

Achieving Miscible Ternary Polymer Blends with Hydrogen Bonding

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ABSTRACT: Poly(vinyl phenol) (PVPh) has previously been found to be successful in making immiscible poly-(methyl methacrylate) (PMMA)/poly(vinyl acetate) (PVAc) miscible. Poly(ethyl methacrylate) (PEMA) with one more methyl group than PMMA is also immiscible with PVAc. PEMA and PVAc are miscible with PVPh according to the literature. To determine whether PVPh can also cosolubilize PEMA/PVAc, PVPh samples of two different molecular weights have been mixed in this study with PEMA and PVAc to produce a ternary blend. On the basis of the calorimetry data, the ternary PEMA/PVAc/PVPh blend, re-

gardless of the molecular weight of PVPh, has been determined to be miscible. The reason for the observed miscibility is probably that the interactions between PVAc and PVPh are similar in magnitude to those between PEMA and PVPh. A modified Kwei equation based on the binary interaction parameters proposed previously is used to describe the experimental glass-transition temperature of the miscible ternary blend almost quantitatively well. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 643–652, 2006

Key words: blends; ternary; hydrogen bonding

INTRODUCTION

Ternary blends have been 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) to the immiscible pair poly-(methyl methacrylate) (PMMA)/poly(ethyl methacrylate) (PEMA) was studied and found to be miscible. The 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 in which this third component is miscible with other polymers.

Painter et al.⁹ reported an interesting review on the effect of hydrogen bonding on the phase behavior of ternary polymer blends. They asked the following 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 the consideration of systems in which there are strong specific interactions (hydrogen bonds) present, one might reasonably presume that immiscible binary blends might well be homogenized by an appropriate poly B that can hydrogen-bond to both poly A and poly C. The ΔK effect (by analogy to the commonly known $\Delta\chi$ effect, where $\Delta\chi$ reflects the interaction between the polymers) 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, in which 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 the introduction of a small amount of a third polymer (compatibilizer).
3. Although the presence of specific intermolecular interactions enhances the probability of forming a homogeneous ternary polymer blend, they can concurrently exacerbate the situation

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through the ΔK effect, which promotes phase separation.

In a previous study of ours,¹⁰ poly(vinyl phenol) (PVPh) was used to homogenize an immiscible PMMA/poly(vinyl acetate) (PVAc) pair. PVPh is known to form intra-hydrogen bonding (i.e., self-association). PVPh (a proton-donating polymer) is miscible with proton-accepting polymers such as PMMA¹¹ and PVAc.¹² The addition of PVPh to PMMA/PVAc pairs has been proven to be successful in making them miscible. The reason is likely that the physical and chemical interaction differences between PMMA/PVPh and PVAc/PVPh are negligible or finely balanced.

Motivated by previous success, now we turn our attention to PEMA, PVAc, and lower molecular weight PVPh. With one more methyl group than PMMA, PEMA is also immiscible with PVAc. It is often believed that more alkyl groups have an adverse effect on miscibility with PVPh or PVAc. A low-molecular-weight polymer in blending is usually beneficial for miscibility because of entropic contributions. However, lower molecular weight PVPh has a stronger tendency for self-association and thus likely an adverse effect on miscibility. PVPh is known to be miscible with PEMA and PVAc. Therefore, in this study, PVPh was used to improve the miscibility of immiscible PEMA/PVAc. A ternary blend consisting of PEMA, PVAc, and PVPh was prepared and determined calorimetrically. Fourier transform infrared (FTIR) was used to characterize the existing hydrogen bonding between PVAc (or PEMA) and PVPh. On the basis of calorimetry data, miscibility was achieved in the prepared ternary blend, and conclusive results are presented in this article. A modified Kwei equation for ternary polymer blends based on the binary interaction parameters proposed previously¹³ is used in this report to describe the glass-transition temperatures (T_g 's) of the miscible ternary. The results seem quite satisfactory.

