC crystals, it should be noted that heating to 250°C might also induce phase separation and give two T_g s for the blends, which thus interfered with the intended interpretation. The reported T_g in this figure was obtained from the first-scan d.s.c. thermograms for blends with only low PC contents, which had a much suppressed solvent-induced PC crystallinity. It was found that these blends with low PC contents also showed two T_g s on the first d.s.c. scanning. Therefore, it can be reasonably assured that regardless of the masking effect of PC crystallinity on the

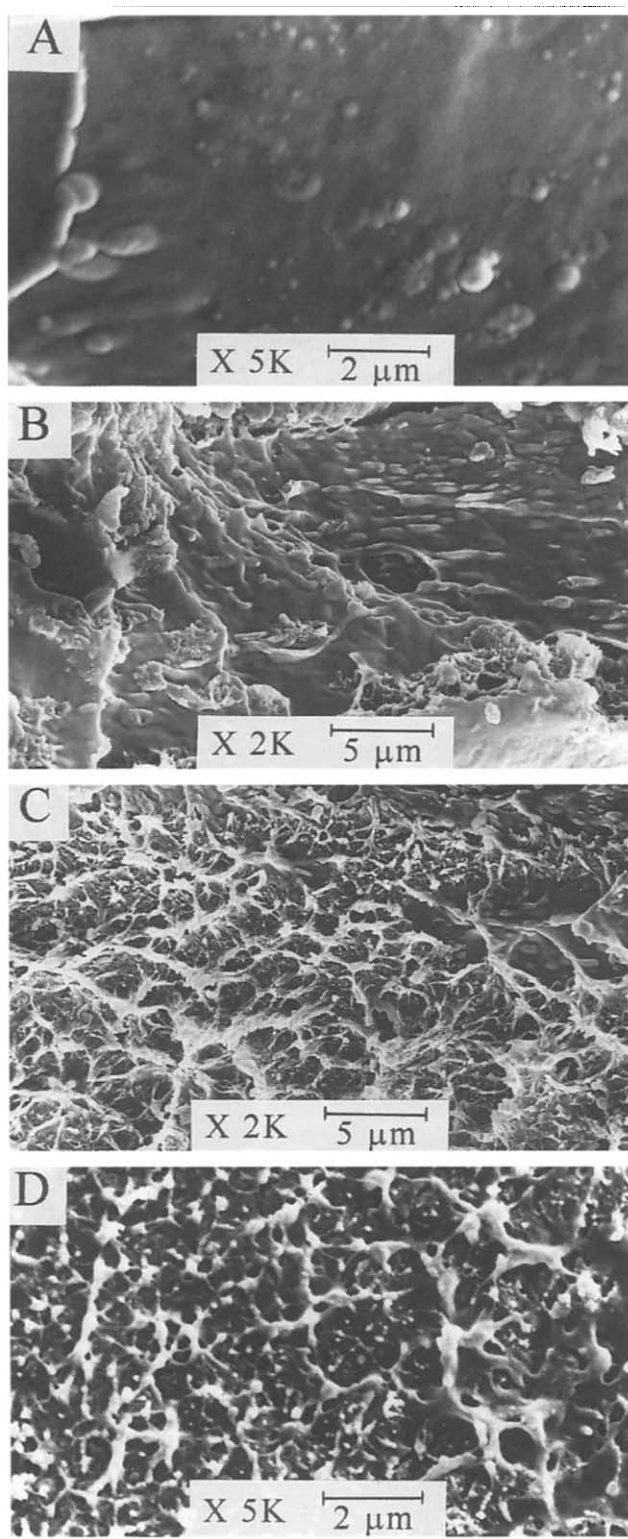


Figure 9 Scanning electron micrographs (cross-sections) of the as-cast PC/PMMA (50/50) blend sample (THF, 50°C) with various film thicknesses: (A) 10 μm; (B) 20 μm; (C) 30 μm; (D) greater than 40 μm

appearance or the T_g behaviour of the 25°C-cast blends with high PC contents, phase heterogeneity is apparent by the presence of two T_g s in the blends cast at 25°C.

