Filler effects on the compatibility and phase separation kinetics of poly(vinyl acetate)–poly(methyl methacrylate) mixtures

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(*Received 5 September 1989; revised 12 March 1990; accepted 11 December 1990*)

The filler effects on the compatibility and phase separation kinetics of poly(vinyl acetate) (PVA)–poly(methyl methacrylate) (PMMA) mixtures were studied. Cloud-point curves for filled and unfilled PVA–PMMA mixtures were plotted. It was shown that this system exhibited lower critical solution temperature behaviour. The phase separation of filled mixtures occurs at lower temperatures than that of unfilled mixtures. The temperatures of phase separation of mixtures with predominant PVA or PMMA contents exhibit an especially sharp decline. The results of the studies on the kinetics of phase separation show that the phase separation rate of filled mixtures is much lower than that of unfilled mixtures at temperatures equidistant from the corresponding cloud-point curves. It is established that the phase separation of mixtures occurs in two stages. This can be associated with the structure rearrangement of the phases formed during phase separation. The differences in phase separation of filled and unfilled mixtures can be explained by the specific interactions between a filler and one of the components of a binary polymer mixture.

(Keywords: compatibility; phase diagrams; filler; critical solution temperature; selective adsorption; poly(vinyl acetate); poly(methyl methacrylate)

INTRODUCTION

Hitherto effects of mineral fillers on the thermodynamic compatibility of binary polymer mixtures have mainly been evaluated by changes in the Flory–Huggins thermodynamic interaction parameters[1–4] χ_{12} or the excess free energy of mixing[5,6] ΔG_m^E determined from the data on equilibrium sorption of solvent vapours[7]. The samples were prepared from melts[1–3] or from solutions in a common solvent[4,5]. As shown by several workers[8–15], the phase behaviour of polymer mixtures is strongly dependent on the method of preparation. This was not taken into account by some investigators and resulted in incorrect conclusions on the compatibility of a number of polymer pairs[12,14,15]. Thus, if the mixtures are prepared from melts at temperatures higher than phase separation temperatures [e.g. systems exhibiting lower critical solution temperature (*LCST*) behaviour[12,14,15]], the system on cooling cannot return to thermodynamic equilibrium because of its high viscosity and will be heterogeneous. If the mixture is prepared from solution in a common solvent, even a compatible pair becomes two-phase during evaporation of the solvent because of a '$\Delta\chi$ effect'[8,12,14,15]. In both cases the parameters χ_{12} or ΔG_m^E will be positive, and the system will be considered to be incompatible. In the latter case one can falsely judge the type of critical solution temperature by the variation in the χ_{12} or ΔG_m^E *versus* temperature curve[16]. Therefore it is necessary to plot phase diagrams to evaluate the compatibility reliably and also evaluate the effect of filler on the compatibility. We first compared the phase diagrams for filled and unfilled mixtures of two polymers using a polystyrene–polycarbonate mixture[13].

In the present work, we studied effects of mineral filler on phase separation for another polymer pair, a poly(vinyl acetate) (PVA)–poly(methyl methacrylate) (PMMA) mixture to which silane-treated and untreated aerosols were added. We first evaluated the effect of filler on the kinetics of phase separation of this system.

EXPERIMENTAL

PVA ($M_\eta = 1.4 \times 10^5$)–PMMA ($M_\eta = 1.1 \times 10^5$) mixtures were prepared. An aerosil with $S_{sp} = 175\ m^2\ g^{-1}$ (A-175) and the same aerosil modified with dimethyldichlorosilane were used as fillers. Cloud-point curves were obtained by a light scattering technique[17]. Test samples were prepared by dipping glass plates in chloroform solutions of polymer mixtures and by removing the solvent at room temperature by a standard procedure[17]. The fillers were added to the polymer solutions, and after mixing for 10 h to achieve equilibrium adsorption[18], films were prepared by the same procedure. In order to prevent oxidation of the polymer films at high temperatures, they were placed between two glass plates to obtain a sandwich arrangement. The procedure for determining cloud points was similar to that described previously[17]. Since the temperature of phase separation can be dependent on the film thickness[17], this was estimated first (*Figure 1*). As seen in *Figure 1*, the phase separation temperature depends on the film thickness. In this study it was not our aim to explore this phenomenon. However Reich and Cohen[17] have investigated this effect and proposed two possible explanations: first, the selective adsorption of one of the components of the

