The dielectric response of a polycarbonate/ poly(butylene terephthalate) blend

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Contour maps of real relative permittivity and loss tangent within the range $-190°C$ to $+185°C$ and 0.1 Hz to 3 MHz are presented for an unannealed 5/4 melt blend of commercial polycarbonate (PC) and poly(butylene terephthalate) (PBT). Evidence is provided for partial miscibility of the homopolymers and for a two-phase morphology involving PBT-rich domains imbedded in a continuous phase consisting primarily of PC.

INTRODUCTION

Polycarbonate is widely employed for its high impact strength and dimensional stability as well as for its low dielectric loss. Although comparatively resistant to ageing and photodegradation, it is subject to hydrolytic degradation and chemical attack. In recent years blends and alloys based on polycarbonate have yielded materials of superior performance. One of the most successful commercial polymer blends is that of bisphenol A polycarbonate (PC) and poly(butylene terephthalate) (PBT). PBT enhances the chemical resistance and processability without impairing the desirable properties of the polycarbonate.

The miscibility and morphology of PC/PBT blends have received considerable attention owing to their importance in determining ultimate properties[1-7]. Conflicting results have been reported in the literature regarding shifts of glass transition temperature (T_g) and miscibility. The apparent disagreement is thought to arise from differences in composition, blending procedure and thermal history.

This study applies the dielectric method at frequencies between 0.1 Hz and 3 MHz to a melt blend of commercial polycarbonate and PBT. Material composition and sample treatment are specified in order to validate comparison with the work of others. Variable-temperature measurements of dielectric response within the present frequency range can yield valuable information regarding modes of molecular and segmental motion in polymers. The inclusion of additives or other polymers, or exposure to environmental influences, may be expected to modify the response. Wetton et al.[8] have used the method to investigate compatibility in polymer blends, although not over a range of frequencies.

EXPERIMENTAL

Plaques of a 5/4 melt blend of Lexan 145 polycarbonate and Valox 315 PBT supplied by General Electric Plastics (Australia) Pty Ltd were cut into smaller pieces, pre-dried at 130°C and pressed into sheets at 260°C. No process of annealing was undertaken. For the measurement of both complex relative permittivity and d.c. resistance, samples of approximate dimensions $25 \times 20 \times 0.4$ mm were cut from the sheet and aluminized on opposite faces *in vacuo* to form matching electrodes. Permittivity data were obtained using the capacitative-T wide-band bridge of Pratt and Smith[9]. A Keithley Instruments 602 electrometer was used to obtain the d.c. resistance, whilst ensuring that sufficient time was allowed to exclude the influence of transient currents. Control of sample temperature was achieved by a baffled flow of dry nitrogen gas at the desired temperature.

RESULTS AND DISCUSSION

Presentation of results

The temperature–frequency variation of complex relative permittivity for the 5/4 PC/PBT blend is presented in *Figures 1* and *2* in the form of contour maps of ε' and $\tan \delta$. Arrhenius plots of the logarithm of the frequency at which maximum loss occurs against reciprocal temperature are shown in *Figure 3* for the α- and β-processes of the blend and its homopolymers. Four dispersion regions are apparent in the contour map of $\tan \delta$ (*Figure 2*).

