Miscible blends between polyacetal and a styrene–vinyl phenol copolymer

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Blends containing polyacetal and a random styrene–vinyl phenol copolymer consisting of 35 mol% vinyl phenol segments were prepared by melt mixing and found to exhibit miscibility within the amorphous phase. The blends exhibited a single, composition-dependent glass transition temperature as determined by dynamic mechanical measurements. Thermal analysis revealed a significant depression of the melting point and, in certain cases, a lowering of the degree of crystallinity of the polyacetal phase upon blending with the styrene–vinyl phenol copolymer.

(Keywords: blends; copolymer; miscibility)

Introduction

In an earlier paper, we reported that polyacetal (PAc), or polyoxymethylene, is miscible in the amorphous phase with poly(vinyl phenol) (PVP)[1]. Calorimetry-of-mixing studies performed on model compounds and analysis of melting point depression in the polymer blends indicated that the interaction driving miscibility was very strong, yielding a negative χ parameter on the order of unity[1,2]. Applying our model compound calorimetry results quantitatively with a binary interaction model, we predicted that a random styrene–vinyl phenol (S-VP) copolymer containing as little as 10% VP segments could exhibit miscibility with PAc.

The phase behaviour of blends between homopolymers and copolymers has been well studied both experimentally and theoretically. In the cases where interactions are relatively weak and all components are amorphous, the binary interaction model, or modifications thereof, has been very successful at describing the phase behaviour of blends providing that the segmental interaction parameters are known[3–6]. However, fewer studies have been performed on homopolymer/copolymer blend systems in which strong specific interactions are present or when crystallizable components are involved. Hydrogen bonding is known to strongly drive miscibility in certain homopolymer/copolymer systems. For example, S-VP copolymers having as little as 2% VP in the copolymer were found to be miscible with poly(methyl methacrylate)[7,8].

The present paper considers melt-blended mixtures of a semicrystalline polymer, PAc, with a copolymer whose minority repeat unit, VP, is capable of strongly interacting with the first polymer. The majority repeat unit, S, is non-interacting. Evidence for miscibility will be presented and the results are rationalized in terms of hydrogen bonding interactions.

Experimental

The materials used in this study are described in *Table 1*. The PAc is an injection moulding grade copolymer (Celcon M-90) obtained from Hoechst Celanese. ^{13}C nuclear magnetic resonance (n.m.r.) revealed its ethylene oxide content to be 2–3%. The S-VP copolymer was also obtained from Hoechst Celanese. ^{1}H and ^{13}C n.m.r. verified that its composition was 35 mol% VP (37 wt% VP).

The blends were prepared by melt compounding of pre-dried powder blends using a laboratory scale 15 mm Baker-Perkins co-rotating twin-screw extruder. A barrel temperature of 240°C and screw rotation speed of 300 rev min^{-1} were maintained throughout. Compounded blends were compression moulded at a temperature of 230°C.

Dynamic mechanical testing was performed using a Polymer Laboratories DMTA operating in the single cantilever beam mode at a frequency of 10 Hz and a heating rate of 3°C min^{-1}. Differential scanning calorimetry (d.s.c.) was performed using a Seiko RTC 220 using heating and cooling rates of 20°C min^{-1}.

Results and discussion

The dynamic mechanical spectrum of the pure PAc constituent is shown in *Figure 1*. As discussed in an earlier paper, we associate the relatively weak β transition of PAc at -6°C with the glass transition of the amorphous phase[1]. The pure S-VP copolymer was too brittle for dynamic mechanical analysis. However, d.s.c. analysis clearly showed that the amorphous copolymer exhibits a glass transition at 125°C.