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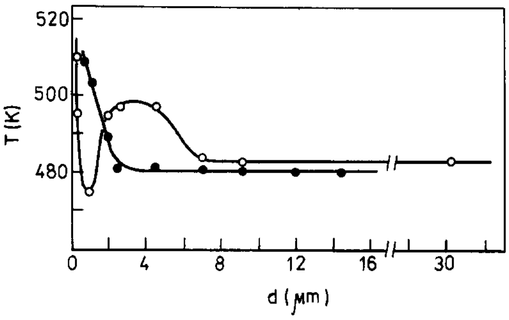

Figure 1 Phase separation temperature as a function of film thickness for the mixtures PVA:PMMA = 0.6:0.4 (○) and PVA:PMMA = 0.8:0.2 (●)

polymer blend (in our case PVA[18]) at the glass surface led to variations in compositions in the bulk region of the film. The temperature of phase separation must then correspond to this new composition, since the adsorbed layer near the wall is relatively immobile; second, the electrostatic effect of a charged surface inducing an electric field in the thin film, destabilizes the mixture. This is a reasonable explanation for the occurrence of a minimum in the curve in *Figure 1*, but not for the subsequent increase of phase separation temperature with decrease in film thickness. In our study, the film thicknesses were chosen in such a way that the phase separation temperature did not depend on this parameter. Films of corresponding thicknesses were prepared by varying solution concentrations. The cloud points were determined at a heating rate of 1.3 K min^{-1} and plotted as an average of three to four parallel determinations.

RESULTS AND DISCUSSION

PVA–PMMA films prepared from solution and dried at room temperature were transparent but on heating they became cloudy due to phase separation (*Figure 2*). As can be seen from *Figure 2*, light scattering intensity *versus* temperature curves possess at least two breaks and the temperatures of cloud points determined from the first break (T_1) for A-175-filled mixtures are much lower than for unfilled mixtures. Similar breaks were also observed for unfilled mixtures[17], but were not interpreted. Recently computer simulation of phase separation has demonstrated[19] that the process is accompanied by structural rearrangement of separated phases which should correspond to several breaks in light scattering intensity *versus* temperature (or time) curves. The two stages of phase separation of the binary mixtures polycarbonate–PMMA characterized by the formation of microclusters and their further coalescence were observed experimentally[20]. It is quite possible that in our case phase separation also takes place in several stages, both for filled and unfilled mixtures. In the first stage (between T_1 and T_2) the phase separation follows a spinodal mechanism[21] but in the second stage (up to T_2) phase separation follows a nucleation mechanism[22]. In the case of filled mixtures the temperatures T_1 and T_2 and $\Delta T = T_2 - T_1$ were greater than for unfilled mixtures (*Figure 2*), and the rate of phase separation in the former lower than in the latter case. One of the causes for this must be the limited mobility of macromolecules at the polymer–filler interface.

Figure 3 shows cloud point curves for unfilled and 10 wt% A-175-filled PVA–PMMA mixtures. The cloud points for filled mixtures were determined from both the first (T_1 in *Figure 2*) and second (T_2 in *Figure 2*) breaks. It is seen that both curves for filled mixtures are at much lower temperatures than those for unfilled ones. It should be noted that the temperature of phase separation decreases sharply in the regions with a predominant PVA or PMMA content. The addition of silane-treated aerosil to the mixture also results in lower temperatures of phase separation (curve E in *Figure 3*). As in the previous case, light scattering intensity *versus* temperature curves also possess two breaks (curve C in *Figure 2*) but the temperatures of phase separation decrease to a lesser extent than in the case of unmodified aerosil. Lower temperatures of phase separation of a binary polymer mixture on the addition of a filler may be explained in the following way. Studies on the behaviour of

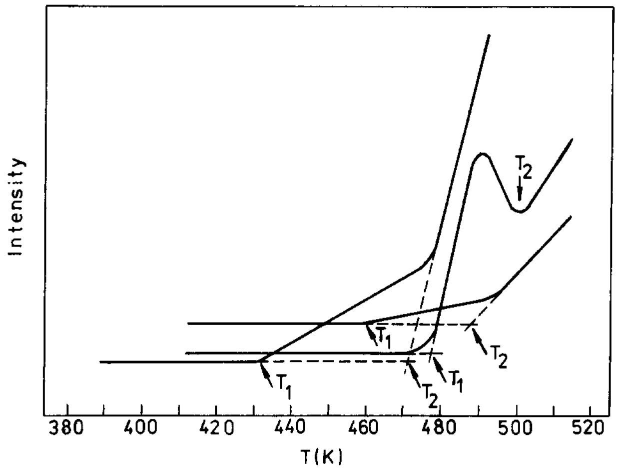

Figure 2 Light scattering intensity as a function of temperature for the mixtures PVA:PMMA = 0.6:0.4 without filler (A) and with 10 wt% A-175 (B) and PVA:PMMA = 0.8:0.2 with 10 wt% silane-treated A-175 (C)

