

Phase Behavior of Ternary Polymer Blends with Hydrogen Bonding

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ABSTRACT: Atactic poly (methyl methacrylate) (aPMMA) was found to be almost completely immiscible with poly(vinyl acetate) (PVAc). Both aPMMA and PVAc are known to be miscible with poly(vinyl phenol) (PVPh) according to literature. Adding of PVPh into immiscible aPMMA/PVAc mixtures is likely to improve their miscibility. Therefore, PVPh can be used as cosolvent to cosolubilize aPMMA and PVAc. A ternary blend consisting of aPMMA, PVAc, and PVPh was

prepared and determined calorimetrically in this article. According to the calorimetry data, the ternary blend was determined to be miscible. The reason for the observed miscibility is because the interactions between PVAc and PVPh are similar to those between aPMMA and PVPh. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2797–2802, 2004

Key words: ternary blends; hydrogen bonding

INTRODUCTION

Ternary blends are gaining importance in the field of polymers through the years. The first systematic study on ternary blends was reported by Kwei et al.¹ in 1977. In their study, the addition of poly(vinylidene fluoride) (PVDF) to the immiscible pair poly(methyl methacrylate) (PMMA)/poly(ethyl methacrylate) (PEMA) was studied and found to be miscible. A list of ternaries investigated has been considerably enlarged since then.^{2–8} In nearly all these blends, a third component either a homopolymer or copolymer is added to homogenize an immiscible pair. Miscibility is often achieved in cases where this third component is miscible with other polymers.

Painter and Coleman⁹ have reported an interesting review on the effect of hydrogen bonding on the phase behavior of ternary polymer blends. They mentioned in their article, “Is it possible to increase the region over which ternary blends are miscible by introducing specific interaction?” “Can we add a polymer (say, poly B) to an immiscible binary blend (poly A/poly C) and render the whole system homogeneous (single phase)?,” and “Will poly B act as a “compatibilizer” and reduce the overall size of the domains in the heterogeneous ternary blend?” As the discovery or design of miscible binary polymer blends has been enhanced by considering systems in which there are

strong specific interactions (hydrogen bonds) present, one might reasonably presume that immiscible binary blends might well be “homogeneized” by an appropriate poly B that can hydrogen bond to both poly A and poly C. The ΔK effect (by analogy to the common known $\Delta\chi$ effect) was proposed by them. The ΔK effect reflects the difference in the “chemical” interaction between the self-association polymer and the other polymers in the mixture. They concluded from their simulations that:

1. It will be difficult to find ternary polymer blends that exist in a single phase over a wide composition range. Only in very rare cases, where the “physical” ($\Delta\chi$) and “chemical” (ΔK) interaction differences are negligible or finely balanced, can we expect to find miscible ternary polymer blends.
2. In most cases, an immiscible binary blend cannot be made homogeneous by introducing a small amount of a third polymer (compatibilizer).
3. Although the presence of specific intermolecular interaction enhances the probability of forming a homogeneous ternary polymer blend, they can concurrently exacerbate the situation through the ΔK effect, which promotes phase separation.

In a previous study of ours,¹⁰ weakly self-associated poly(styrene-co-vinyl phenol) (PSVPh) with 5 or 15 mol % VPh units (PSVPh5 or PSVPh15) was added into the immiscible PEMA/PMMA pairs. Note that PSVPh forms interhydrogen bonds with both PEMA and PMMA, respectively. The results showed that the miscibility region of the ternary blends consisting of PS-

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VPh5, PEMA, and PMMA was larger than the similar ternaries containing PSVPh15. The reason may be that the PSVPh15 ternaries exhibit a strong ΔK effect.