The dynamic mechanical spectra of two PAc/S-VP blends are shown in *Figure 2*. *Figure 2a* shows a blend containing 20% S-VP copolymer which exhibits a peak in the loss tangent centred around 88°C. *Figure 2b* shows a blend containing 40% S-VP copolymer which exhibits a single peak at 109°C. The association of these peaks with the glass transition of the amorphous phase of the blend follows from the observation that they increase in magnitude and approach the glass transition temperature (T_g) of pure S-VP as the copolymer content increases. Furthermore, the magnitude of the drop in storage modulus which is associated with this transition increases as the amount of copolymer in the blend increases.

Figure 3 plots the T_gs of the PAc/S-VP blends *versus* blend composition and compares these results to data reported previously for PAc blends with PVP homopolymer[1]. The plots are similar with the exception that

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Table 1 Materials used

Designation	Material	Composition	M_n[a]	M_w[a]	T_g (°C)	T_m (°C)
PAc	Polyacetal (Celcon M-90)	2–3% oxyethylene	–	–	−6	170
S-VP	Styrene–vinyl phenol copolymer	35 mol% VP	37200	80900	125	–

[a] Gel permeation chromatography in *N*-methyl-2-pyrrolidone expressed relative to polystyrene standards

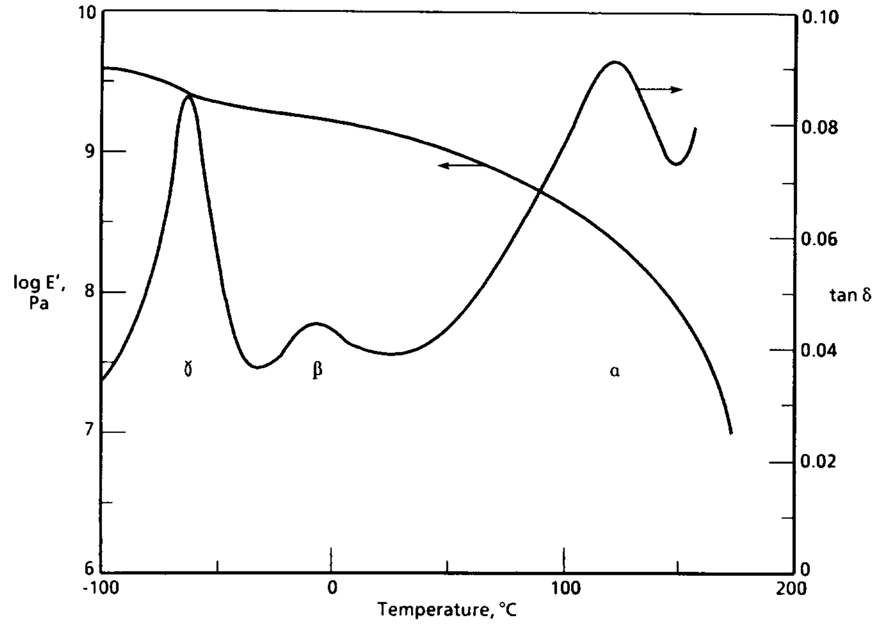

Figure 1 Dynamic mechanical storage modulus, E', and loss tangent, tan δ, as a function of temperature at a frequency of 10 Hz for the unblended PAc constituent

Table 2 Thermal analysis results

Sample	T_m (°C)	ΔH_m (J g^{-1})	T_c (°C)	ΔH_c (J g^{-1})	Crystallinity[a] (%)
PAc	169.6	171.8	141.3	144.7	53
80/20 PAc/S-VP	166.3	138.6	139.7	123.9	53
60/40 PAc/S-VP	162.8	96.0	123.1	73.8	49
40/60 PAc/S-VP	154.1	52.4	72.8	23.2	40

[a] Normalized with respect to PAc content of blend

the T_g values for the copolymer-containing blends are slightly lower than those of the homopolymer-containing blends to a degree that is consistent with the lower T_g of the copolymer compared to that of the VP homopolymer. Thus, we conclude that both blend systems are miscible in the amorphous phase.

