Polycarbonate–poly(methyl methacrylate) blends: the role of molecular interactions on miscibility and antiplasticization

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(Received 20 July 1990; revised 4 October 1990; accepted 12 October 1990)

Polycarbonate (PC) and poly(methyl methacrylate) are miscible; the β-relaxation characteristic for PC is strongly reduced in these blends. Based on calorimetric, dielectric, and dynamic mechanical studies, X-ray investigations, volume fluctuations and a computer-aided molecular modelling investigation we conclude that specific interactions exist between the phenyl rings and the ester group in such blends. We also conclude that these interactions contribute to miscibility and that they are the origin of the β-suppression effect.

(Keywords: polycarbonate; poly(methyl methacrylate); blends; miscibility)

INTRODUCTION

This paper is concerned with the effect of mutual molecular interactions on miscibility as well as on dynamic mechanical and dielectric properties in binary blends of polycarbonate (PC) and poly(methyl methacrylate) (PMMA). The two polymers have recently been found to be compatible at all concentrations, contrary to previous reports in the literature, and to display a lower critical solution temperature (LCST) behaviour[1–3]. Such a behaviour is frequently indicative of the presence of specific interactions between selected groups of both blend components. Our infra-red spectroscopic investigations failed to provide any evidence for such interactions.

The strong secondary relaxation, the β-relaxation, which is displayed by PC at temperatures well below room temperature is strongly suppressed in blends containing PMMA; this might be interpreted in terms of the formation of specific interactions. However, as demonstrated by Fischer *et al.*[4], a β-suppression effect may also originate solely from a reduction of the free volume fluctuations due to additives in blends as compared to the corresponding fluctuations in pure PC.

It seemed important to investigate the origin of the miscibility of the two polymer species, to look for the occurrence of specific molecular interactions, and to consider their effect on the dynamic mechanical and dielectric properties of the blends. The methods of analysis employed included—in addition to thermodynamic studies, dynamic mechanical and dielectric investigations—molecular modelling calculations on the occurrence of specific interactions and small angle X-ray studies on volume fluctuations.

EXPERIMENTAL

Polymers

Two kinds of commercial grade bisphenol A PC (Bayer AG, Leverkusen) and three different kinds of PMMA (Röhm GmbH, Darmstadt) were used. The polymers differed mainly in their molecular weights and thus in their glass transition temperatures (*Table 1*). Studies using different molecular weights were chosen because of discrepancies in the literature concerning the critical temperatures of such blends[1–3].

Sample preparation

Single-phase blends with various concentration ratios were prepared in two different ways. In method 1 both polymers were dissolved at a 2 wt% level in tetrahydrofuran (THF). Films were then cast on glass slides which were heated to temperatures above 50°C. This yielded transparent films with a thickness of up to 20 μm. In method 2 we prepared single-phase blends using the technique of precipitation. A 2 wt% solution of the polymers was sprayed into the non-solvent methanol. The precipitate was dried for 3 days under vacuum and afterwards the powder was pressed slightly above the glass transition temperature (T_g) to obtain single-phase sheets.

Two-phase blends were obtained either by film casting at room temperature or by mixing both polymers in the melt (method 3). All samples were dried for a couple of days at 80°C prior to the investigations.

Methods

Differential scanning calorimetry was carried out using a DSC-4 (Perkin–Elmer) equipped with a thermal analysis data station. The heating rate employed was

Table 1 Characteristics of the samples used for PMMA/PC blends

Sample	M_n	M_w	T_g (°C)
PC I	9 000	20 000	145
PC II	22 900	51 000	153
PMMA I	13 000	26 000	112
PMMA II	25 800	50 000	114
PMMA III	29 000	72 000	115

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0032-3861/91/071155-05

15 K min^{-1}. All samples were heated initially to 170°C to provide an equal thermal history. The data used from the PC/PMMA blends were obtained on the second heating run.

