Note

THERMOGRAVIMETRIC STUDY OF THE THERMAL STABILITY OF BISPHENOL-A POLYCARBONATE/POLY(METHYL METHACRYLATE) BLENDS

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ABSTRACT

The thermal stability. of bisphenol-A polycarbonate (PC)/poly(methyl methacrylate) (PMMA) blends was studied by thermogravimetry. The stability of a blend depends on the method of preparation and its composition. Blends containing 25 and 50% by weight of PC are less stable than predicted by the additivity rule, and immiscible blends show better stability than miscible blends. However, blends containing 75% by weight of PC are more stable than predicted by the additivity rule, and the miscible blend shows better stability than the immisicible blend.

INTRODUCTION

When two polymers are mixed, the resulting blend can be a homogeneous miscible blend or a phase-separated immiscible blend depending on the thermodynamics of polymer–polymer interaction [1–3]. Several recent papers discussed the effect of miscibility on the thermal stability of polymer blends. Goulet and Prud'homme [4] compared the thermal stability of a miscible poly(vinyl chloride) (PVC)/poly(ϵ-caprolactone) blend to that of an immiscible PVC/poly(ethylene adipate) blend. Eguiazabal and Iruin [5] compared the stability of a miscible poly(hydroxy ether of bisphenol-A) (phenoxy)/poly(butylene terephthalate) blend and an immiscible phenoxy/poly(ethylene terephthalate) blend. Moskala and Lee [6] studied the stability of a miscible PVC/ethylene-vinyl acetate copolymer (70% by wt. of vinyl acetate) blend and an immiscible PVC/poly(vinyl acetate) blend. In these studies, comparison was made between a miscible A/B blend and an immiscible A/C blend. However, the degradation product of one polymer in a blend can stabilize or destabilize the other polymer [7–12]. Thus the difference observed in the thermal stability of A/B and A/C blends may not be solely due to the miscibility of the blend.

In some cases, the miscibility of a blend depends on the method of preparation. One example is the bisphenol-A polycarbonate (PC)/poly

(methyl methacrylate) (PMMA) blend [13–15]. PC/PMMA blends prepared by solution casting and melt mixing are immiscible [13]. Blends prepared by precipitation from tetrahydrofuran (THF) solutions using *n*-heptane as non-solvent are miscible but those prepared by using methanol as non-solvent are immiscible [13]. Therefore, it is possible to compare the thermal stability of a miscible PC/PMMA blend to that of an immiscible PC/PMMA blend.

Recently, Rincon and McNeill [16] studied the thermal degradation of a 1:1 by weight blend of PC and PMMA by thermogravimetry and thermal volatilization analysis. They reported that the rate of degradation of PC in the blend was increased and the PMMA depolymerization was retarded. However, their study did not deal with the effect of the miscibility on the thermal degradation of the blend. In this communication, the thermogravimetric study of the thermal stability of miscible and immiscible PC/PMMA blends is reported.

EXPERIMENTAL

Materials

PMMA was obtained from Du Pont (Elvacite 2010) and PC was obtained from BDH Chemicals. The weight-average molecular weights of PMMA and PC are 120 000 and 22 000, respectively, as determined by intrinsic viscosity measurements. The polymers were purified by precipitation of their THF solutions with excess methanol.

Preparation of blends

Miscible blends
0.5 g of polymer mixture was dissolved in 25 cm³ of THF. The solution was then poured slowly into 250 cm³ of *n*-heptane with vigorous stirring. The precipitated polymer blend was then washed with *n*-heptane and dried in vacuo at 110°C for 72 h.

Immiscible blends
The method followed the same procedure as described above except that methanol was used as the non-solvent.

Thermogravimetric measurements

The TG curves of various samples in a nitrogen atmosphere were obtained using a Du Pont 9900 thermal analysis system fitted with a 951 thermogravimetric analyser. The sample size was 10 mg. The nitrogen flow rate was 75 cm³ min^{-1} and the heating rate was 20°C min^{-1}. Duplicate

runs were made for each sample to check the reproducibility of the TG curves.

RESULTS AND DISCUSSION

Figure 1 shows the TG curves of PC and PMMA. PMMA starts to lose weight at 280°C and leaves a negligible amount of residue by 430°C, while PC starts to lose weight at 400°C and leaves a substantial amount of residue (20%) at 700°C. The two polymers show only slight overlapping of their temperature regions of degradation.

The TG curves of various PC/PMMA blends are shown in Figs. 2–4. Also shown in the figures are the predicted TG curves based on linear additivity of the TG curves of unblended PC and PMMA.

