Miscibility of poly(vinyl acetate) with poly(chloromethyl methacrylate), poly(2-chloroethyl methacrylate) and poly(2-bromoethyl methacrylate)

M. K. Neo and S. H. Goh*
Department of Chemistry, National University of Singapore, Singapore 0511, Republic of Singapore
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The miscibility of poly(vinyl acetate) (PVAc) with poly(chloromethyl methacrylate) (PCMMA), poly(2-chloroethyl methacrylate) (PCEMA) and poly(2-bromoethyl methacrylate) (PBEMA) was studied by differential scanning calorimetry. PVAc/PCMMA and PVAc/PCEMA blends cast from tetrahydrofuran (THF) and 2-butanone (MEK) are miscible and do not show lower critical solution temperature (*LCST*) behaviour. PVAc/PBEMA blends cast from THF are immiscible, but those cast from MEK are miscible at low temperatures and shown *LCST* behaviour upon heating to 80–100°C.

(Keywords: polymer blends; miscibility; lower critical solution temperature behaviour; poly(vinyl acetate); halogen-containing polymethacrylates)

INTRODUCTION

There have been many studies on the miscibility of poly(vinyl chloride) (PVC) with poly(ethylene-*co*-vinyl acetate) (PEVAc)[1–10]. PVC is miscible with PEVAc over a certain copolymer composition range although there are disagreements on the width of the miscibility range. Several of these studies also reported that PVC is immiscible with polyethylene and poly(vinyl acetate) (PVAc). However, Bhagwager *et al.*[11] have recently reported that the observed immiscibility of PVC/PVAc blends arises from a powerful solvent effect. PVC/PVAc blends cast from tetrahydrofuran (THF) are grossly phase separated and each blend shows two distinct glass transitions while those cast from 2-butanone (MEK) show only a single glass transition in each blend, indicating miscibility.

In a recent series of papers, we reported the miscibility behaviour of poly(chloromethyl methacrylate) (PCMMA) and poly(2-chloroethyl methacrylate) (PCEMA)[12–18]. In many respects, the miscibility behaviour of PCMMA and PCEMA is similar to that of PVC in forming miscible blends with several polymethacrylates[15,16], poly(*N*-vinyl-2-pyrrolidone)[17] and poly(ε-caprolactone) (PCL)[18]. We have also studied the miscibility of poly(2-bromoethyl methacrylate) (PBEMA) with polymethacrylates and found that PBEMA has a more limited miscibility with polymethacrylates than PCEMA[19]. In this paper, we report the miscibility of PVAc with PCMMA, PCEMA and PBEMA.

EXPERIMENTAL

PCMMA, PCEMA and PBEMA were prepared by free radical polymerization as described previously[15,16,19]. The number-average molecular weights of PCMMA, PCEMA and PBEMA are 58000, 40000 and 25000, respectively; the respective weight-average molecular weights are 110000, 65000 and 37000. PVAc was obtained from Union Carbide; its number-average and weight-average molecular weights are 74000 and 124000, respectively.

Polymer blends were prepared by solution casting using THF or MEK as solvent. Solvent was first allowed to evaporate slowly at room temperature. The cast films were then dried *in vacuo* at 90°C for 7 days.

The glass transition temperatures (T_gs) of various samples were measured with a Perkin-Elmer DSC-4 differential scanning calorimeter using a heating rate of 20°C min^{-1}. The T_g value is taken as the initial onset of the change of slope in the d.s.c. curve. The reported T_g value is the average value based on the second and subsequent runs.

All the miscible blends were examined for the existence of lower critical solution temperature (*LCST*) behaviour using the method described previously[15].

RESULTS AND DISCUSSION

All the PVAc/PCMMA blends cast from THF and MEK were transparent and remained so upon heating to 280°C where they began to develop brown colouration. Each of these blends showed only one glass transition. The T_g–composition curves are shown in *Figure 1.* Based on the optical clarity and the glass transition behaviour of the blends, it is concluded that PVAc is miscible with PCMMA.

As mentioned earlier, the miscibility of PVAc/PVC blends depends on the choice of solvent. It is also of interest to compare the miscibility of PVAc/PCMMA blends to that of PVAc/poly(methyl methacrylate) (PMMA) blends. Krause *et al.*[20] reviewed the work on the miscibility of PVAc/PMMA blends and found that the results were ambiguous. Recently, Guo[21] re-examined the miscibility

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*To whom correspondence should be addressed

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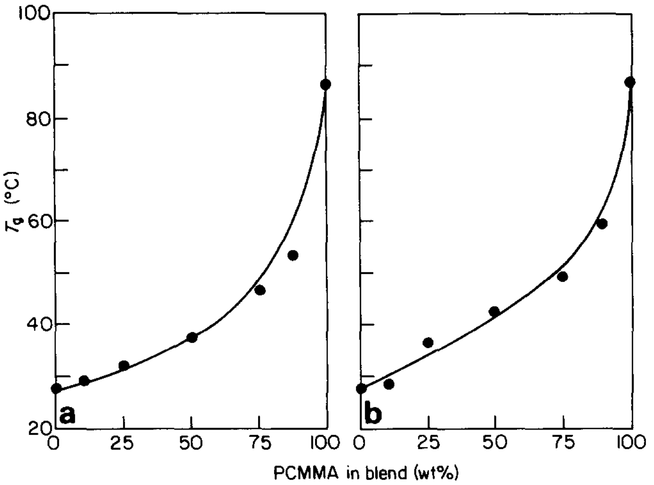

Figure 1 T_g–composition curves for PVAc/PCMMA blends: (a) THF cast; (b) MEK cast

