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CALORIMETRIC STUDY OF THE MISCIBILITY OF POLY(2,6-DIMETHYL-1,4-PHENYLENE OXIDE) WITH STYRENE–METHYL METHACRYLATE COPOLYMERS *

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ABSTRACT

The miscibility of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with styrene–methyl methacrylate (S–MMA) copolymers was studied by differential scanning calorimetry. An S–MMA copolymer with a low MMA content is miscible with PPO when the PPO content in the blend is 40% or more. An increase in the MMA content in an S–MMA copolymer narrows the composition range in which the blend is miscible. An S–MMA copolymer containing 29.2 wt.% MMA is immiscible with PPO over the entire composition range.

INTRODUCTION

The measurement of the glass transition temperature T_g of a polymer blend provides a simple means of ascertaining the miscibility of the blend [1,2]. Provided that the T_g values for the two component polymers differ by at least 20 K, a miscible blend shows a composition-dependent value of T_g which is intermediate between the T_g values for the component polymers, while an immiscible blend shows two unperturbed T_g values for the component polymers.

The poly(2,6-dimethyl-1,4-phenylene oxide)/poly(styrene) (PPO/PS) blend is a well-known example of miscible polymer blends [3–9]. A modification in the chemical structure of either polymer can change the miscibility behaviour of the blend. Karasz, MacKnight and co-workers [10–15] have made extensive studies on the miscibility of PPO with various styrene–halogenated styrene copolymers. The ability of the halogen substituent to induce immiscibility in the PPO/PS blend was found to be in the order *o*-Br > *p*-F > *p*-Br > *o*-Cl ≈ *p*-Cl > *o*-F.

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We have earlier reported the miscibility of PPO with styrene–2,2,6,6-tetramethylpiperidinyl methacrylate (S–TPMA) copolymers [16]. The incorporation of TPMA drastically reduced the miscibility of the PPO/PS blend. In the studies of the miscibility of blends containing homologous polymethacrylates [17–20], the miscibility of a polymethacrylate with other polymers has been found to decrease with increasing size of the pendant alkyl group. As the pendant group in TPMA is a bulky sterically hindered amine group, it will be of interest to study if the incorporation of methyl methacrylate, the first member of the methacrylates, will produce a less drastic effect on the miscibility of a PPO/PS blend.

EXPERIMENTAL

Materials

The PPO was obtained from General Electric; its weight-average molecular weight ($\overline{M}_w$) was 40700. Poly(methyl methacrylate) (PMMA) was obtained from Du Pont (Elvacite 2010); its $\overline{M}_w$ was 120000.

Five styrene–methyl methacrylate (S–MMA) copolymers were prepared by bulk polymerization at 333 K for 24 h using azobisisobutyronitrile (0.3 wt.%) as initiator. The copolymers were purified by precipitation from 2-butanone solutions by methanol. The compositions of the copolymers as determined by ^{1}H-NMR based on the phenyl protons of styrene, together with their T_g and intrinsic viscosity $[\eta]$ values are given in Table 1.

Preparation of blends

The blends were prepared by solution casting from tetrahydrofuran (THF). 0.5 g of polymer mixture was dissolved in 25 cm^3 of THF. The solution was poured into an aluminium dish and the solvent was allowed to evaporate slowly at room temperature. The blend was then dried in a vacuum oven at 383 K for 48 h.

TABLE 1

Characteristics of S–MMA copolymers

Copolymer	Wt.% MMA	T_g(K)	$[\eta]$ [a] (dl g^{-1})
S–MMA4	3.9	373	0.57
S–MMA12	11.6	373	0.33
S–MMA17	16.5	373	0.38
S–MMA29	29.2	374	0.54
S–MMA55	55.0	374	0.55

[a] In 2-butanone at 303 K.

Calorimetric measurements

A Perkin–Elmer DSC-4 differential scanning calorimeter was used to measure the T_g values of various samples. Each sample was scanned several times between 323 and 523 K using a heating rate of 20 K min^{-1} and a cooling rate of 320 K min^{-1}. The initial onset of the slope in the DSC curve was taken as T_g. The reported T_g value is the average value based on the second and subsequent runs.