The first is a broad dispersion at temperatures below ambient. The peak extends from about $-110°C$ at 0.1 Hz, through $-75°C$ at 1 kHz, to $+5°C$ at 3 MHz. The locus of the peak coincides reasonably closely with that observed for the β-process in Lexan 145 polycarbonate and lies some 15–30°C below that for Valox 315 PBT. Although there are differences in detail between the molecular motions responsible for the secondary relaxation processes in polycarbonate and PBT, there is no evidence for separate β-peaks arising from the individual constituents of the blend. Wahrmund et al.[1] and Birley and Chen[3] also observe insubstantial differences in the temperature locations of the β-peak for polycarbonate and the blend. The activation energies calculated from the Arrhenius plots of *Figure 3* are 37 kJ mol^{-1} for the combined β-process of the blend,
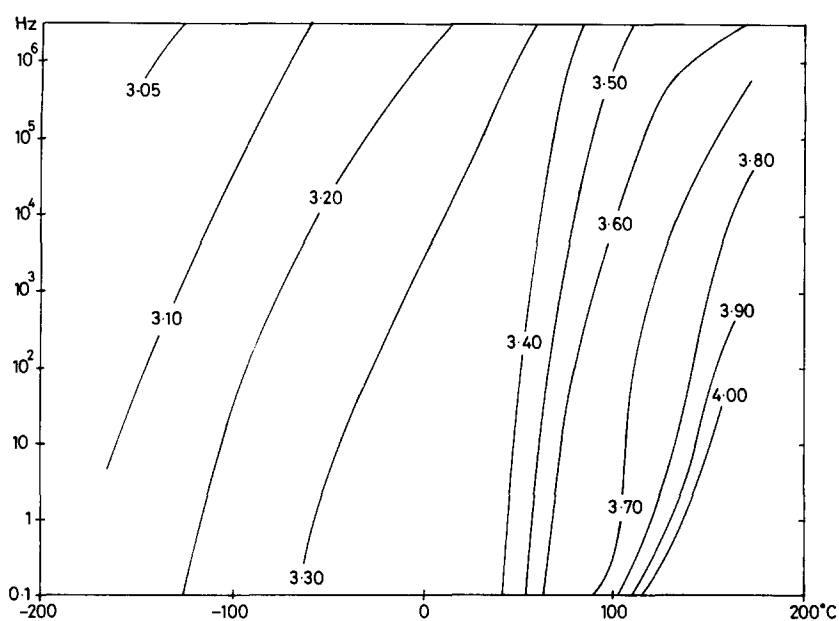
Figure 1 Contour map depicting the temperature-frequency variation of real relative permittivity ε' of the PC/PBT blend
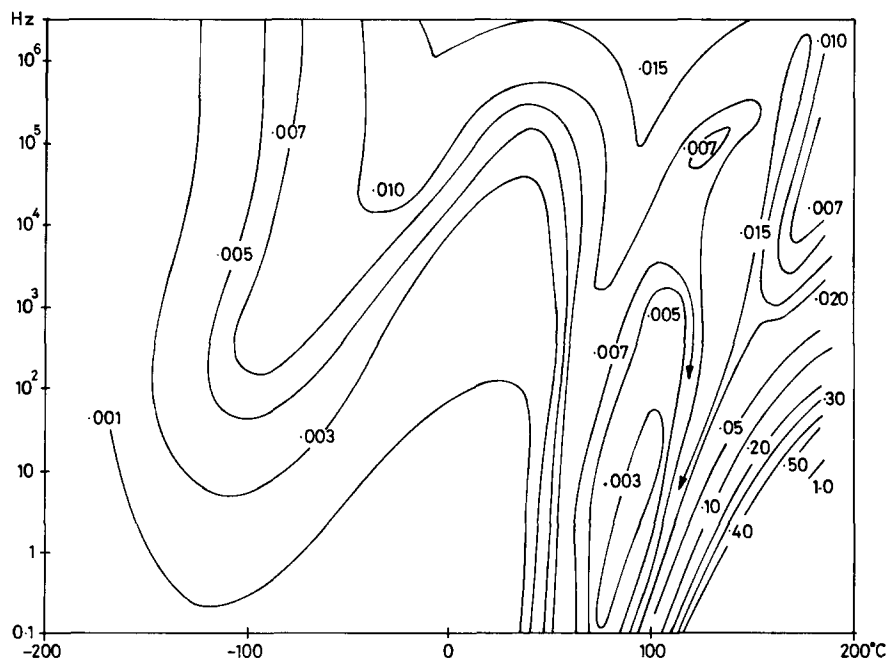

Figure 2 Contour map of tan δ for the PC/PBT blend

49 kJ mol^{-1} for Lexan 145 polycarbonate and 57 kJ mol^{-1} for Valox 315 PBT. Literature values between 27 and 54 kJ mol^{-1} for polycarbonate were noted in an earlier paper[10] and values from 50 to 55 kJ mol^{-1} have been reported for PBT[11,12].

The peak of the second and moderately narrow region of dispersion extends approximately from 60°C at 0.1 Hz, through 70°C at 1 kHz, to 105°C at 3 MHz. The location of this peak corresponds very closely with that for the α-process in PBT[13], but with a shift of 0–5°C towards higher temperatures. Although Hanrahan *et al.*[4] found no T_g shifts in solution-cast PC/PBT blends, increases of 5–17°C for the PBT T_g have been reported by others[1,3,5]. As in the case of the homopolymer[13], the Arrhenius plot for the PBT α-process in the blend (*Figure 3*) separates

into two straight lines of differing slope at about 1 kHz. The activation energies are 210 and 480 kJ mol^{-1}, respectively, above and below 1 kHz, as against 220 and 420 kJ mol^{-1} for the homopolymer. Values from 205 to 460 kJ mol^{-1} are reported elsewhere[11,14].

