

Single-Phase Blends of Polycarbonate and Poly(Phenyl Methacrylate)

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SYNOPSIS

Miscibility studies on blends of polycarbonate (PC) and poly(phenyl methacrylate) (PPMA) were undertaken by means of differential scanning calorimetry (DSC), dynamic mechanical, and dielectric relaxation methods. PC and PPMA were mixed by dissolving in tetrahydrofuran (THF) and subsequently coprecipitated in methanol. DSC studies showed a single glass transition (T_g) that shifts systematically with composition. These T_g s are reproducible in repeated DSC heating cycles, suggesting true miscibility of the pair. The dry PC and PPMA pellets were melt mixed in a Mini-Max Mixer/Molder. The extrudates were compression molded. These melt-mixed PC/PPMA blends exhibited glass-like transparency and also showed a single T_g in the DSC scans. The true miscibility of PC and PPMA was further confirmed by dynamic mechanical and dielectric relaxation methods. The net birefringence has been reduced substantially because of the opposite sign of the intrinsic birefringence of PC and PPMA molecules. At the 12/88 PC/PPMA, the birefringence remains zero at all draw ratios, indicating the achievement of birefringence-free polymer alloys.

INTRODUCTION

In pursuit of polymeric optical materials, we have been involved in the miscibility studies in blends of polycarbonate (PC) and various poly(methyl methacrylates) (PMMA).¹⁻⁴ PC and PMMA derivatives are customarily used in optical disk, write-once or erasable memory disk, video disk, optical fiber, and waveguide. The criteria for such optical materials include low birefringence, low moisture absorption, dimensional and thermal stability, high glass transition temperature (T_g), good processability, and glass-like transparency. It is very difficult for a homopolymer to meet all requirements because of such stringent criteria. For instance, PC is a tough material with outstanding optical clarity, good thermal and dimensional stability, high T_g , and good processability.⁵ However, due to the presence of aromatic groups in the main chain, the intrinsic birefringence of PC is very large, i.e., the principal polarizability along the main chain is very large rel-

ative to that in the transverse direction. Thus, a small level of residual stress or birefringence can result in optical distortion. Moreover, thermal stress cracking, poor scratch resistance, and moisture absorption are drawbacks of PC. On the other hand, PMMA shows outstanding transparency, low intrinsic birefringence, and good scratch resistance, but it is brittle and has low dimensional and thermal stability.⁵ Hence, it is natural to witness the growing interest in the blends of PC/PMMA and other blend systems for optical applications.⁶⁻⁸

As part of this effort, we continue our investigation on miscibility of bisphenol-A polycarbonate (PC) and polyphenyl methacrylate (PPMA) blends. Both PC and PPMA are known for their outstanding optical clarity. Moreover, their refractive indices are very close, i.e., 1.5860 for PC against 1.5706 for PPMA. PC is positively birefringent along the molecular axis, whereas PPMA is negatively birefringent as it has a larger polarizability in the transverse direction. If the two polymers were completely miscible, the positive and negative birefringence may be cancelled out, which would be ideal for fabricating birefringence-free polymer alloys.^{6,7}

Another attractive feature of this blend system

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is that PC and PPMA have vastly different mechanical properties. PC is a ductile plastic, whereas PPMA is a glassy brittle polymer.⁵ A truly miscible blend should give material properties intermediate between its components, i.e., the mechanical properties may range from brittle to ductile with varying compositions. In this article, the miscibility between PC and PPMA was investigated by means of differential scanning calorimetry (DSC), dynamic mechanical, and dielectric relaxation methods.

EXPERIMENTAL

Reagent grade bisphenol-A polycarbonate (PC, $M_w \sim 64,000$ and $M_w/M_n \sim 2.1$) and polyphenyl methacrylate (PPMA, $M_w \sim 114,000$) were purchased from the Scientific Polymer Products Co. Blend films were prepared by solution blending as well as by melt mixing. In the former, the two polymers were dissolved in tetrahydrofuran (THF) by stirring at ambient temperature. Then the ternary solution (2 wt % polymer concentration) was either coprecipitated in methanol or solvent casted in Petri dishes. The solvent-cast films generally exhibited glass-like transparency. In the latter case, dry PC pellets were melted at 250°C in a Mini-Max Mixer/Molder (Custom Scientific Co.) and stirred for 5 min, then PPMA pellets were added in various ratios and mixed for additional 5 min at a lower temperature of 220°C. The blend extrudates were then either injection molded in a cylindrical dumbbell shape for mechanical studies or compression molded in a disk shape for dielectric measurements. These blend specimens showed glass-like transparency.