The TG curve of an immiscible PC/PMMA (weight ratio 25/75) blend agrees fairly well with that of the predicted curve. However, a miscible blend of the same composition is less stable than the immiscible blend, particularly in the temperature range 400–550°C. Both miscible and immiscible PC/PMMA (50/50) blends show substantial destabilization in the temperature range 400–550°C as shown in Fig. 3. The miscible blend is also less stable than the immiscible blend. These results are consistent with the mechanism proposed by Rincon and McNeill [16] that PMMA macroradicals abstract hydrogen atoms from isopropyl groups of PC molecules, followed by chain scission of the resultant PC radicals, leading to destabilization of PC. In an immiscible blend, one polymer is dispersed as domains in another polymer matrix. Interactions between PMMA radicals and PC molecules have to occur at the phase boundary. On the other hand, PC and PMMA molecules
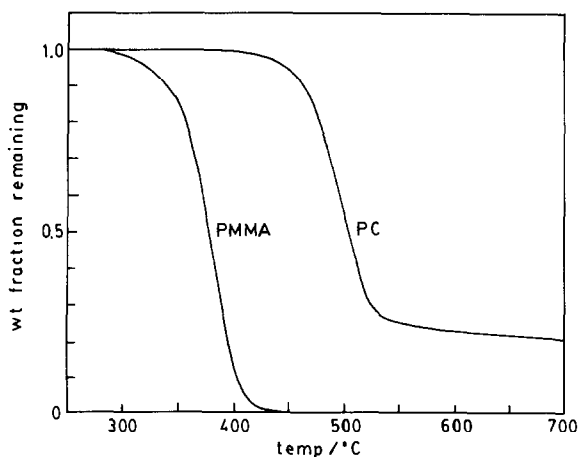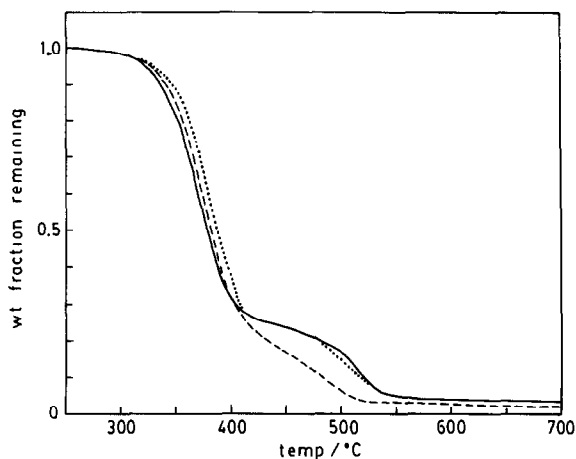

Fig. 1. TG curves of PC and PMMA.

Fig. 2. TG curves of PC/PMMA (25/75) blends: ————, immiscible blend; - - - - - -, miscible blend; · · · · · ·, predicted by additivity rule.

are in intimate contact with each other in a single-phase miscible blend such that hydrogen-abstraction readily occurs, causing the blend to lose weight more readily than an immiscible blend.

The stability of PC/PMMA (75/25) blends in which PC is the major component is very different from those blends with lower PC contents. As shown in Fig. 4, PC/PMMA (75/25) blends show better stability than that predicted by the additivity rule, and the miscible blend shows better stability than the immiscible blend. Both blends also produce more residue than expected. These results indicate that with increasing PC content, more crosslinking between PC radicals takes place resulting in less weight loss and
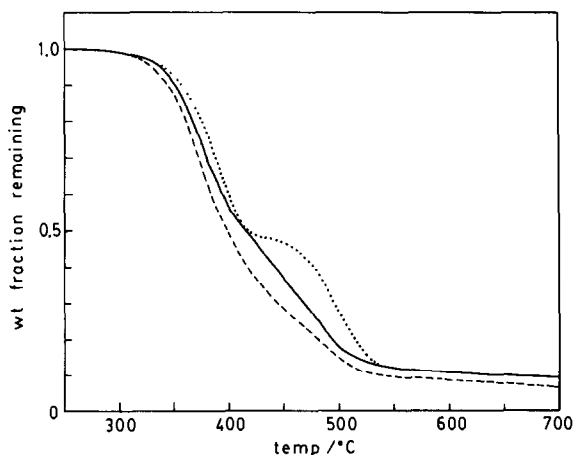

Fig. 3. TG curves of PC/PMMA (50/50) blends: ————, immiscible blend; - - - - - -, miscible blend; · · · · · ·, predicted by additivity rule.
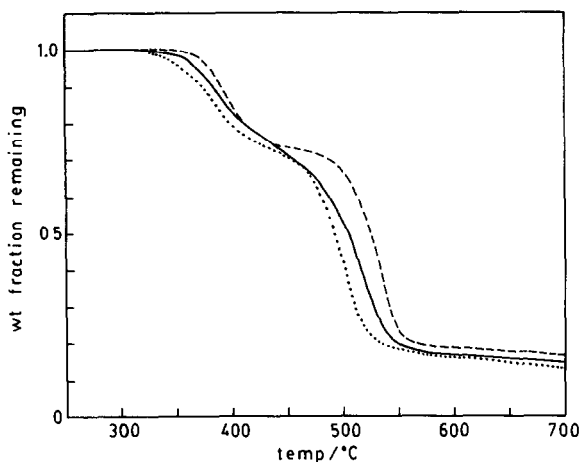
Fig. 4. TG curves of PC/PMMA (75/25) blends: ———, immiscible blend; - - - - - -, miscible blends; · · · · · ·, predicted by additivity rule.

more residue. It is noted that miscible PC/PMMA blends undergo phase separation at high temperature [13,15]. Thus the kinetics of phase separation might have some effect on the thermal stability of miscible blends. In summary, the thermal stability of PC/PMMA blends depends not only on the method of preparation but also on their compositions.

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