Now we turn our attention to atactic PMMA (aPMMA), poly(vinyl acetate) (PVAc), and poly(vinyl phenol) (PVPh). PVPh is known to form intrahydrogen bonding (i.e., self-association). PVPh (a proton-donating polymer) is miscible with proton-accepting polymers like aPMMA¹¹ or PVAc.¹² The interassociation constant as described by Painter and Coleman⁹ between PVAc and PVPh is slightly larger than and has a similar magnitude to that between aPMMA and PVPh. Adding PVPh into aPMMA/PVAc pairs is likely to form a completely miscible ternary. Before pursuing this investigation, the miscibility or immiscibility between aPMMA and PVAc needs to be confirmed first. The miscibility of the blends of atactic poly(methyl methacrylate) (aPMMA) and poly(vinyl acetate) has been widely studied. The conclusions reached by different authors are not consistent. The following paragraph is devoted to expound this aspect more clearly.

A very interesting effect was found by Ichihara and coworkers,¹³ who prepared transparent aPMMA/PVAc blends by a freeze-drying technique. In differential scanning calorimetry (DSC) experiments these blends exhibited only single glass transition, a characteristic indication of miscible polymer blends. However, after annealing the blends at 400 K, two glass transition temperatures (T_g s) were detected corresponding to the T_g of the homopolymers. The authors explained this by demixing of the frozen nonequilibrium state at temperatures higher than the T_g s of PMMA and PVAc. The same blends were prepared by Schneier¹⁴ by mixing the polymers in the melt and in the absence of a solvent. aPMMA was the major constituent of the blend. Data obtained from dynamic mechanical and DSC experiments show that, when they are mixed under given Brabender mix conditions, the blend exhibits properties characteristic of miscible polymer pairs. However, if the mix conditions are altered, a two-phase system is evidenced. Schenk et al.¹⁵ prepared the aPMMA/PVAc blends from solutions of benzene. They used a nuclear magnetic resonance technique to study the miscibility of the same blends. Heterogeneity was detected, and the results of immiscibility were also confirmed by DSC studies. The aPMMA/PVAc blends in chloroform cast at 50°C were prepared by Song and Long.¹⁶ They studied the blends by using DSC and IR techniques. PMMA is miscible with PVAc at all compositions. Based on IR spectra, conformational changes were detected in the miscible blends. The influence of solvent and temperature on the miscibility of aPMMA and PVAc was investigated by Muniz et al.¹⁷ Experiments using differential scanning calorimetry (DSC) and viscometry were performed. The miscibility of the cast aPMMA/

PVAc blends (not definitely in thermodynamic equilibrium state) was observed to depend on the solvent. The blends are miscible in chloroform at 30 and 50°C, whereas in *N,N*-dimethyl formamide (DMF) at the same temperature, the blends are immiscible. In toluene, the miscibility depends on the temperature: the blends are miscible at 30°C and immiscible at 50°C.

In view of conflicting data, a previous study of ours¹⁸ was determined to give some insight into the miscibility of aPMMA/PVAc blends. The blends were prepared from solutions of chloroform or tetrahydrofuran, and the blends were cast at room temperature but annealed at 126–130°C to make the blends closely approach the equilibrium state. Different tactic PMMAs were used to blend with PVAc to study the effect of tacticity on miscibility. Our results showed that PMMA is almost completely immiscible with PVAc regardless of tacticity of PMMA. Recently, Prud'homme¹⁹ reported a similar result that PMMA and PVAc were immiscible. They used a Minimax molder to prepare the blends and the samples were finally molded at 150°C.

In conclusion, aPMMA and PVAc are immiscible. Poly(vinyl phenol) (PVPh) was found to be miscible with both aPMMA¹¹ and PVAc.¹² Addition of PVPh into immiscible aPMMA/PVAc is likely to improve their miscibility. Therefore, in this article, a ternary blend consisting of aPMMA, PVAc, and PVPh were prepared and determined calorimetrically. FTIR is used to characterize the existing hydrogen bonding between PVAc (or aPMMA) and PVPh. Finally, the role of PVPh as cosolvent was evaluated, and the approximate ternary phase diagram was established based on the calorimetry data.