DSC scans were carried out on a Dupont thermal analyzer (Model 9900) with a heating module (Model 910) under dry nitrogen circulation. The heating rate of 20°C/min was chosen arbitrarily.

Table I Film-Stretching Temperatures in Comparison with T_g of PC/PPMA Blends

Blend Composition	Stretching Temperature	DSC T_g
PC	147°C	150°C
90/10	145	147
50/50	131	134
30/70	130	132
12/88	127	127
10/90	125	125
PPMA	119	123

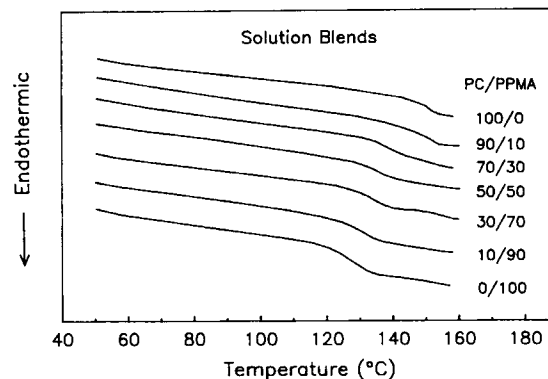


Figure 1 DSC thermograms of various blends of PC and PPMA prepared by solvent casting from THF solutions. The heating rate was 20°C/min.

An indium standard was used for temperature calibration. Dynamic mechanical studies were undertaken using a dynamic mechanical thermal analyzer (DMTA, Polymer Laboratories, Inc.) at a fixed frequency (1 Hz) and at a heating rate of 1°C/min. In dielectric relaxation studies, a dielectric thermal analyzer (DETA, Polymer Laboratories, Inc.) was employed at a frequency of 10 kHz and at a heating rate of 2.5°C/min. Disk-shaped blend specimens were coated with gold-palladium alloys by a sputter machine to ensure good electrical contact between the specimens and the condenser plates.

The blend films were cut into ribbon shapes and stretched for various draw ratios at temperatures slightly below their respective T_g s as shown in Table I. The drawn specimens were subsequently quenched to room temperature. Birefringence measurements were made at room temperature on a Leitz polarized microscope (Laborlux Pol 12) using a Berek compensator (Brace-Koehler, 1592 K).

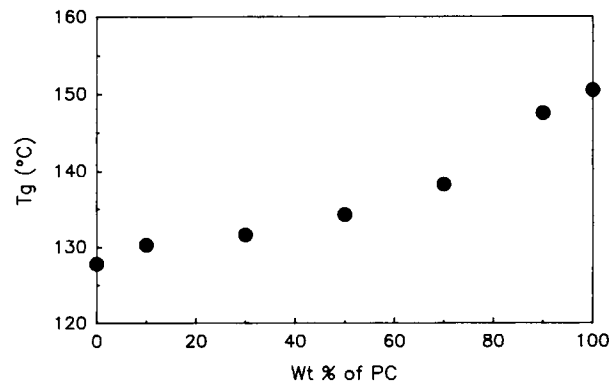


Figure 2 Variation of T_g s as a function of composition of PC/PPMA prepared by solution blending.

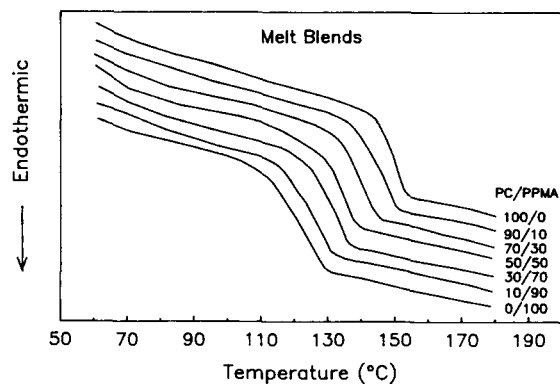


Figure 3 DSC traces of PC/PPMA prepared by melt mixing. The heating rate was 20°C/min.