The third dispersion region is narrow and is observed at high temperatures. Its peak extends from 142°C at 1 kHz to 173°C at 1 MHz and is shifted by 25–30°C towards lower temperatures compared with the α-peak in either Lexan 141 or 145 polycarbonates[4]. Previous studies using non-dielectric methods have reported lowering of the PC T_g by 17–47°C in PC/PBT melt blends[1,3,5], but no change for solvent-cast blends[4,5]. The activation energies derived from the Arrhenius plots of *Figure 3* are 330 kJ mol^{-1} for the blend, 490 kJ mol^{-1}
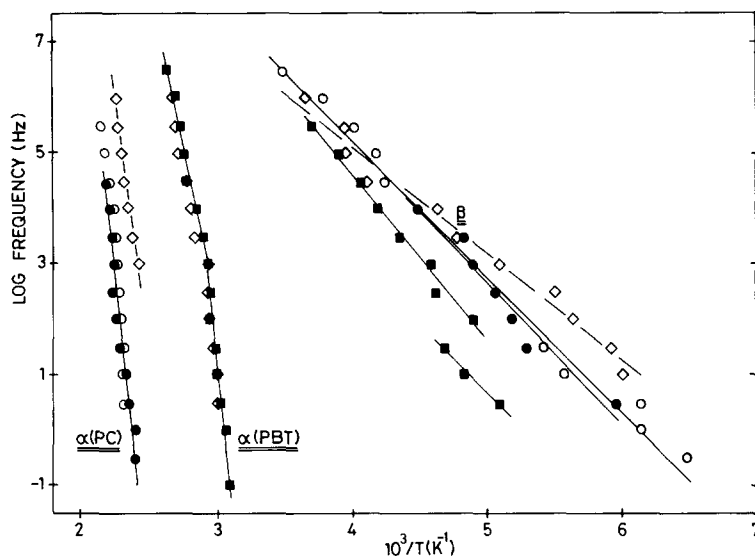
Figure 3 Arrhenius plot of the α- and β-processes for PC and PBT homopolymers and the blend: (●, O) Lexan 145 and 141 PC: (■) Valox 315 PBT; (◇) PC/PBT blend

for Lexan 141 and 390 kJ mol^{-1} for Lexan 145. Literature values of 480–835 kJ mol^{-1} for the α-process in polycarbonate were noted in the earlier paper[10].

The final dispersion represents MWS losses, which increase rapidly with increasing temperature and/or decreasing frequency. The contour at tan $\delta = 0.1$ extends from about 105°C at 0.1 Hz to 190°C at 300 Hz. The onset of these losses occurs at temperatures and frequencies corresponding to those for PBT[13]. Since interfacial Maxwell–Wagner–Sillars (MWS) losses in PBT increase rapidly in the approach to high temperature and low frequency, it is not possible to locate the onset of similar losses from the polycarbonate constituent of the blend.

Miscibility and morphology

The persistence of the glass transition temperatures of the component polymers in the tan δ map (*Figure 2*) of the blend, and the lack of a third T_g peak at an intermediate temperature, confirm that the blend consists of two phases. The temperature shift in each T_g is considered to be a consequence of the partial miscibility of the component polymers, as noted previously by others[1,3,5]. The very slight increase in the T_g of PBT in the melt blend indicates that the PBT-rich phase contains only a small amount of polycarbonate. In contrast, the substantial decrease in the T_g of polycarbonate in the blend suggests the presence of moderate proportions of PBT in the polycarbonate-rich phase, in agreement with the conclusion of Birley and Chen[3] and others[1,5].

The published literature appears unanimous in the view that PC/PBT blends are multiphase materials. However, a consensus has yet to appear regarding mutual miscibility and morphology.