EXPERIMENTAL

Materials

aPMMA and PVPh were purchased from Polysciences, Inc., Warrington, PA. According to supplier information, the molecular weights (M_w s) of aPMMA and PVPh were 100,000 and 30,000 g/mol, respectively. The PVAc used for this study was obtained from Scientific Polymer Products, Inc., Ontario, NY. The M_w value for PVAc is also approximately 100,000 g/mol.

Film preparation

Thin films of the following binary and ternary polymer blends were made by solution casting onto glass plates. (1) aPMMA/PVPh by 2-butanone, (2) PVAc/PVPh by 2-butanone, (3) aPMMA/PVAc/PVPh by 2-butanone.

The actual compositions of the binary and ternary blends are shown later in Tables I and II. 2-Butanone

TABLE I
Glass Transition Temperatures of a
PMMA/PVAc Blends

	T_g (°C)	ΔT_g (°C)
aPMMA/PVAc		
1. (100/0)	105.9	13
2. (74.4/25.6)	42.8, 102.9	9, 12
3. (50.0/50.0)	44.2, 103.6	9, 13
4. (25.2/74.8)	44.5, 103.6	8, 13
5. (0/100)	44.7	6

is A.C.S. (American Chemical Society) reagent purchased from Aldrich Chemical Company, Inc., Milwaukee, WI. The final drying step for all the films took place in a vacuum oven at 126–130°C for about 16 h. Then the films were cooled to room temperature slowly by air to make as-cast samples. The as-cast samples were later used for DSC studies.

Differential scanning calorimetry (DSC)

Glass transition temperatures (T_g s) of the polymer blends were determined by a DuPont 2000 thermal analyzer coupled with a mechanical cooling system. The scanning range for temperature was from 10 to 200°C and a heating rate of 20°C/min was used in every measurement. The experiments were often performed in two consecutive scans in the ambient environment of nitrogen gas at a flow rate of 90–110 mL/min. In the first thermal scan, the samples stayed at 200°C for 1 min. Then the samples were cooled to 10°C using a cooling rate of 20°C/min. The inflection point of the specific heat jump of a second thermal scan was taken as the glass transition temperature. The cooling rate was proven to be fast enough to produce virtually the same results as quenching. ΔT_g is calculated as the difference between the onset and end points of the glass transition temperature region.

Fourier transform infrared spectroscopy (FTIR)

The binary polymer blend samples of aPMMA/PVPh and PVAc/PVPh were cast directly onto KBr win-

TABLE II
Glass Transition Temperatures of Ternary
Polymer Blends

	T_g (°C)	ΔT_g (°C)
aPMMA/PVAc/PVPh		
1. (18.6/6.1/75.3)	117.2	19
2. (12.7/12.6/74.7)	104.1	17
3. (6.3/19.0/74.7)	130.8	15
4. (37.2/12.3/50.5)	110.0	20
5. (25.0/25.0/50.0)	93.1	9
6. (12.4/37.5/50.1)	81.2	17
7. (56.0/18.6/25.4)	104.9	13
8. (37.4/37.4/25.2)	99.6	11
9. (18.8/56.4/24.8)	102.3	13

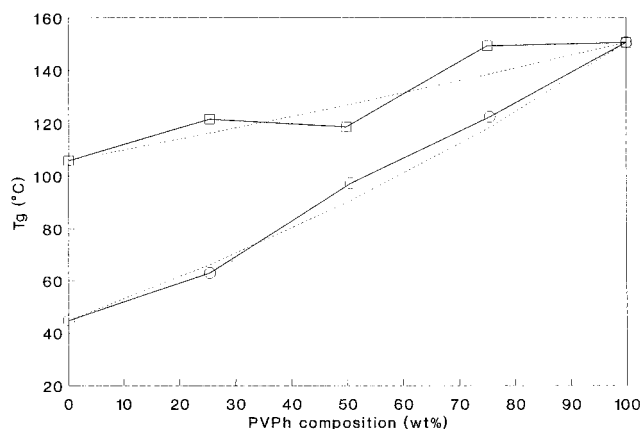


Figure 1 Glass transition temperatures of miscible binary polymer blends: \square : aPMMA, \circ : PVAc.

