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MISCIBILITY IN BLENDS OF POLY(VINYL ACETATE) WITH POLY(METHYL METHACRYLATE) STUDIED BY FTIR AND DSC

MO SONG* and FUJIN LONG
Guangzhou Institute of Chemistry, Academia Sinica, Guangzhou P. O. Box 1122,
People's Republic of China

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Abstract—Miscibility in blends of poly(methyl methacrylate) (PMMA) with poly(vinyl acetate) (PVAc) has been studied by using differential scanning calorimetry and i.r. spectra techniques. PMMA is miscible with PVAc at all compositions. PMMA/PVAc blends show a lower critical solution temperature. The FTIR spectrum of a blend could not be obtained by adding spectra of the two pure components. There are spectral differences between miscible and immiscible blends either prepared by casting from tetrahydrofuran solution or phase separation. It is suggested that conformational changes resulting from hydrogen bond interactions between two similar polymers and solvents in solution are involved in miscible blends.

INTRODUCTION

In polymer–polymer mixtures, the entropy of mixing is very small because of the small number of molecules involved; miscibility generally requires specific interactions such as hydrogen bonding, donor-acceptor interaction, charge-transfer etc., resulting in a negative exchange interaction contribution to the free energy of mixing. However, some miscible polymer pairs are known in which there are supposedly no specific interactions, e.g. polystyrene–poly(*o*-chlorostyrene) and polystyrene–poly(α-methylstyrene) [1, 2]. In these systems, the chemical constitutions are so similar that the free volume contribution is very small, therefore small positive exchange interaction energy allows the net free energy of mixing to be negative. A polyacrylate and a poly(vinyl ester), when their repeating units contain the same number of carbon atoms, were found to be miscible [3]. Those systems which have very similar molecular structures also belong to this category. For poly(methyl methacrylate) (PMMA) with poly(vinyl acetate) (PVAc), inverse gas chromatography shows that the polymer–polymer interaction parameter has a small positive value so that the absence of specific interactions has been inferred [4].

The miscibility of PMMA with PVAc blends has been widely studied. Results obtained by different methods have provided evidence for limited miscibility [5–9]. It should be noted that most of investigations involved films prepared by casting mixtures of the two polymers in tetrahydrofuran (THF) solution or mixing in the melt. Friese [10] found, when chloroform was used as solvent, that homogenous solutions and transparent films were obtained. Jenckel and Herwing [11] studied also the dynamic mechanical properties of the mixtures and observed that the damping curves exhibited two maxima. Single or two-phase system were considered by various authors [12, 14].

In this work, the miscibility of PMMA with PVAc cast for chloroform solution is reported. Based on FTIR spectra, conformational changes in miscible blends of PMMA with PVAc are discussed.

EXPERIMENTAL PROCEDURES

PMMA ($\bar{M}_w = 1.98 \times 10^5$, $\bar{M}_n = 0.77 \times 10^5$) and PVAc ($\bar{M}_w = 2.6 \times 10^6$, $\bar{M}_n = 0.8 \times 10^6$) were commercial products. The blends of the polymers were prepared by dissolving in a common solvent viz, chloroform. The blend samples were cast on glass, and the solvent was allowed to evaporate slowly. The films were kept under vacuum at 50° until no further weight losses were observed.

DSC runs were carried out on a Perkin–Elmer differential scanning calorimeter, model DSC-2C, at a heating rate of 20°/min. The onset of the change of slope in the DSC plot was taken as T_g.

Infrared spectra were obtained on Analect RFX-65 FTIR spectrometer, and 96 scans were averaged.

RESULTS AND DISCUSSION

Examination of phase behaviour of PMMA with PVAc blends

Casting from chloroform solution, all films of PMMA with PVAc blends with various compositions were optically clear. Even after annealing at 110° for 24 hr, they were transparent and no indication of phase separation was observed under an optical microscope. The blend films on the glass were placed on a hot plane and the temperature was raised at the rate of 10°/min. With temperature increasing, the films became opaque. We judged that the blend was in the two phase region in the phase diagram (Paul's method [14]). When the temperature reached about 170°, all films of various compositions became opaque. Figure 1 is the phase diagram of PMMA with PVAc. The results show that PMMA with PVAc

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*To whom all correspondence should be addressed.