RESULTS AND DISCUSSION

The DSC curves of various PPO/S–MMA4 blends are shown in Fig. 1. For a blend containing 40, 50, 75 or 90 wt.% PPO, each showed a single glass transition, indicating its single-phase nature. The glass transitions of these blends are broader than those of PPO and S–MMA4. The glass transition width is about 10 K for either PPO or S–MMA4, but it is 30–40 K for a miscible PPO/S–MMA4 blend. Such a broadening in the glass transition of a miscible blend has been observed for blends of PPO with polystyrene and other styrenic polymers [10,12,21,22]. The reason for the glass transition broadening is uncertain, and it has been attributed to changes in relaxation time, glass structure and degree of interaction or to composition fluctuation [22,23]. As shown in Fig. 1, a PPO/S–MMA4 blend containing 25% PPO showed two broad glass transitions, indicating its two-phase nature. Thus the copolymerization of a small amount of MMA with styrene does affect the miscibility behaviour of a PPO/PS blend.

The results for PPO/S–MMA12 blends are similar to those for

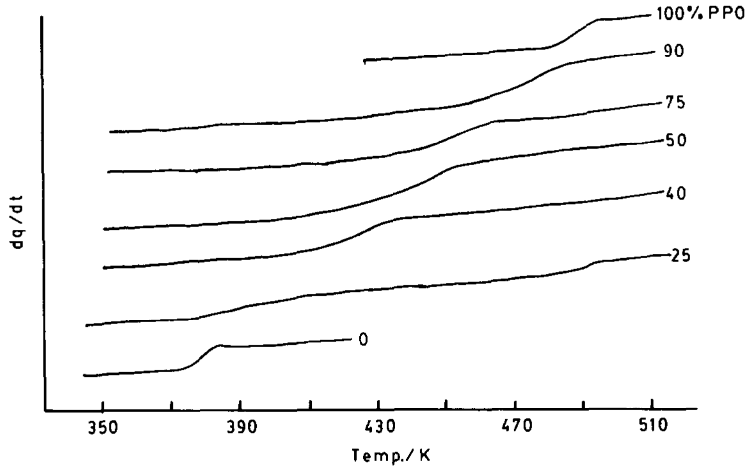

Fig. 1. DSC curves of PPO/S–MMA4 blends.

TABLE 2

T_g values of various blends

Wt.% PPO in blend	T_g (K) [b]					
	PPO/ S-MMA4	PPO/ S-MMA12	PPO/ S-MMA17	PPO/ S-MMA29	PPO/ S-MMA55	PPO/ PMMA
0	373	373	373	374	374	373
25	379, 473	375, 478	375, 478	374, 476	374, 471	373, 471
40	403	415	375, 448	— [a]	— [a]	— [a]
50	421	425	374, 449	374, 470	374, 473	373, 474
75	438	440	444	375, 467	374, 473	373, 471
90	451	457	— [a]	— [a]	— [a]	— [a]

[a] Blends of these compositions were not prepared.

[b] T_g of PPO, 483 K.

PPO/S-MMA4 blends. The T_g values of these blends are given in Table 2. Blends containing 40% or more of PPO are miscible, while a blend containing 25% PPO is immiscible.

The DSC curves of various PPO/S-MMA17 blends are shown in Fig. 2. A blend containing 75% PPO showed a broad glass transition. For a blend containing 25, 40 or 50% PPO, two glass transitions were observed. The lower T_g values are in good agreement with that of S-MMA17. However, the upper glass transition for a blend containing 40 or 50% PPO is quite broad and the T_g value is about 35 K lower than that of PPO which indicates the presence of a substantial amount of S-MMA17 in the PPO-rich phase. However, the upper glass transition of a PPO/S-MMA17 blend containing 25% PPO is narrower and the T_g value is close to the T_g value of