dows and subjected to thermal treatments similar to those for the DSC samples. For PVPh, the polymer was ground with KBr powder instead to make samples for FTIR studies. Spectra were obtained on the aforementioned prepared samples with 64 scans at a resolution of 4 cm^{-1} at room temperature. The wave number range was 400–4000 cm^{-1} .

RESULTS AND DISCUSSION

aPMMA/PVAc blends

Table I presents the glass transition temperatures (T_g s) of aPMMA/PVAc blends taken from a previous study.¹⁸ It is obvious that aPMMA and PVAc are not miscible because of the observation of two T_g s. Taking into account the error of T_g determination, the blends phase separated into highly pure aPMMA and PVAc phases. ΔT_g values (definitions aforementioned in the Experimental section) of the aPMMA/PVAc blends are listed in Table I for reference. ΔT_g values of the blends correspond almost exactly to those of component polymers also indicating immiscibility between aPMMA and PVAc. Interestingly Prud'homme¹⁹ studied the same blends and reported similar T_g and ΔT_g behavior. Our results are in good agreement with theirs.

Binary blends with PVPh

Figure 1 presents the results of aPMMA/PVPh and PVAc/PVPh blends. For these two blends, single composition-dependent T_g was detected indicating miscibility. The dashed lines shown in Figure 1 represent the Fox equation prediction.²⁰ The Fox equation is shown as below in eq. (1)