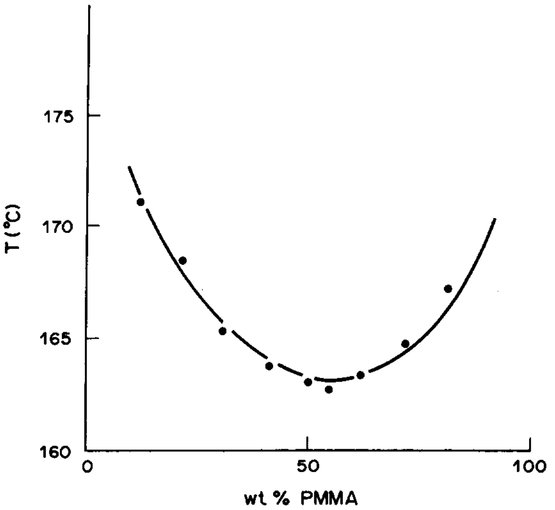

Fig. 1. Phase diagram of PMMA with PVAc blends.

exhibited a lower critical solution temperature (LCST). The cloud point curve was skewed with a minimum at about 55 wt% PMMA content.

Each blend showed a single composition-dependent T_g indicating its single phase nature. Thus, PMMA is miscible with PVAc cast from chloroform. The T_g data for the blends are shown in Fig 2.

Based on the results of T_g and the phase diagram, PMMA is miscible with PVAc over the entire composition range. By examining the i.r. spectra of blends, we could obtain the information about polymer chain interactions or conformation changes. In general, if there are no interactions between two polymers or there are no conformational changes in a polymer blend, the i.r. spectrum of a blend should be the addition of the spectra of the two components [15]. Therefore, subtraction of the spectrum of one pure component (say PVAC) for that of the blend should lead to the spectrum of the other component (PMMA). Figure 3 shows the spectrum of pure PMMA and the difference spectrum obtained by subtracting that for PVAc from that for PMMA/PVAc blend (40:60 by wt) until the band at 1024.0 cm^{-1} was reduced to the baseline. The film was cast from chloroform. It can be seen that bands associated with ester groups are changed. In the difference spectrum, bands at 1732.2 and 1241.0 cm^{-1} in the spectrum of pure PMMA shifted to 1733.7 and 1245.8 cm^{-1} respectively; the intensities of these bands also increased. This result shows that the spectrum of the blend is not the linear addition of the spectra of the two pure components. In general, if there are no interactions between two polymers or there are no conformational changes in a polymer blend, the i.r. spectrum of the blend should be the addition of the spectra of the pure components. It appears that there must be conformational changes in the miscible blend.

The spectrum of a miscible blend is different from that of an immiscible blend. PMMA with PVAc blend (40:60 by wt) prepared by casting from THF solution has been shown to be immiscible [8,9]. The spectrum showed no difference from the addition of those for the two pure components. Subtracting the spectrum of PVAc from that for PMMA/PVAc blend cast from THF gives a spectrum almost indentical with that of pure PMMA. However, it is different from the spectrum of a blend cast from chloroform solution (Fig 4) . Bands at 1735.6 and 1240.0 cm^{-1} are shifted to 1737.6 and 1241.9 cm^{-1}, respectively. The intensities of bands at 1147 and 1194 cm^{-1} are increased. The difference spectrum shows these changes clearly.

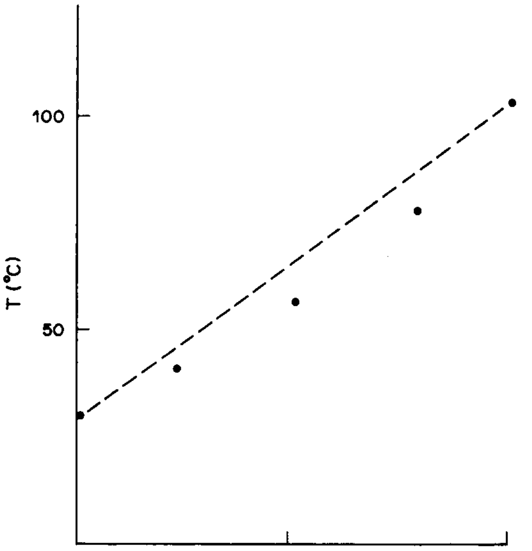

Fig. 2. T_g-composition curve for PMMA with PVAc blends.