Wahrmund *et al.*[1], Birley and Chen[3] and Hobbs *et al.*[5] provide evidence for partial miscibility of the homopolymers in melt blends of PC and PBT. Devaux *et al.*[15] argue in favour of PC/PBT copolymer formation rather than limited miscibility. The investigation of solution-cast blends by Hanrahan *et al.*[4] led them to conclude that PC and PBT are immiscible. The contrasting behaviour between melt-processed blends and melt-processed blends that are subsequently

solution-cast has been well demonstrated by the extensive d.s.c. studies of Hobbs *et al.*[5]. If the depression of PC T_g in the melt blend arises from copolymer formation, then a similar depression should occur in the solution-cast blend. However, neither Hanrahan *et al.*[4] nor Hobbs *et al.*[5] observe such a depression in solvent-cast blends. Alternatively, if the T_g shift is due to partial mixing of the phases in the melt and subsequent segregation of PC and PBT during solvent casting, then the T_g should be significantly depressed for the melt blend alone, as observed by Hobbs *et al.* The presence of PC between PBT lamellae in the blend[5,7] supports the view that partial miscibility in the melt leads to the presence of a small amount of PC in the predominantly PBT phase and that this PC is rejected from the growing PBT lamellae as crystallization occurs during cooling from the melt.

Regarding phase morphology Hobbs *et al.*[5] conclude, on the basis of transmission electron microscopy with appropriate staining techniques, that PBT forms the continuous phase in all the melt blends they examined. Furthermore, they state that an interpenetrating network is formed at PC compositions above 40%. Although figures 4 and 5 of Hobbs *et al.*[5] do show continuity of the PBT phase for blends 1 and 3, we contend that figure 6 shows continuity of the PC phase in blend 4 despite their statement to the contrary. Further information on this point is provided by a similar study of Delimoy *et al.*[7] in which figures 3 to 5 confirm the authors' statement that PC is the continuous phase in blends with more than 60% PC, and that PBT is the continuous phase for compositions below that limit. Both groups of authors refer to an interpenetrating network of the two phases in the region of the 56%/44% PC/PBT composition of commercial Xenoy materials and of the 5/4 PC/PBT blend of interest here, but provide no detail regarding the nature of the interpenetration.

D.c. resistance measurements form an integral part of our experimental procedure and can provide information on the nature of the interpenetration of the two phases for a blend of our composition. The conductivity of PBT is 4–5 orders of magnitude greater than that of either polycarbonate or the blend. This observation is explained

by a morphology involving the polycarbonate-rich phase in the form of a continuous matrix through which are scattered domains of the phase consisting predominantly of PBT. The observations is not consistent with the existence of a continuous PBT phase.

Miscibility and morphology of the two homopolymers in PC/PBT blends is greatly affected by thermal history[1,3,7] and the method of sample preparation. As noted above, the use of melt-processed as against solution-cast blends leads to conflicting conclusions regarding phase miscibility. Annealing also plays an important role in determining morphology. Wahrmund *et al.*[1] observed substantially different behaviour in annealed and unannealed samples. Whereas d.s.c. of PC/PBT melt blends revealed substantial lowering of PC T_g, Rheovibron measurements with annealed samples showed no difference between PC and the blends. More recently, in a d.s.c./d.m.t.a. investigation of melt-processed dry blends of Lexan 145 PC and Valox 315 PBT subjected to annealing at 160°C, Cherry[16] observed much less lowering of PC T_g. For the 60%/40% PC/PBT blend, d.s.c. showed a fall in PC T_g from 148°C to 142°C, whilst d.m.t.a. showed a fall in PC T_g from 150°C to 144°C and an increase in PBT T_g from 55°C to 67°C. Both T_g shifts are significantly different from those reported in the present work for unannealed samples prepared from the same batch of material.

CONCLUSIONS

Contour maps of real relative permittivity and loss tangent within the range -190°C to $+185$°C and 0.1 Hz to 3 MHz have been presented for an unannealed 5/4 melt blend of commercial polycarbonate and PBT. The dispersions due to secondary relaxation processes in polycarbonate and PBT are fully merged in the blend to produce a broad β-dispersion. Other dispersion regions in the blend are attributed to MWS polarizations and to the α-relaxation processes of the individual homo-polymers. The depression of the PC T_g in the blend and the slight increase in the PBT T_g indicate partial phase miscibility. Evidence is also provided for a two-phase morphology in which PBT-rich domains are distributed throughout a continuous phase consisting primarily of polycarbonate.

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