The phase diagrams of the PC/PMMA blends were obtained by using quantitative turbidity measurements, where a beam of light impinged on the heated samples and the intensity of the transmitted light was measured with a photosensitive detector.

A Kratky compact small angle X-ray camera equipped with a one-dimensional position-sensitive counter was used to determine the magnitude of volume fluctuations. This technique of using small angle X-ray scattering (SAXS) to monitor thermal fluctuations has been described previously[4–6]. The studies were performed on a film prepared from a homogeneous blend of PMMA and PC (film 1) and on two parallel films of pure PMMA and PC (film 2) having the same overall thickness and composition as film 1.

The dynamic–mechanical properties were investigated by the means of a dynamic mechanical thermal analyser (Polymer Lab. Inc.). All samples were measured in the tensile mode using a heating rate of 0.75 K min^{-1} and frequencies from 0.1 to 30 Hz. Dielectrical measurements were performed in the range 10–10^3 Hz using a capacitance bridge (General Radio).

Molecular modelling[7,8]

The aim of the computer simulations was to find out whether preferred interactions occur in the blends between specific sites along the PC and PMMA backbones or side groups. We used the program INSIGHT (Biosym Technologies) to construct the molecules and we employed the programs MOPAC (QCPE) and DISCOVER (Biosym Technologies) for the calculations of minimized configurations and the mutual interaction between the two polymers. The calculations were carried out using a Silicon Graphics IRIS 4D/70GT work station.

RESULTS AND DISCUSSION

Phase behaviour

We undertook this study because of the discrepancies in the literature with respect to the compatibility and phase behaviour of PC/PMMA blends, and the distribution of the components on a segmental scale and because of the strong dependence of the phase morphology on the modes of sample preparation. We investigated the phase behaviour of PC/PMMA blends and used them for the following studies.

The d.s.c. curves of the PC/PMMA blends exhibited either one or two glass transitions depending on the method of preparation (*Figure 1*). The T_g values of the single-phase blends, prepared by methods 1 and 2 vary continuously between those of the pure components. The two-phase mixtures, prepared by method 3, on the other hand, exhibit two glass transitions which were nearly independent of the overall composition. It is apparent however, that the T_g of PC is lowered to some extent compared to that of the homopolymer. This can probably be attributed to a slight partial mixing of the two components during melt blending.

The phase diagrams of three PC/PMMA blends with different molecular weights were obtained by measuring cloud point temperatures (*Figure 2*). A LCST behaviour is obvious. The phase separation temperatures shown in *Figure 2* represent the first slight deviation from the constant intensity of the transmitted light beam. They were verified by means of small angle light scattering measurements[9]. These results clearly show that the polymers studied and prepared by methods 1 and 2 are mixed on a molecular scale at lower temperatures.

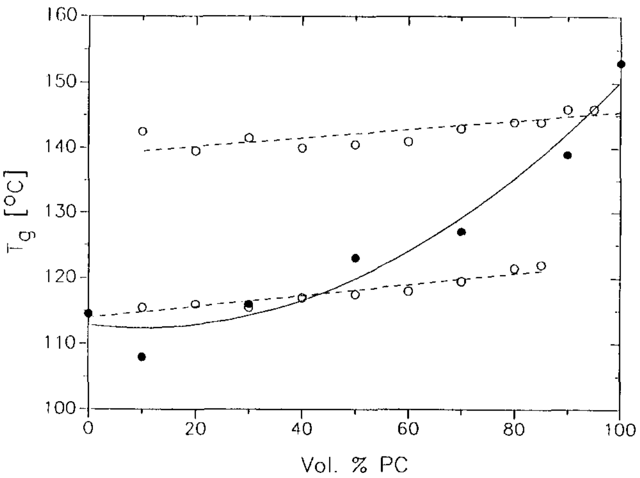

Figure 1 Glass transition temperatures as a function of the composition for single-phase (●) and two-phase (○) mixtures of PC and PMMA, taken as the midpoint of the heat capacity change