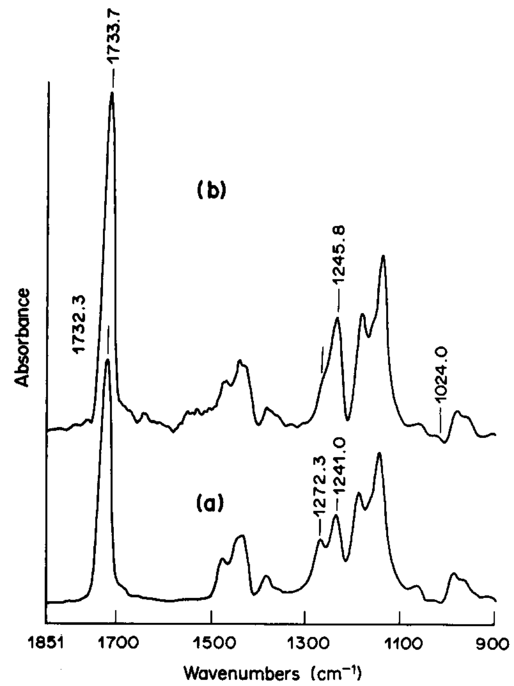

Fig. 3. (a) FTIR spectrum of pure PMMA from 1850 to 900 cm^{-1}, (b) difference spectrum of PMMA obtained by subtracting PVAc from PMMA/PVAc blend (40:60 by wt) until band at 1024.0 cm^{-1} reduced to baseline.

The PMMA/PVAc blends show an LCST. When the blend is heated above the critical temperature, phase separation occurs. The composition of each phase is governed by temperature. When PMMA/PVAc blend (40:60 by wt) was heated at 182° for 17 min, separation into two components occurred. The spectra obtained before and after phase separation are quite different, as shown in Fig 5. Both spectra were obtained at room temperature so that the temperature effect was minimal. After phase separation, the band at 1737.6 cm^{-1} shifted to 1735.6 cm^{-1} and that at 1241.9 to 1240.0 cm^{-1}. It should be noted that the bands at 1194 and 1147 also showed small shifts and intensity changes. They are stronger in the miscible system than in the phase separated [Fig. 5(c)].

The chemical constitution of PMMA and PVAc are similar; such similarity could not cause specific interactions favouring miscibility of PMMA with PVAc.

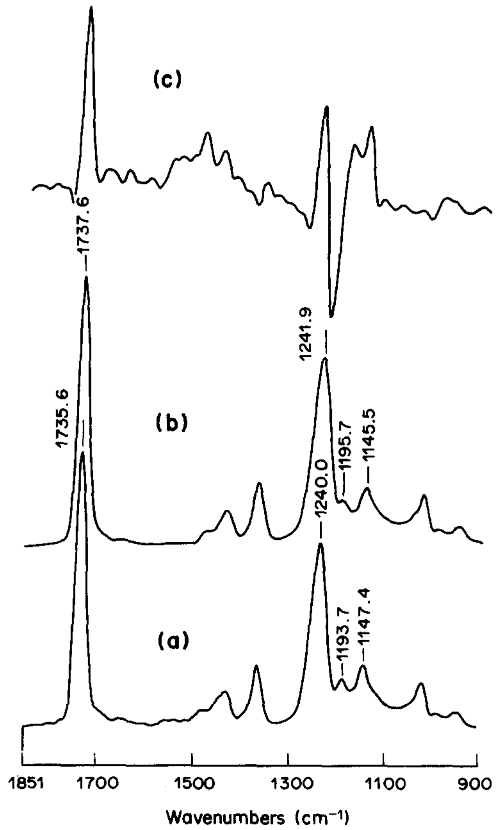

Fig. 5. FTIR spectra of PMMA/PVAc blend (40:60 by wt): (a) heated at 182° for 17 min then cooled to room temperature; (b) in one phase; (c) difference (b)–(a).