Differential scanning calorimetry was performed on the blends in order to examine the effect that the added copolymer exerts on the melting behaviour of the crystalline PAc phase. In a previous paper, we showed that the melting point of PAc was depressed by blending with PVP homopolymer. The results for the present blend system, PAc/S-VP, are summarized in *Table 2*. *Figure 4* demonstrates that, as the copolymer content of the blend increases, both the melting point (upon heating) and the temperature of crystallization (upon cooling) are significantly depressed. This result is consistent with miscibility in the melt state.

The approximate crystallinity of the present blends was calculated based upon the measured enthalpies of melting, the blend compositions, and the reported heat of fusion of polyoxymethylene crystals (326 J g^{-1})[9]. The crystallinity of the PAc component is given in *Table 2*. The crystallinity of the PAc component of the blend was less than that of the neat PAc control only when S-VP was the major component of the blend.

The observation of intermediate T_gs and melting point depression relative to the pure blend constituents clearly indicates miscibility in the present system. PVP homopolymer was previously shown to be miscible and strongly interactive with PAc, whereas polystyrene homopolymer is immiscible with PAc. We propose that miscibility in the present blends is driven to a lesser extent by the so-called 'copolymer effect' (the repulsive interactions between S and VP segments within the copolymer), and to a greater extent by strong hydrogen bonding interactions between phenol moieties in S-VP and ether units in PAc.