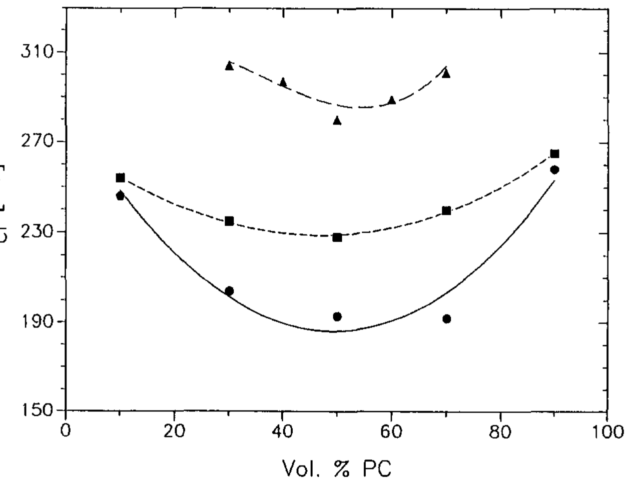

Figure 2 Phase diagrams of three different PC/PMMA blends: ▲, PC I-PMMA I; ■, PC I-PMMA II; ●, PC II-PMMA III. The mixtures differ with respect to the molecular weights of PMMA and PC (see *Table 1*). T_{cl} corresponds to the temperature at which turbidity occurs on heating

The experimental finding is that the critical temperature varies strongly as a function of the molecular weight. The critical temperature increases with decreasing molecular weight, predominantly due to entropic effects as expected from theory[10,11].

Deviations exist however, in our data and other published data on the location of the critical temperature of polymers with similar molecular weights. It is important to point out that in our case all samples were heated using a constant heating rate of 5 K min^{-1}. That means the equilibrium phase separation temperatures will be located below the ones shown in *Figure 2*. This is in agreement with the fact that because of the slowness of the phase separation, distinct variations in intensity of the transmitted light show up in turbidity studies only at substantially higher temperatures. This may explain why Kyu and Saldanha[2,3] found using a comparable molecular weight to one of our mixtures higher phase separation temperatures. Substantially lower heating rates or even isothermal measurements, which would allow more accurate determination of the phase diagram, fail because of the modest thermal stability of PMMA.

Dynamic mechanical and dielectric properties

To investigate the effect of miscibility on the properties of the PC/PMMA blends, we carried out dynamic mechanical and dielectric measurements on homogeneous and phase-separated blends (*Figures 3* and *4*). In *Figures 3* and *4* the temperature-dependent loss tangent of both single and two-phase mixtures is presented. The frequency used is 1 Hz (dynamic mechanical) and 1 kHz (dielectric), respectively. These two diagrams show the influence of miscibility on the properties of the single-phase blends: (1) as expected, only one glass transition peak can be observed. This indicates that both polymers are intimately mixed; (2) the β-relaxation of the PC, which can be clearly observed in the two-phase mixtures at about −80°C, is nearly completely suppressed in the case of the single-phase blends. No such effect occurs for the β-relaxation of PMMA at about 25°C.

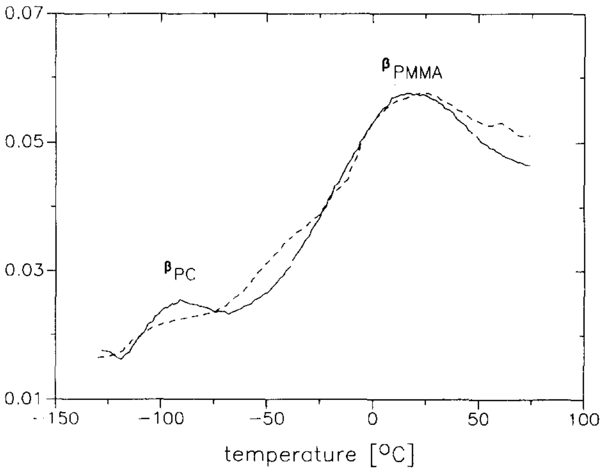

Figure 3 Temperature dependence of the dynamic mechanical loss tangent of 50/50 blends of PC II and PMMA III. Both (---) single phase and (———) two-phase blends were measured at a frequency of 1 Hz. Note the assignment of the β-peaks