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} \quad (1)$$

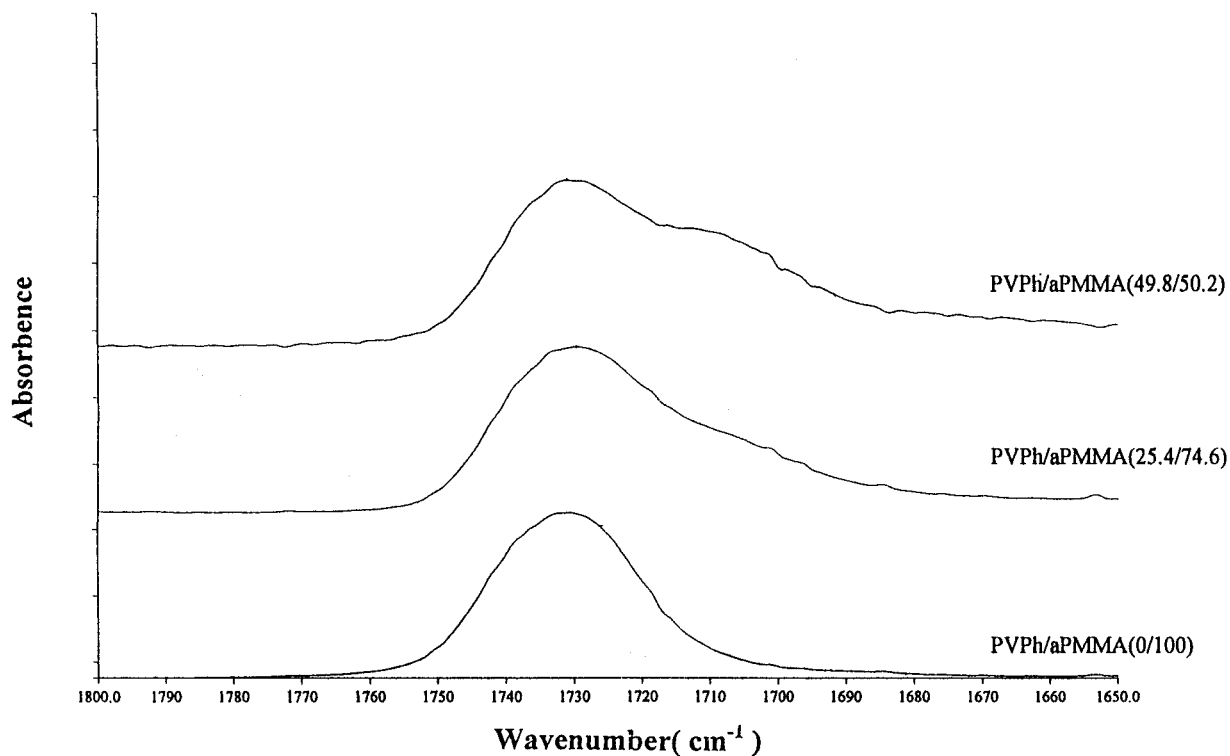


Figure 2 FTIR spectra of aPMMA/PVPh blends at the carbonyl absorption region ($1650\text{--}1800\text{ cm}^{-1}$).

where T_g is the glass transition temperature of a blend, T_{g_i} and w_i are the glass transition temperature and the weight fraction of polymers i , respectively ($i = 1, 2$). The

T_g s of the PVAc/PVPh blends can be approximately described by the Fox equation with some slight deviation. For the aPMMA/PVPh blends, the deviation from