Figure 11 shows scanning electron micrographs of THF-cast blend samples with five different compositions, all cast at a lower temperature of 25°C, but with the same average thickness. Overall, the extents of heterogeneity in these blends are seen to be significantly greater than in

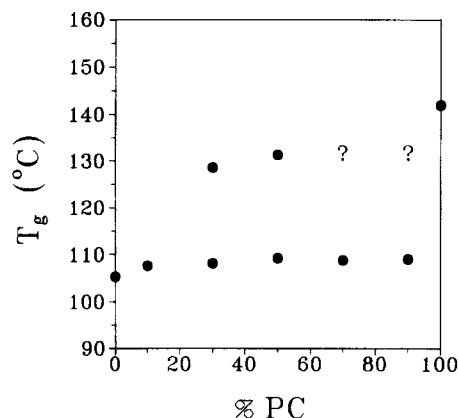


Figure 10 T_g vs. composition for the as-cast PC/PMMA blends (THF, 25°C)

the blends with corresponding compositions cast at 50°C. Due to much larger domain sizes, a shift in phase continuity can be clearly identified as the composition is changed. For example, the PC/PMMA (10/90) blend sample (A) exhibits a continuous PMMA phase containing discontinuous PC domains of about 1–2 μm in size. Note that these blends were prepared by casting THF solution at 25°C, followed with degassing first at 50°C, and then at 120°C for extended periods of time. Solvent-induced PC crystallization was apparent during the first step, i.e. the casting and evaporation process, although subsequent annealing/degassing at 120°C might further slightly increase the extent of crystallinity. Solvent evaporation was much slower at 25°C, and thus solvent-induced crystallization occurred only in the 25°C-cast blends with high PC contents, but not in the corresponding 50°C-cast blends. Due to solvent-induced crystallinity in the PC phase, the PC domain could be easily identified by the tiny white crystalline dust-like particles. At compositions of 50/50 and 30/70, the continuous phase is gradually shifted to the PC component. The domain sizes have an average size of between 2 to 5 μm, thus indicating a grossly phase-separated cloudy blend. Note that there are some microvoids in these samples, with these probably being caused by evaporation of the residual trapped THF solvent during degassing. Eventually, at a 90/10 blend composition, there is now no doubt that the PC component is the only continuous phase.

CONCLUSIONS

The widely studied blend system of PMMA with PC was re-investigated, with attempts being made to clarify a long-running controversy. Visually, these blends appeared to be transparent and exhibited only one single T_g upon d.s.c. scanning. Our microscopy observations of the 'transparent' blend samples of PC/PMMA cast from THF solution at 50°C unambiguously revealed a micro-heterogeneous morphology, with microscopically discernible domain sizes. It is pointed out that the conventional cloud point vs. composition transition might have been erroneously labelled as an *LCST* in several reports in the literature. In other words, the visual phase change at 170–180°C may not be a thermodynamic phase change from homogeneity to heterogeneity, but rather a kinetic phenomenon involving a sudden