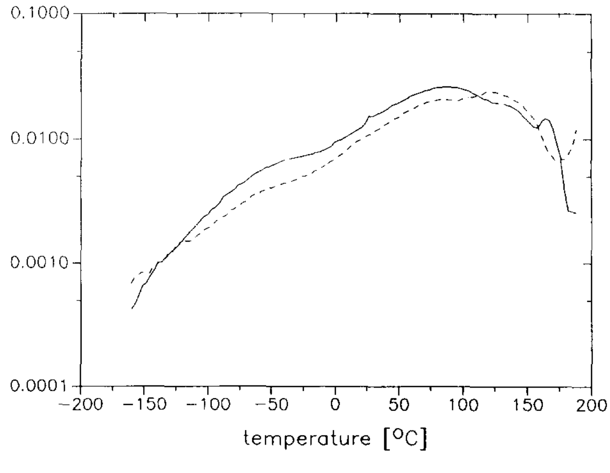

Figure 4 Temperature dependence of the dielectric loss tangent of 50/50 blends of PC II and PMMA III at 1 kHz. Symbols as in *Figure 3*

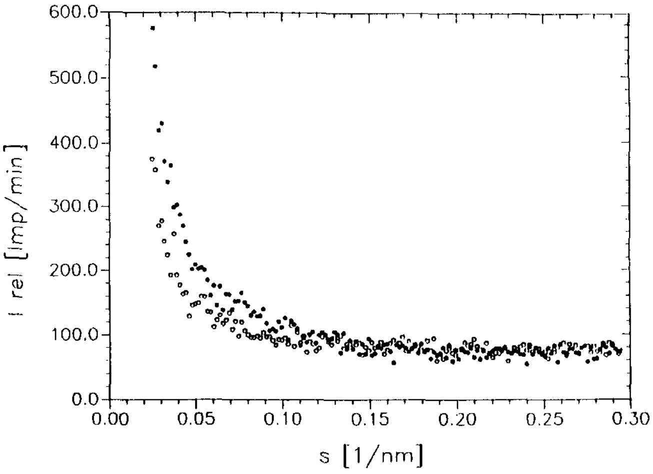

Figure 5 Small angle X-ray scattering curves of 50/50 blends of PC II and PMMA III as a function of the absolute value of the scattering vector. ●, Results for a homogeneous mixture; ○, scattering curve for a stack of parallel films of the pure homopolymers

These findings are in agreement with results reported in the literature[12].

Studies on volume fluctuations

The 'β-suppression' or 'antiplasticizer' effect reported above for PC is a well known effect for mixtures of polymers with low-molecular additives. It has frequently been attributed to the occurrence of specific interactions between polymers and additives[13]. Fischer *et al.*[4] demonstrated that such effects may also originate from a strong depression of thermal density fluctuations induced by additives.

In order to discriminate between the two cases we performed SAXS studies on the homogeneous blends and on film stacks composed of pure films of PMMA and PC at room temperature. The results are shown in *Figure 5*.

It is obvious that the two scattering curves agree closely. It is known that the small angle scattering is controlled in blends by density and concentration fluctuations. However, the scattering contrast between the two homopolymers is negligible, because the electron densities are very close to each other. It is expected that due to the closeness of the critical temperature and the T_g the concentration fluctuations have decayed in the range of the scattering vector values considered here. We therefore conclude:

1. that the mean square value of the volume fluctuations is not depressed in the case of a single-phase mixture of PC and PMMA;
2. that it seems reasonable to assume that specific interactions exist between PC and PMMA leading to miscibility and the β-suppression effect;
3. that such specific interactions might involve the phenyl rings of PC since their motion controls the β-relaxation.