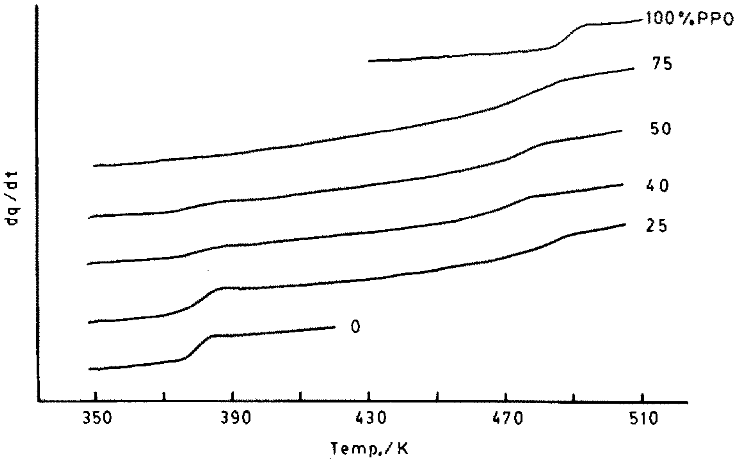

Fig. 2. DSC curves of PPO/S-MMA17 blends.

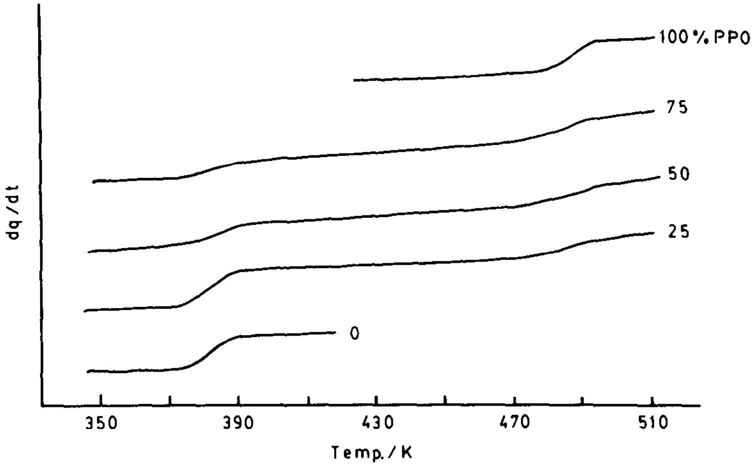

Fig. 3. DSC curves of PPO/S–MMA29 blends.

PPO. Thus the phase separation in this blend is more complete compared with that in a similar blend containing a higher proportion of PPO.

The DSC curves of various PPO/S–MMA29 blends are shown in Fig. 3. Two glass transitions were observed for a blend containing 25, 50 or 75% PPO. Thus, an S–MMA copolymer containing 29% MMA is immiscible with PPO at all compositions. A further increase in the MMA content in the S–MMA copolymer is then expected to lead to the formation of immiscible PPO/S–MMA blends. This is confirmed by the immiscibility of PPO/S–MMA55 blends as shown in Table 2. Table 2 also shows the T_g values for PPO/PMMA blends which indicate the immiscibility of these blends. The immiscibility of PPO/PMMA blends has been reported earlier [24].

The miscibility behaviour of PPO with S–MMA copolymer is similar to that with S–TPMA copolymer as reported earlier. A copolymer with a low TPMA or MMA content is miscible with PPO if the weight percentage of PPO in the blend is 40% or more. An increase in the TPMA or MMA content in the copolymer narrows the composition range in which the blend is miscible. However, a closer look at the results shows that the miscibility of S–MMA copolymer with PPO is slightly better than that of S–TPMA copolymer when comparison is made with a copolymer of similar molar composition. For example, a PPO/S–MMA12 (12.0 mol.% MMA) blend containing 40% PPO is miscible, while a PPO/S–TPMA18 (8.9 mol.% TPMA) blend of the same composition is immiscible [16].

The formation of a miscible blend requires some specific interactions between the component polymers. The miscibility of PPO/PS blends has been attributed to dispersive interaction between the phenyl groups of the two polymers [8]. The incorporation of TPMA or MMA therefore interferes with the dispersive interaction, leading to a reduction in the miscibility.

Lastly, a recent patent [25] covers the applications of blends of S–MMA copolymers containing less than 15% of MMA with PPO. Such blends offer good heat and chemical resistance as well as good mechanical properties.

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