RESULTS AND DISCUSSION

To assure molecular level mixing, solvent-mixed specimens were used in the DSC measurements. Figure 1 depicts the DSC traces for various PC/PPMA blends prepared by dissolving in a common solvent (THF), then coprecipitating in a nonsolvent (methanol). A single T_g appears in all blends that shifts systematically with composition, suggestive of miscible character. The midpoint of the DSC transition is taken as T_g and plotted against composition in Figure 2. These T_g s are reproducible in repeated DSC heating runs, implying the lack of thermally induced phase separation up to the ther-

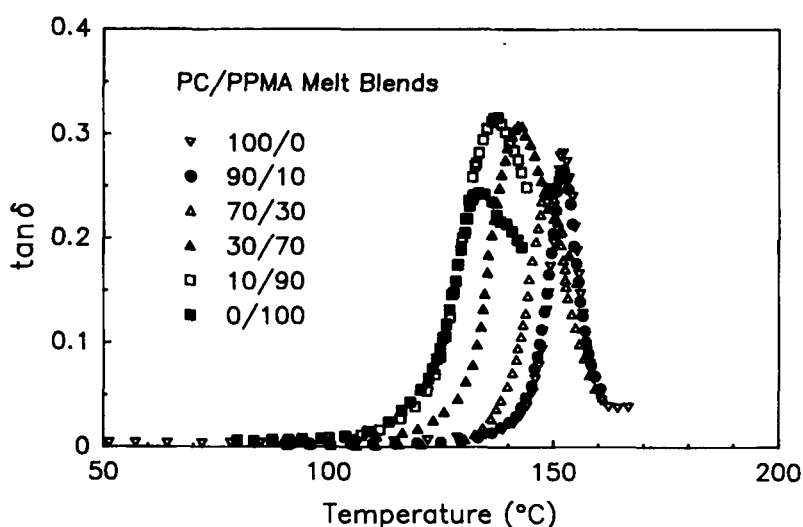


Figure 4 Temperature dependence of mechanical loss tangent at 1 Hz for melt-blended PC/PPMA. The heating rate was 1°C/min.

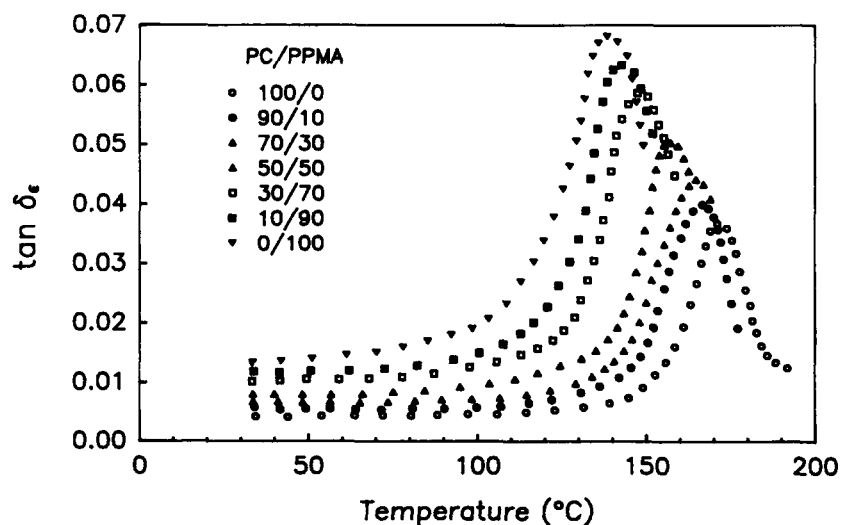


Figure 5 Temperature dependence of dielectric loss tangent at 10 kHz for melt-mixed PC/PPMA. The heating rate was 2.5°C/min.

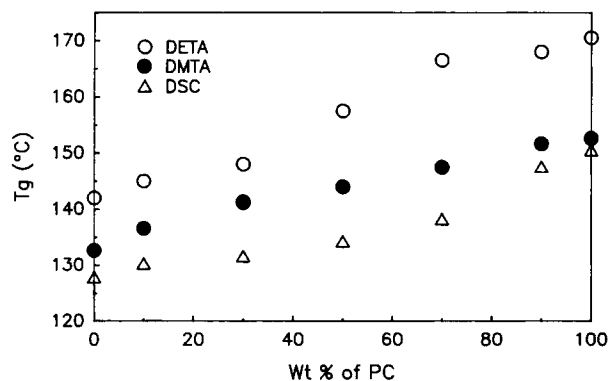


Figure 6 Comparison of T_g s vs. composition obtained by DSC, dynamic mechanical, and dielectric relaxation methods.

mal degradation temperature. This, in turn, suggests that it may be feasible to obtain a miscible blend by simply melt blending.