It is however, important to obtain additional evidence for such conclusions. In the following the results from molecular modelling studies on mutual interactions occurring in PC/PMMA blends are discussed.

MOLECULAR MODELLING STUDIES ON SPECIFIC INTERACTIONS

The procedure used in the computer simulations and the results obtained are limited in accuracy; they provide guide lines only. In addition, so far there is no well tested route for analysing specific interactions in blends[14]. Keeping this in mind, we proceeded using several stages.

In a first approach we considered monomer units of both polymers and determined their minimum-energy configurations using the MNDO technique[7,8]. Simultaneously the net charges and the electron densities of all atoms were calculated. The graphic representation of the electron density distribution about both molecules (*Figure 6*) suggests that preferred interactions might occur between the carbonyl group of the PMMA and the phenyl rings of the PC, based on the concept of interactions happening via surface contacts. From the display of the grids, which represent a surface of equal electron densities, it is apparent that the particular spatial variation of the surface of the PMMA, which is caused by the carbonyl oxygen, can be matched with the corresponding variation due to phenyl rings of the PC where some 'electronic deficiency' seems to exist.

The next step in our analysis was to estimate the interactions between the monomer units of PC and PMMA. We selected one molecular group of each kind and placed them in a large number of different mutual positions. After minimizing in each case the energy of the whole system we found several favourable configurations, although of different strength. The most favourable configuration is depicted in *Figure 7*.

This configuration is characterized by the fact that the side group of the PMMA lies perpendicular to the plane, defined by the two phenyl rings of PC, the carbonyl oxygen pointing towards the phenyl rings. The total intermolecular energy depends on the distance between the molecules as depicted in *Figure 8*. A distinct minimum of the interaction energy occurs at a well defined equilibrium distance of about 3.1 Å. This spacing represents the average value of the distance between the carbonyl oxygen and the two nearest carbon atoms of each phenyl ring.

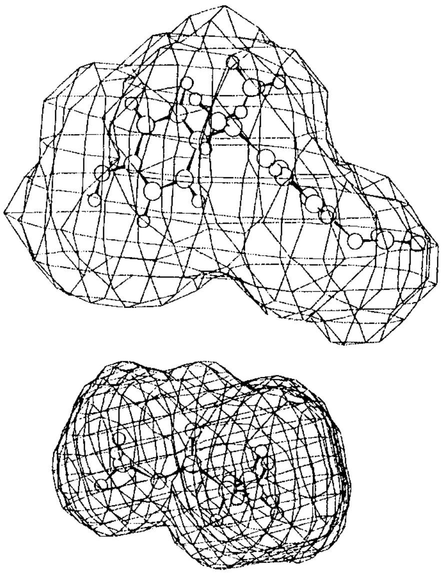

Figure 6 Minimum energy configurations of the monomer units of PC and PMMA, respectively. The grids around the molecules represent planes of equal electron densities

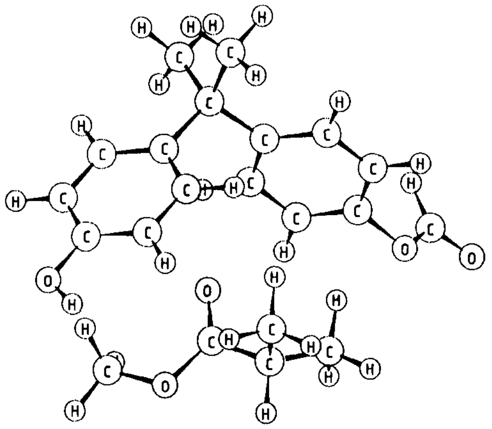

Figure 7 Most favourable conformation of the monomer units of PC and PMMA possessing the largest mutual interaction energy