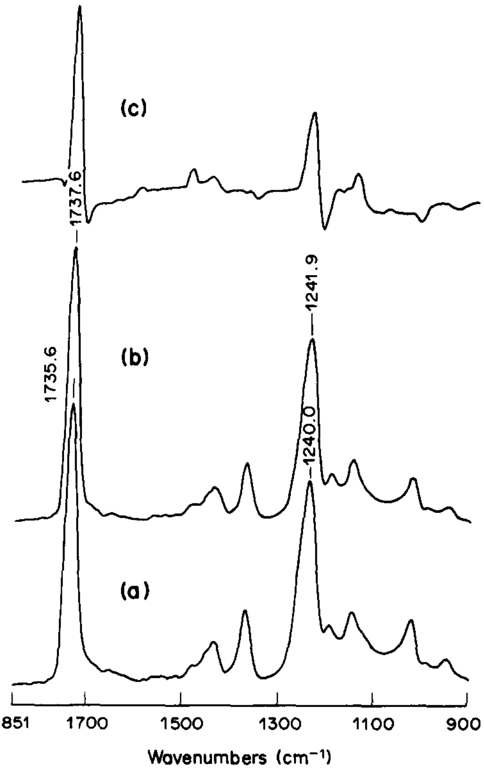

Fig. 4. FTIR spectra of PMMA/PVAc blend (40:60 by wt): (a) cast from THF solution; (b) cast from chloroform solution; (c) difference (b)–(a).

The spectral changes for PMMA are very interesting. The bands at about 1735 and 1240 cm^{-1} overlap for the two polymers and it is difficult to decide which component give the main contribution to these changes; we could see however that the band for C═O stretching vibration of PMMA (also PVAc) shifted to higher frequency in miscible blends and that bands between 1300 to 1000 cm^{-1} changed in peak position and intensity. The four bands of PMMA between 1000 and 1350 cm^{-1} are assigned to C—O stretching and skeletal vibration and are sensitive to backbone and side-chain conformational changes [16]. The dependence of these four bands and the carbonyl stretching frequency at 1733 cm^{-1} on temperature was attributed to a conformational equilibrium between low-energy *trans–trans* states and high-energy *trans–gauche* states. Comparing with the difference spectra of PMMA at elevated temperature [16], we could find that the difference spectrum between a miscible blend and phase separated one is very similar to that at high temperature. Consequently, it could be deduced that, in a miscible blend cast from chloroform solution, PMMA is in the high energy conformational state. Comparing the spectra of PMMA/PVAc miscible and immiscible blends prepared by casting from THF solution (Fig. 4), it is clear that the difference spectrum is similar to that in Fig. 5. This result indicates that the stucture of mixes separated above the critical temperature is the same as that prepared by casting from THF. We believe that the solvent THF did not induce conformational changes of polymer chains.

Figure 6(a) shows the i.r. spectrum of PMMA/PVAc (30:70) in chloroform solution. Bands of C═O for both PMMA and PVAc shifted to lower wavenumbers compared with THF solution. It showed that hydrogen bonds are formed between C═O of both polymers and C—H of the solvent [17]. Owing to the hydrogen bonding, the chain conformation of both PMMA and PVAc would be changed, perhaps to higher energy states. As a result, the two similar polymer chains could interpenetrate. This

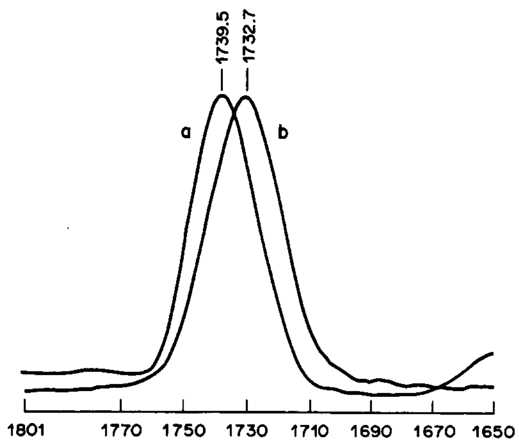

Fig. 6. Spectrum of PMMA/PVAc (30:70 by wt) blend: (a) in THF solution (b) in chloroform solution.

situation, the similarity of constitution of the two polymers, is advantageous for forming such an interpenetrated system. When solvent evaporated, chain movement was frozen and the high-energy conformational structure remained. Conformational energy calculated by O'Reilly and Mosher [16] was around 1450 cal/mol (6090 J/mol). It is possible that the force of hydrogen bonding in chloroform solution is sufficient to overcome such energy. However, in THF solution, there is no specific interaction between the polymers and the solvent so that polymer chains of each component exist in their own random coil states.

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