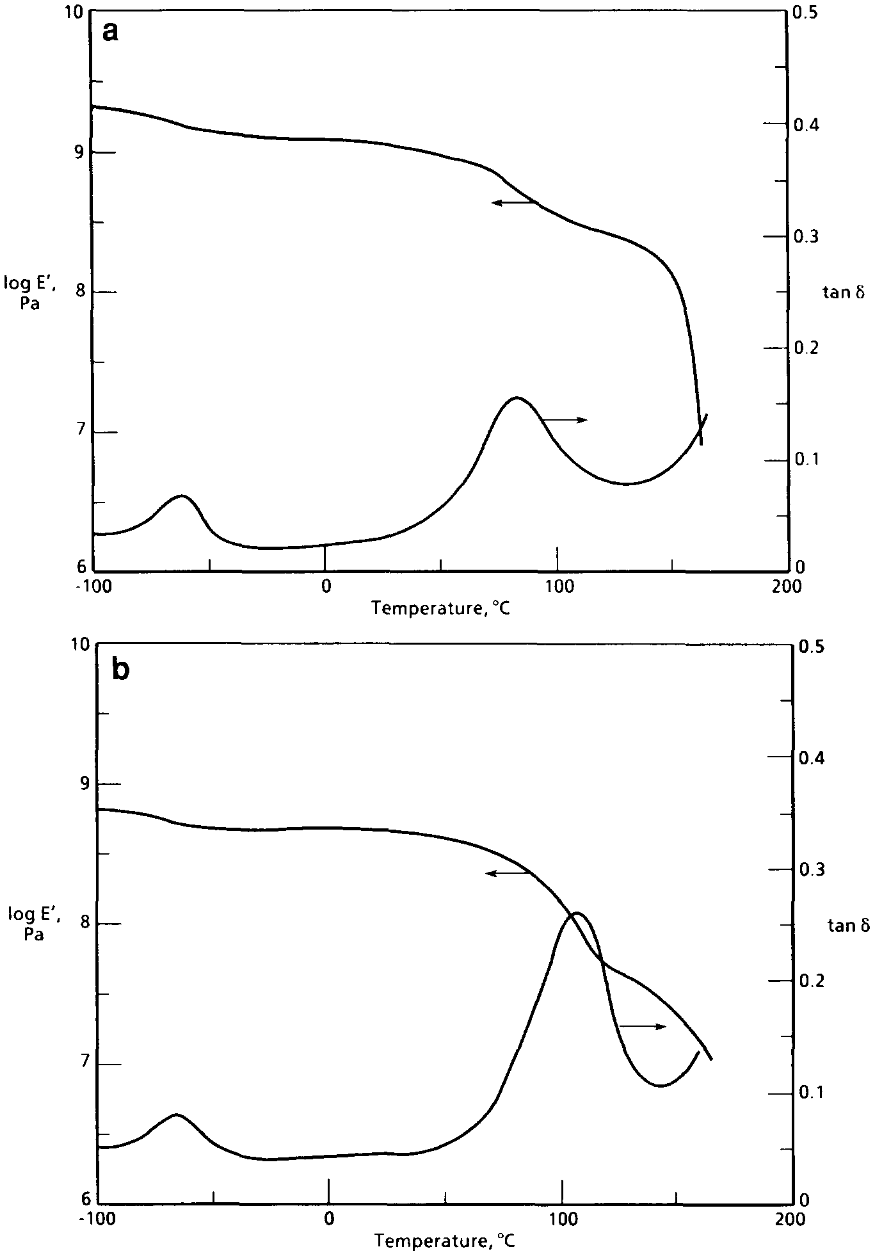

Figure 2 Dynamic mechanical storage modulus, E', and loss tangent, tan δ, *versus* temperature at 10 Hz frequency for: (a) an 80/20 PAc/S-VP blend; (b) a 60/40 PAc/S-VP blend

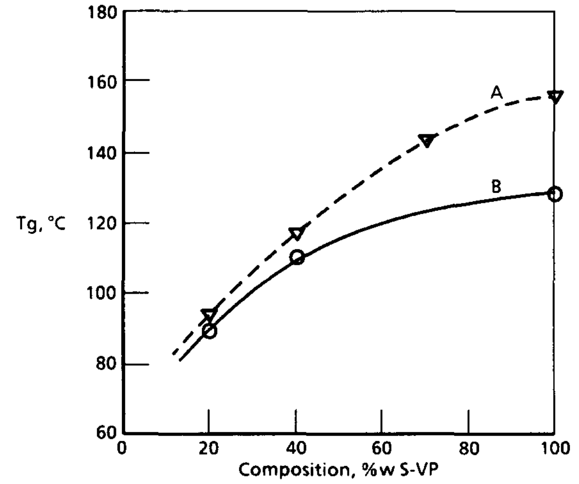

Figure 3 Glass transition temperature, T_g, as a function of blend composition for: (A) PAc/PVP homopolymer blends; (B) PAc/S-VP copolymer blends

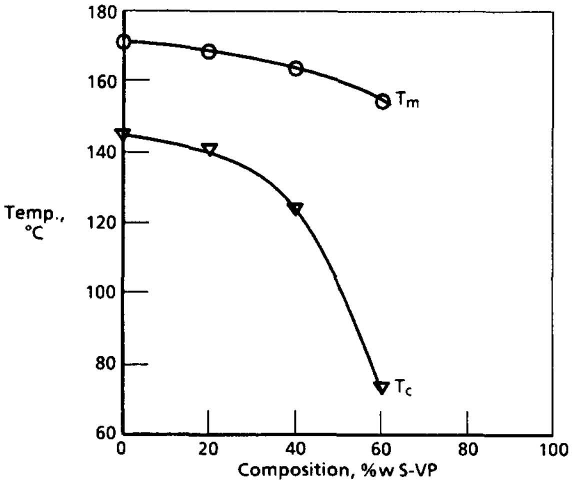

Figure 4 Melting temperature upon heating, T_m, and crystallization temperature upon cooling at constant rate, T_c, as a function of blend composition for PAc/S-VP blends

Conclusions

Blends containing a commercial grade PAc and a S-VP copolymer containing 35 mol% VP segments were prepared by melt compounding. Miscibility in the blends was evidenced by a single glass transition at temperatures which were dependent upon composition and intermediate between those of the pure blend constituents. Thermal analysis revealed crystallinity in the blends. A significant depression of the melting point of the crystalline component as the amorphous copolymer content increased provided further indication of miscibility.

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