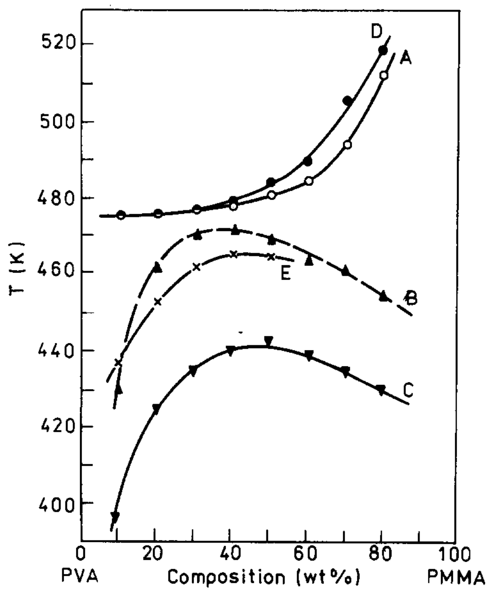

Figure 3 Cloud point curves for the mixture PVA:PMMA without filler (A), with 10 wt% A-175 (B, C), after A-175 removal (D), with 10 wt% silane-treated A-175 (E). C, E, From the first break in *Figure 2*; B, from the second break in *Figure 2*

PVA–PMMA mixtures absorbed from a chloroform solution on the aerosil surface have shown[18] that PVA displaces PMMA adsorbed on the filler surface. Thus, during the preparation of our samples, PVA will predominantly be adsorbed on the aerosil surface. If a filled PVA–PMMA mixture is treated as 'ternary', one may expect a noticeable change in phase separation temperatures due to the difference in pair interactions[22–25]. A possible mechanism for filler effects on phase separation is proposed elsewhere[26]. We demonstrated the effect of asymmetry of interactions on the phase separation temperatures experimentally using a ternary PVA–PMMA–poly(ethylene glycol) (PEG) mixture[27]. In particular, it was established that a higher asymmetry of pair interactions (a greater difference in the thermodynamic interaction parameters χ_{12} of PEG–PVA and PEG–PMMA with a higher PEG content in the mixture) led to a lower phase separation temperature and changed the shape of the phase diagram. The modification of aerosil surface with silane, probably decreases the asymmetry of interactions in the system, since a large difference in the pair interactions of silane-treated A-175–PVA and silane-treated A-175–PMMA cannot be expected. Lower asymmetry of interactions should result in a smaller effect of a filler on the phase separation temperature which is also observed experimentally (curve E, *Figure 3*). It should be noted that the phase separation temperature also decreases with increase in aerosil content in the mixture (*Figure 4*). This fact may be interpreted as indirect confirmation of the 'ternary' blend model, because the variation of the composition (in our case the increasing aerosil content) should affect the asymmetry of the interactions and therefore have an effect on the temperature of phase separation.

At present it is assumed that during the adsorption of polymers from solution, the high molecular weight polymer fraction leaves for the adsorbent surface[28]. The high molecular weight fractions are also supposed to leave the adsorbent surface in the case of solutions of polymer mixtures. As can be seen in *Figure 3* (curve D), the phase separation temperatures of PVA–PMMA mixtures prepared from solutions which were centrifuged after adsorption to remove aerosil with adsorbed polymers (predominantly PVA) were higher than those of unfilled mixtures. Higher phase separation temperatures are observed for mixtures with a predominant PMMA content. If in this case high molecular weight fractions, for example, PVA, had predominantly been adsorbed on the aerosil, the reduction in phase separation temperatures would have been observed for all the compositions, with this reduction being more pronounced for the mixtures with a predominant PVA content. (Points in *Figure 3* correspond to the initial ratio of components.) The fact that the shift in phase separation temperatures is observed only in the region with a predominant PMMA content indicates that this shift is determined only by the change in the mixture composition due to selective PVA adsorption (by a shift along the abscissa, curve D can overlap curve A for an unfilled mixture).