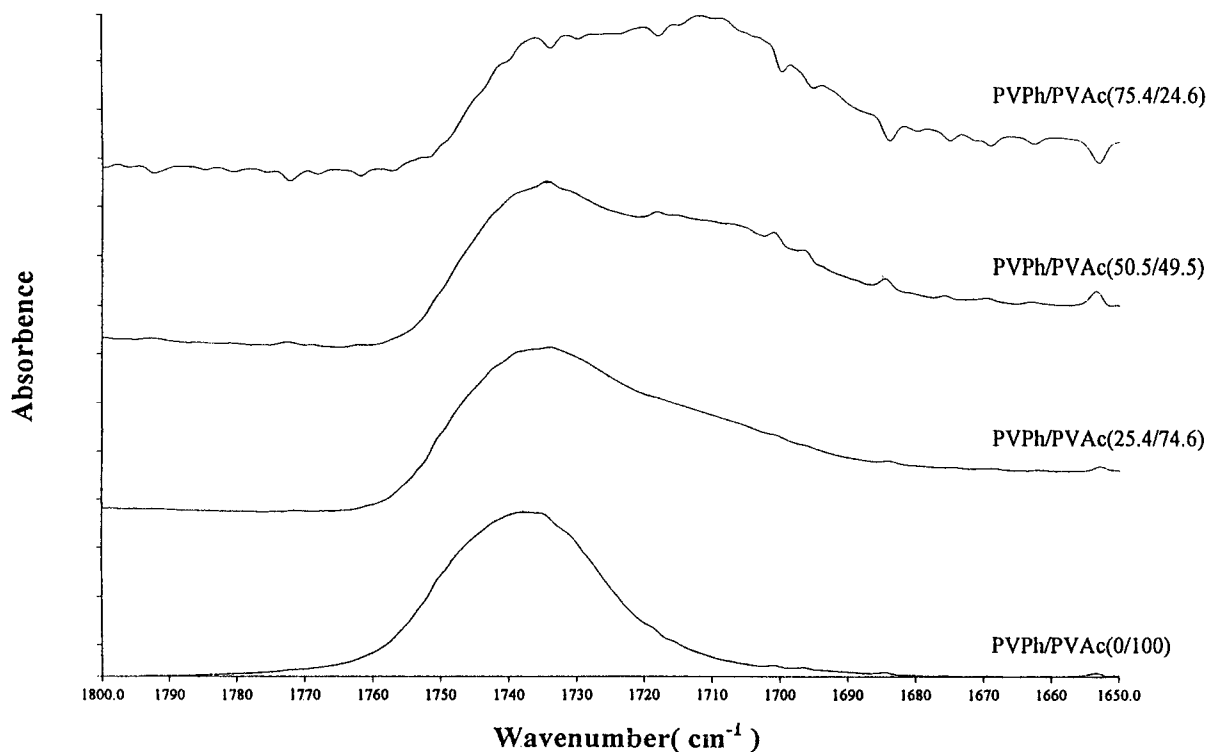


Figure 3 FTIR spectra of PVAc/PVPh blends at the carbonyl absorption region ($1650\text{--}1800\text{ cm}^{-1}$).

the Fox prediction is much larger because of different degrees of hydrogen bonding in the prepared films.

To understand the role of hydrogen bonding operating in aPMMA/PVPh and PVAc/PVPh blends. FTIR spectra of these two blends were performed. For the discussion of interhydrogen bonding, only the carbonyl absorption spectra were reported. Figures 2 and 3 present the spectra of the aPMMA/PVPh and PVAc/PVPh blends, respectively. The spectra of the PVPh/aPMMA(75/25) blend were not included because of poor resolution, but they showed similar results as the PVPh/aPMMA(49.8/50.2) one. The free carbonyl absorption peaks of aPMMA and PVAc are located at 1731 and 1738 cm^{-1} , respectively. Upon addition of PVPh, the spectra of the blends show a new peak located at a lower frequency, 1715 cm^{-1} for both aPMMA and PVAc. This peak represents the hydrogen-bonded carbonyl groups. Judging from the area of this peak as shown in Figures 2 and 3, it can be concluded that PVAc forms slightly stronger hydrogen bonding with PVPh than aPMMA. Painter and Coleman et al.^{9,21} reported a higher interassociation constant between PVAc and PVPh than that between aPMMA and PVPh. Therefore, their results also show that the interhydrogen bonding between PVAc and PVPh is slightly stronger than that between aPMMA and PVPh.

Ternary blends

The glass transition temperatures of the aPMMA/PVAc/PVPh blends are tabulated in Table II. For all nine studied blend compositions, they all showed a single T_g , indicating miscibility. ΔT_g values of the aforementioned blends are tabulated for reference.

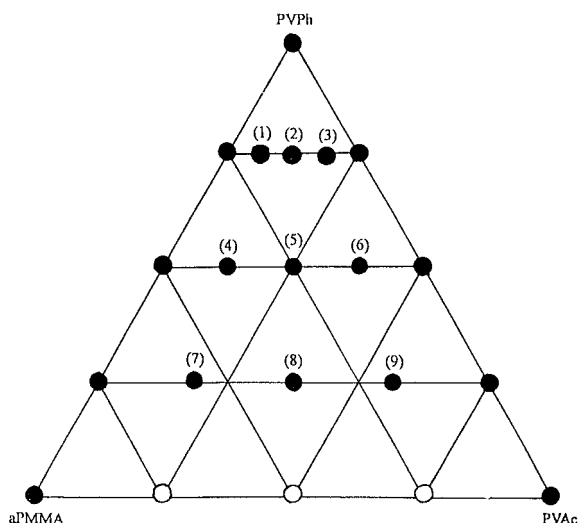


Figure 4 Phase diagram of ternary polymer blends ●: one T_g , ○: two T_g s, numbers in the figure indicate the same compositions as in Table II.