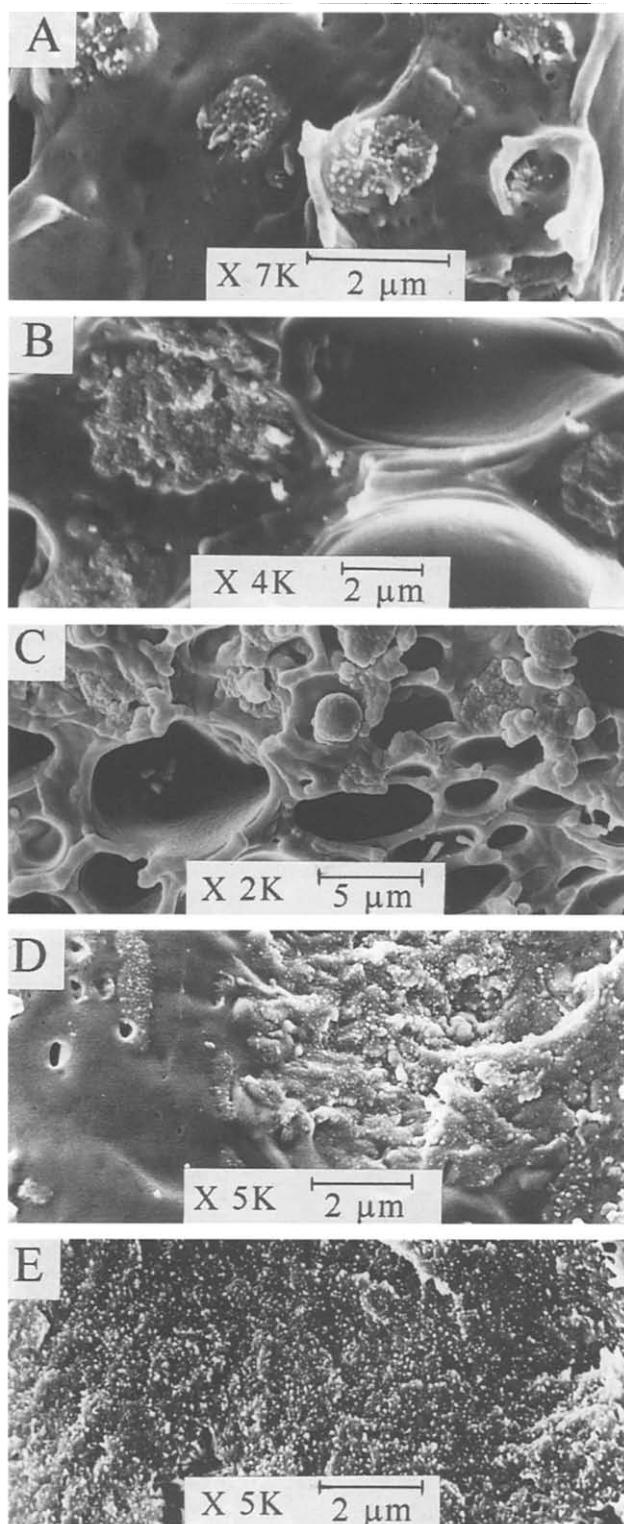


Figure 11 Scanning electron (cross-sections) of as-cast PC/PMMA blends (THF, 25°C) with various compositions: (A) 10/90; (B) 30/70; (C) 50/50; (D) 70/30; (E) 90/10

expansion of the originally existing micro-domains when the molecular chain segments gain sufficient mobility at temperatures above the T_g (s) of the blends. Furthermore, our study has also helped to clarify the controversy concerning the widely reported 'UCST' in PC/PMMA blends, where the latter is a thermodynamic phenomenon involving a cloudy-to-transparent transition of the blends at temperatures above 240°C. Our microscopy

results did not support the view that the blends at temperatures above the 'UCST' (actually the upper cloud-point curve) were homogeneous, although d.s.c. scanning revealed only a single T_g .

To summarize, PC and PMMA might display a certain level of polar interactions and thus have solubility parameters which are sufficiently well matched that partial miscibility is likely. Thus, their molecular chains can be easily entangled, particularly when they are co-dissolved and mixed in a common good solvent. Subsequent rapid removal of the solvent might have caused the polymer chains to become temporarily trapped into a non-equilibrium, micro-heterogeneous state with an entangled chain conformation. Therefore, the sizes of the domains are highly dependent on the type of solvent and kinetic parameters such as film thickness, temperature of film casting, and the time and temperature of the post-thermal treatment. This entanglement conformation can be eventually altered when the polymer chain segments gain enough mobility to gradually shift from the temporarily entangled state to eventually give segregated chains on reaching the equilibrium state of phase separation.

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