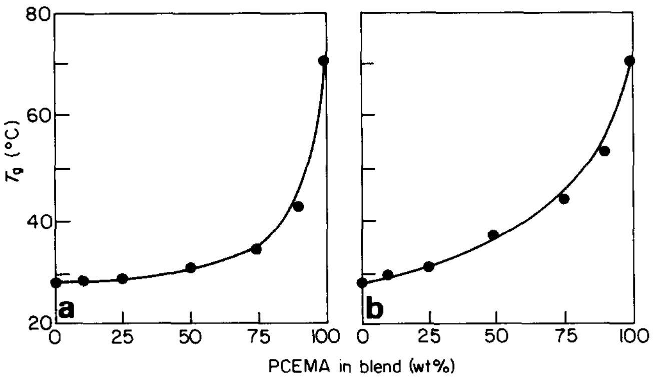

Figure 2 T_g–composition curves for PVAc/PCEMA blends: (a) THF cast; (b) MEK cast

of PVAc/PMMA blends and found that the miscibility depended on the method of preparation. PVAc/PMMA blends cast from THF and prepared by melt blending are immiscible as shown by the opacity and the glass transition behaviour of the blends. However, blends cast from chloroform and cyclohexanone are miscible and show *LCST* behaviour. Guo concluded that the specific interaction between PVAc and PMMA is very weak and the miscibility is greatly influenced by the method of preparation.

The formation of a miscible blend arises from specific interactions between the component polymers. For PCL/PVC blends, Fourier transform infra-red (*FT*i.r.) studies have shown that there exists a hydrogen-bonding interaction between the polyester carbonyl group and the α-hydrogen of PVC[22]. *FT*i.r. studies of PEVAc/PVC blends also reveal the interaction of the carbonyl groups of vinyl acetate segments with PVC[7]. In the case of PVAc/PMMA blends, the interaction is likely to be a dipole–dipole interaction involving the carbonyl groups of the two polymers. For PVAc/PCMMA blends, in addition to the dipole–dipole interaction involving carbonyl groups, hydrogen-bonding interaction is also likely to occur. The presence of electron-withdrawing chlorine and the ester carboxyl group makes the pendent methylene hydrogen atoms acidic to interact with the carbonyl group of PVAc. This type of interaction has been ascribed to the miscibility of PVAc with polyepichlorohydrin[23].

The *LCST* behaviour of polymer blends provides information on the intensity of interaction. An increase in the strength of interaction leads to a higher temperature for phase separation[24,25]. For example, polystyrene can be modified to contain a small amount of vinylphenylbis(trifluoromethyl)carbinol as comonomer units. The modified polystyrene interacts more intensely with poly(vinyl methyl ether) and the *LCST* of the blend is raised[25]. PVAc/PMMA blends start to undergo phase separation at 150°C[21], whereas PVAc/PCMMA blends do not undergo phase separation up to 280°C. The results suggest that PCMMA interacts more intensely with PVAc as compared with PMMA.

All the PVAc/PCEMA blends cast from THF and MEK were also transparent and remained so upon heating to 280°C. Furthermore, each of the blends showed only one glass transition, confirming that PVAc is miscible with PCEMA. The T_g–composition curves of the blends are shown in *Figure 2*.

In contrast, PVAc/PBEMA blends cast from THF were opaque, indicating the heterogeneous nature of the blends. D.s.c. measurements also revealed the existence of two glass transitions in each of these blends and the T_g values are close to those of PVAc and PBEMA. The d.s.c. curves of the blends are shown in *Figure 3*. Therefore, THF-cast PVAc/PBEMA blends are immiscible.

On the other hand, PVAc/PBEMA blends cast from MEK were transparent. However, these blends became cloudy after drying in the vacuum oven at 90°C. Apparently, the blends have rather low *LCST*s such that phase separation occurs during the drying process. A new batch of blends was prepared and the cast films were then examined for *LCST* behaviour. All the films turned cloudy when heated to 80–100°C. Therefore, PVAc/PBEMA blends cast from MEK are miscible only at low temperatures. The results also suggest that the interaction between PVAc and PBEMA is rather weak which can be attributed to the large size and low electronegativity of bromine. Since bromine is less electronegative than chlorine, the pendent methylene hydrogen atoms are less acidic than those in PCMMA and PCEMA.

In summary, blends of PVAc with PCMMA and PCEMA cast from THF and MEK are miscible; blends of PVAc with PBEMA cast from THF are immiscible and

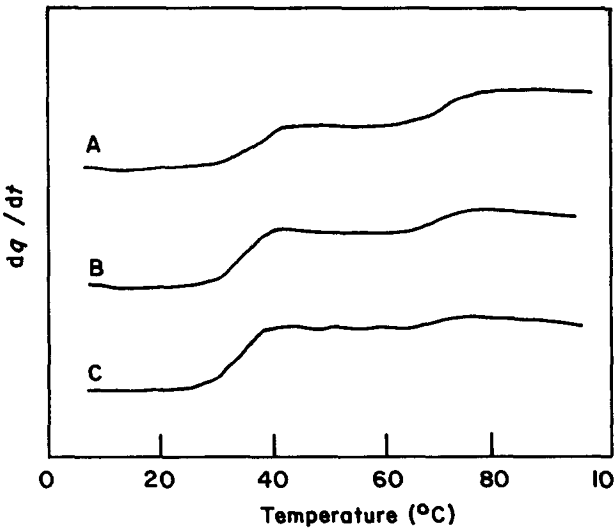

Figure 3 D.s.c. curves for THF-cast PVAc/PBEMA blends: (A) 25 wt% PVAc; (B) 50 wt% PVAc; (C) 75 wt% PVAc

those cast from MEK are miscible only at low temperatures.

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