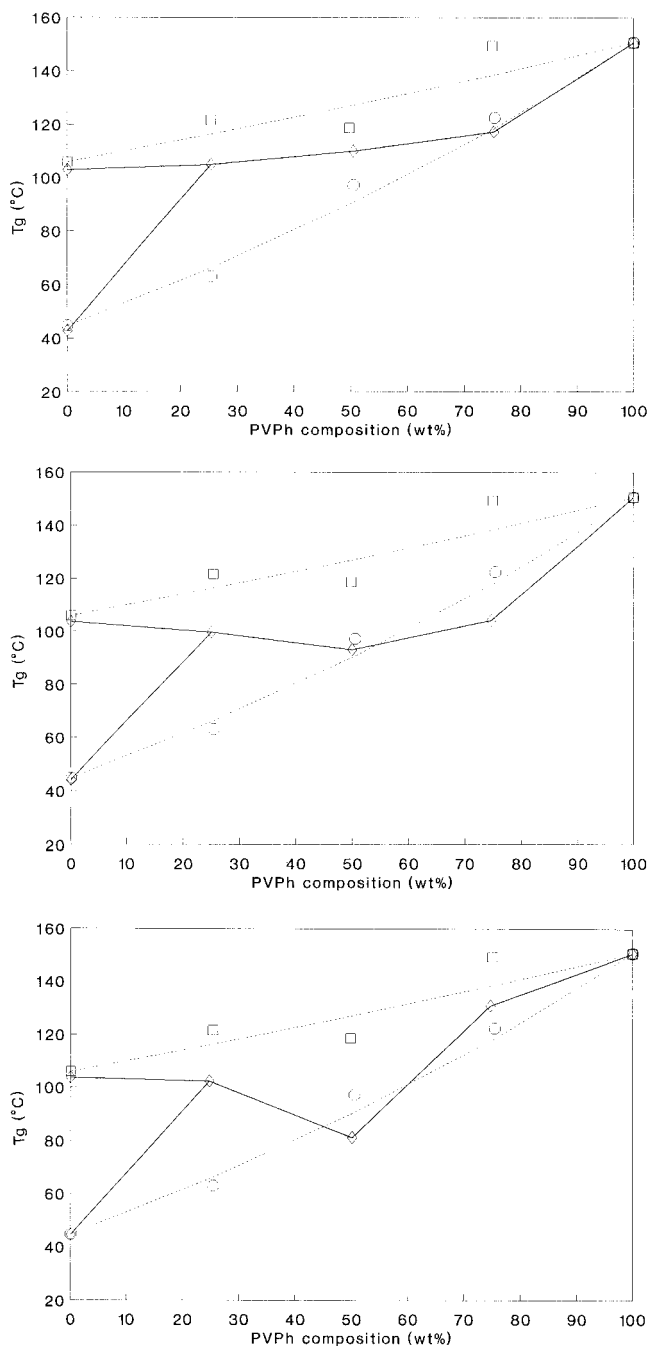


Figure 5 (a) Change of T_g of the ternary blends with PVPh composition (aPMMA/PVAc wt ratio ca. = 3/1). □: aPMMA/PVPh blends, ○: PVAc/PVPh blends, ◇: data point. (b) Change of T_g of the ternary blends with PVPh composition (aPMMA/PVAc wt ratio ca. = 1/1). □: aPMMA/PVPh blends, ○: PVAc/PVPh blends, ◇: data point. (c) Change of T_g of the ternary blends with PVPh composition (aPMMA/PVAc wt ratio ca. = 1/3). □: aPMMA/PVPh blends, ○: PVAc/PVPh blends, ◇: data point.

There is no ΔT_g broadening phenomenon observed indicating miscibility. Using single T_g as the criterion for miscibility, the phase diagram composed of aPMMA, PVAc, and PVPh was established and is

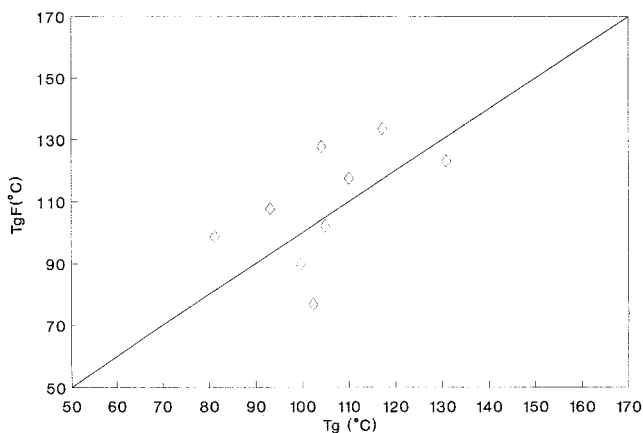


Figure 6 Fox predicted T_g vs. experimental T_g .