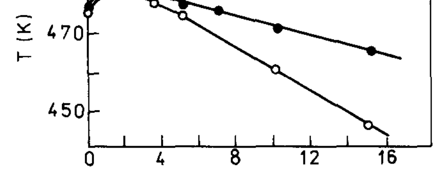

Figure 4 Phase separation temperature as a function of concentration for the mixtures PVA:PMMA = 0.8:0.2 (○) and PVA:PMMA = 0.6:0.4 (●)

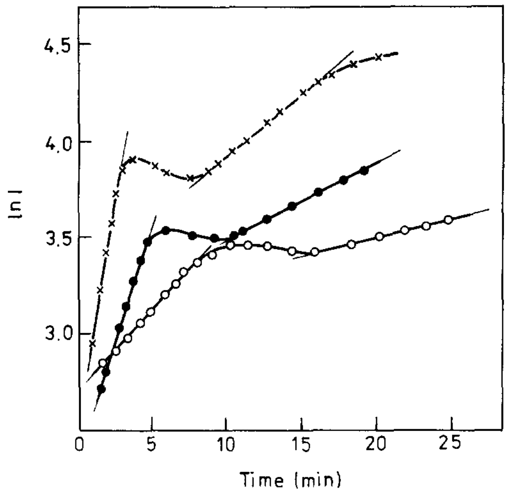

Figure 5 Kinetics of light scattering intensity variations for the mixture PVA:PMMA = 0.6:0.4 at 486 (○), 491 (●) and 498 K (×)

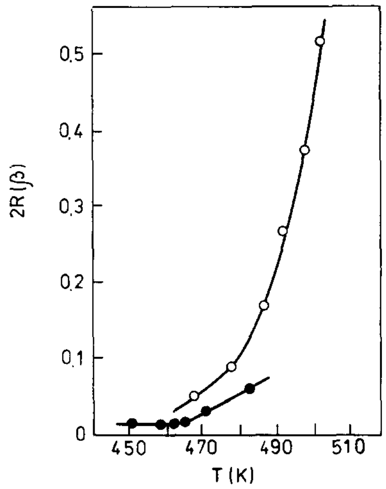

Figure 6 Amplification factor as a function of temperature for the mixture PVA:PMMA = 0.6:0.4 without filler (○) and with 10 wt% A-175 (first stage) (●)

In *Figure 5* the variation of light scattering intensity ln I as a function of time τ is given for PVA–PMMA mixtures for temperatures higher than the cloud point curve. It is seen that the curves ln $I(\tau)$ for unfilled mixtures have at least two linear regions (several linear regions are also observed for filled mixtures). In all the cases the slopes of these curves increase with the distance from the cloud point curve which is characteristic of the spinodal phase separation mechanism. Assuming that in both cases the mechanism of phase separation in its initial stages is described by the Cahn–Hilliard theory of spinodal decomposition, we calculated the so-called amplification factor $2R(\beta)$ (where β is the wavenumber) characterizing the growth rate of concentration fluctuations. As is seen in *Figure 6*, the value of $2R(\beta)$ for unfilled mixtures increases sharply with temperature, i.e. with the distance from the cloud point curve as predicted by the Cahn–Hilliard theory. For filled mixtures the growth rate of $2R(\beta)$ with temperature is much lower (in the temperature range of the first linear region $2R(\beta)$ hardly changes with temperature), i.e. the growth rate of the amplitude of concentration fluctuations for filled mixtures decreases sharply. As is shown elsewhere[29], the filler–polymer interaction leads to the retardation of relaxation processes in the boundary layer and, as a result, to the retardation of diffusion processes causing the growth of composition fluctuations during phase separation.

CONCLUSIONS

The present investigation has shown that the PVA–PMMA mixtures are compatible and separate on heating exhibiting *LCST* behaviour, and the addition of a mineral filler decreases the phase separation temperature. With the difference in the energy of selective interaction between the polymers and the filler becoming smaller, the phase separation temperature decreases to a lesser extent.

The rate of phase separation slows down when mineral filler is added, and the molecular weight distribution of a selectively adsorbed component of the mixture does not change.

The change of compatibility is determined by the asymmetry of pair interactions in the system.

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