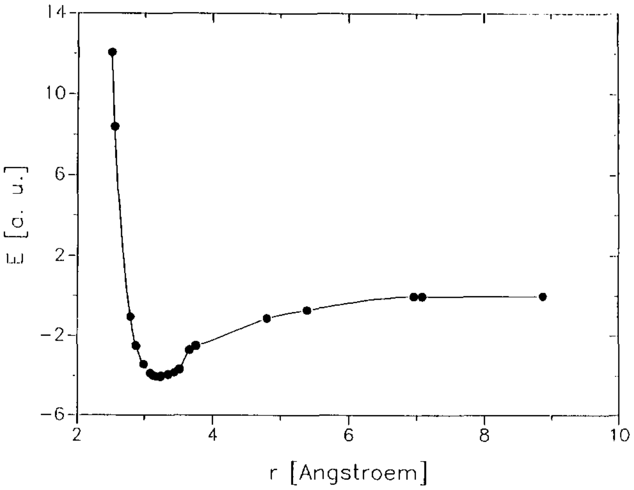

Figure 8 Dependence of the interaction energy, *E*, on the distance, *r*, between the two monomer units of PC and PMMA

Based on these results we performed energy minimization calculations for longer chains, taking the following route: we constructed chains, which contained 10 monomer units and in each case we placed four of them randomly in a large volume. The ratio was 2 PC:2 PMMA chains or 1:3 chains, respectively. Subsequently we calculated the molecular motions in a force field under the influence of temperature. Time steps of 1 fs were used and the 'temperature' was 900 K. This very high temperature provided enough energy for the motions of the chains to avoid local energy minima. This ensured that the system was able to approach its absolute minimum after sufficient time. All calculations were made without periodic boundary conditions, which increases the credibility of our results. The result was that the system approached in each case the same final configuration: one PMMA chain and one PC chain formed a complex, the other chains drifted away. We therefore tentatively conclude that the mutual 'complexation' of a PMMA and a PC chain is energetically a more desirable condition than the 'complexation' between like chains.

The calculations described allowed us to derive also some tentative conclusions with respect to site–site interactions and their molecular origin. The intermolecular interactions between both polymer chains are composed of a coulombic part and a van der Waals part.

The calculations clearly show that the latter, which is controlled by the difference between a repulsion and an attractive dispersion term, dominates.

To locate the favoured sites of the attraction between the two polymers, we built a large number of test molecules from well defined residues, for example carbonyl groups or methyl groups. The conclusion was that approximately 80–85% of the whole intermolecular interaction energy as well as the van der Waals interaction energy can be considered as being localized at the phenyl rings of PC, the preferred partner being mainly the carbonyl group of PMMA. An extended analysis of our data leads to the finding that the interaction between the carbonyl group of PMMA and the phenyl rings of PC is in most cases not only restricted to one ring but occurs with similar magnitude to both rings.

This interaction may be responsible for the miscibility of the two polymers and it is tempting to speculate that this weak but clearly localized interaction is responsible for the suppression of the β-relaxation of PC. The closeness of the phenyl and carbonyl groups and the occurrence of energetically preferred configurations may restrict the probability for ring flips to occur in the same way as for reduced free volume fluctuations in PC additive systems[4].

However, at least one question remains: why is the β-relaxation of the PMMA unaffected by the interaction of the polymers? This situation has also been observed in PMMA-additive mixtures and it has been attributed to the fact that the β-relaxation in PMMA is related to local motions of individual side groups, i.e. the rearrangement volume needed for the relaxation process is very small. This is in contrast to the case of PC where the β-relaxation is related to local modes requiring much larger rearrangement volumes and much stronger coupling to the environment[4].

In conclusion, it seems that weak specific interactions occur in PC/PMMA blends causing miscibility and also a β-suppression effect.

ACKNOWLEDGEMENT

We gratefully acknowledge the financial support of the BMFT (Bundesministerium für Forschung und Technologie) via the Arbeitsgemeinschaft Industrieller Forschungseinrichtungen (AIF).

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