shown in Figure 4. The solid and empty circles represent single T_g and two T_g s, respectively. Miscibility is encountered in all the studied ternary blends. Painter and Coleman⁹ reported a similar ternary blend [poly(methyl acrylate) (PMA)/PVAc/PVPh]. PMA is an isomer of PVAc and known to be miscible with PVAc. PMA and PVAc are both miscible with PVPh because of hydrogen bonding. Because of no $\Delta\chi$ effect and weak ΔK effect, PMA/PVAc/PVPh blends were found to be miscible by them using DSC. They also used their theory to estimate the phase diagram and the results are in agreement with experiment. Our study used aPMMA instead of PMA. Because aPMMA is not an isomer of PVAc, there is likely a weak $\Delta\chi$ effect between aPMMA and PVAc. The magnitude of the interassociation constant between aPMMA and PVPh is similar to that between PMA and PVPh. Therefore, a weak ΔK effect is also operating in our ternary system. Weak $\Delta\chi$ and ΔK effects are the reasons for the observed miscibility in the aPMMA/PVAc/PVPh blends.

For the purpose of illustrating the cosolvent effect of PVPh, the T_g values of the ternary blends with aPMMA/PVAc wt ratio ca. 3/1, 1/1, and 1/3 were plotted in Figure 5(a)–(c), respectively. Results of the corresponding binaries (aPMMA/PVPh and PVAc/PVPh blends) were also included in Figure 5(a)–(c) for comparison. The ternary T_g values of the blends with aPMMA/PVAc wt ratio ca. 3/1 are always located mostly between those of the binaries with the same PVPh composition. For the ternary blends with aPMMA/PVAc wt ratio ca. 1/1 and 1/3, two of the three ternary T_g values are located between those corresponding binaries. However, one T_g of the aforementioned ternaries is below the corresponding binaries likely because of breaking and forming of intra- and interhydrogen bonding in the ternary.

For polymer blends with weak or no interaction, the Fox equation²⁰ seems to predict the glass transition temperature quite well. The T_g values of the ternary

blends (designated as T_{gF}) were estimated using aPMMA, PVAc, and PVPh's T_g s in an extended equation for the ternary similar to eq. (1) (i.e., $1/T_{gF} = w_1/T_{g1} + w_2/T_{g2} + w_3/T_{g3}$). The outcome is shown in Figure 6 (T_{gF} vs. experimental T_g). The T_g data can be described qualitatively by the Fox equation. Totally speaking, the prediction by the Fox equation is not satisfactory as frequently encountered difficulty in predicting T_g of multicomponent polymers. Positive and negative deviations of experimental T_g from Fox predictions were both observed in Figure 6, making estimation difficult; therefore, other equations including favorable interaction were not attempted.

CONCLUSIONS

aPMMA and PVAc are immiscible. PVPh is miscible with both aPMMA and PVAc based on the calorimetry data in accordance with literature. The miscibility between PVAc (or aPMMA) and PVPh is driven by interhydrogen bonding as observed in the FTIR spectra. Although PVAc forms slightly stronger hydrogen bonding than aPMMA, a ternary blend consisting of aPMMA, PVAc, and PVPh was found to be completely miscible. The miscibility of the ternary was probably driven by weak $\Delta\chi$ and ΔK effects in concert. The weak ΔK effect is caused by a slight difference in the interaction between aPMMA and PVPh and that between PVAc and PVPh.

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