The melt-mixed PC/PPMA blends were prepared in a Mini-Max Mixer/Molder. The mixes exhibit glass-like transparency. Figure 3 shows the DSC scans of the melt-mixed PC/PPMA blends where a single T_g is evident for all intermediate compositions. These T_g s are reproducible despite repeated heatings, suggesting the true miscibility of the pairs.

A similar observation was also made in the dynamic mechanical studies of the melt-mixed PC/PPMA blends. Figure 4 shows the appearance of single loss tangent peaks corresponding to the T_g s of the respective blends. These loss peaks move to higher temperatures with increasing PC content, which is in good agreement with the above DSC results. This observation is further confirmed by the dielectric relaxation studies, which also show the movement of a single dielectric loss peak with composition (Fig. 5). Figure 6 illustrates the comparison of the T_g movement by the three independent tech-

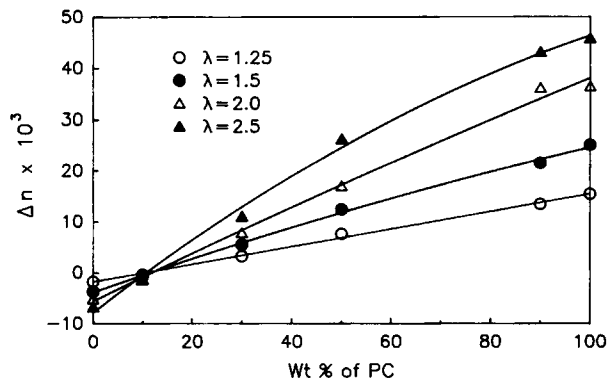


Figure 7 Change of birefringence as a function of elongation for various blend compositions.

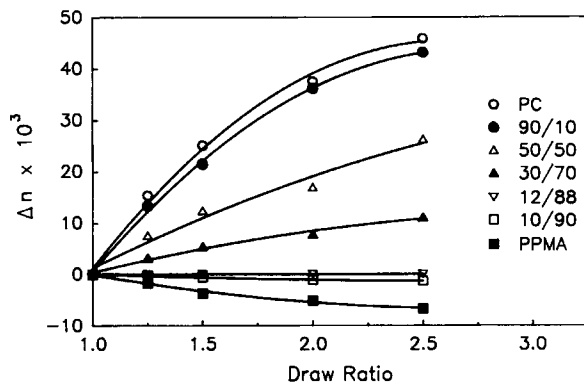


Figure 8 Variation of birefringence as a function of composition for various draw ratios.

niques. There are slight differences in the T_g values since the exact T_g positions depend on the techniques used and the experimental conditions. Nevertheless, all three experiments manifest the same trend and thus point to the fact that PC and PPMA are indeed truly miscible and melt processable.

The single-phase PC/PPMA blend is important not only for its scientific interest but also from a commercial point of view. As pointed out before, PC and PPMA have opposite signs of intrinsic birefringence (or principal polarizability) that may be cancelled out in their miscible states at the right combination. Some birefringence measurements were carried out for melt-mixed PC/PPMA as a function of draw ratio. The blend films were stretched at temperatures a few degree lower than their respective T_g s and then quenched to ambient temperature. As shown in Figure 7, the birefringence increases drastically with increasing draw ratio in the neat PC, whereas it decreases in the case of pure PPMA. As expected, the intermediate blend compositions show reduced birefringence. At the 10/90 PC/PPMA ratio, the birefringence is almost invariant regardless of elongation. The birefringence results were replotted as a function of composition in Figure 8. It is apparent that the 12 wt % PC gives zero birefringence for all draw ratios. Such blends, known as birefringence-free or zero birefringence plastic alloys,^{6,7} may have potential in compact disk applications.

CONCLUSIONS

We have demonstrated that solution- or melt-mixed blends of PC/PPMA are truly miscible. Because of the positive and negative intrinsic birefringence of PC and PPMA, their miscible blends reveal reduced

birefringence. A birefringence-free alloy was obtained at the 12/88 PC/PPMA ratio.

This article is dedicated to the late Mr. Wookap Cho, without whose contribution this work would not have been possible. It is hoped that this article preserves the fond memories he shared with his colleagues at the University of Akron. We thank Professor H. James Harwood of the Institute of Polymer Science, the University of Akron, for supplying some polyphenyl methacrylate samples. The support of the Edison Polymer Innovation Corporation (EPIC) and the NSF-ALCOM (Advanced Liquid Crystal Optical Materials) Center, DMR 8920147 are gratefully acknowledged.

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