EXPERIMENTAL

Materials

PEMA, PVAc, and PVPh were all purchased from Polysciences, Inc. (Warrington, PA). According to sup-

TABLE I
 T_g Values of PEMA/PVAc Blends

Sample	T_g (°C)	ΔT_g (°C)
PEMA/PVAc		
1	100/0	80.7
2	74.9/25.1	45.5, 77.4
3	50.0/50.0	46.1, 79.3
4	25.0/75.0	46.5, 82.1
5	0/100	45.7

TABLE II
 T_g Values of PVPh1/PEMA/PVAc Blends

Sample	T_g (°C)	ΔT_g (°C)	T_{gF} (°C)	w_1' (%)	T_{gk} (°C)
PEMA/PVAc/PVPh1					
1	18.7/6.4/74.9	131.4	27	123.2	55.8
2	12.5/12.7/74.8	127.5	29	120.2	37.1
3	6.4/18.5/75.1	124.3	24	117.6	19.3
4	37.5/12.5/50.0	110.3	23	104.4	37.5
5	25.1/25.0/49.9	118.1	26	98.9	25.0
6	12.8/37.6/49.6	102.9	24	93.3	12.6
7	56.0/18.7/25.3	91.9	24	87.3	19.0
8	37.4/37.5/25.1	78.3	28	79.7	12.5
9	18.7/56.2/25.1	71.8	22	72.6	6.3

plier information, the weight-average molecular weights (M_w 's) of PEMA and PVAc were 340,000 and 160,000 g/mol, respectively. The M_w value for two PVPh samples were 1500–7000 g/mol (designated PVPh1) and 9000–11,000 g/mol (designated PVPh2).

Film preparation

Thin films of the following binary and ternary polymer blends were made via solution casting from 2-butanone onto glass plates. The actual compositions of the binary and ternary blends are shown in Tables I–III. 2-Butanone was an American Chemical Society reagent purchased from Aldrich Chemical Co., Inc. (Milwaukee, WI). The final drying step for all the films took place in a vacuum oven at 131–137°C for about 16–24 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 differential scanning calorimetry (DSC) studies.

DSC

T_g 's of the polymer blends were determined with a PerkinElmer (Wellesley, MA) DSC-7 thermal analyzer coupled with a compressor for cooling. The tempera-

TABLE III
 T_g Values of the PVPh2/PEMA/PVAc Blends

Sample	T_g (°C)	ΔT_g (°C)	T_{gF} (°C)	w_1' (%)	T_{gk} (°C)
PEMA/PVAc/PVPh2					
1	18.6/6.3/75.1	132.3	29	127.2	56.1
2	12.7/12.6/74.7	129.5	25	123.8	37.5
3	6.3/18.6/75.1	125.0	25	121.0	19.0
4	37.6/12.3/50.1	118.2	29	106.7	37.8
5	25.3/25.0/49.7	111.4	28	100.8	25.0
6	12.6/37.4/50.0	103.0	24	95.7	12.6
7	56.0/18.8/25.2	92.9	27	88.1	18.9
8	37.4/37.4/25.2	81.2	30	80.7	12.6
9	18.8/56.2/25.0	72.7	23	73.4	6.3

ture scanning range was 10–200°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 20 mL/min. In the first thermal scan, the samples stayed at 200°C for 1 min. Then, the samples were cooled to 10°C with a cooling rate of 20°C/min. The inflection point of the specific heat jump of a second thermal scan was taken as T_g . The cooling rate was proven to be fast enough to produce virtually the same results as quenching. ΔT_g was calculated as the difference between the onset and end points of the T_g region.

FTIR spectroscopy

Most of the binary polymer blend samples of PEMA/PVPh and PVAc/PVPh were cast directly onto KBr windows and subjected to thermal treatments similar to those for the DSC samples. For PVPh and some brittle binary samples, the polymer was ground with KBr powder instead to make samples for FTIR studies. A PerkinElmer FTIR 2000 was used in this study. Spectra were obtained for 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

Thermal scans of calorimetry are not shown for brevity. The calculated T_g data are presented in the following section.

PEMA/PVAc blends

Table I presents T_g 's of PEMA/PVAc blends. It is obvious that PEMA and PVAc are not miscible because of the observation of two T_g 's. Taking into account the error of T_g determination, we believe that the blends phase-separated into highly pure PEMA and PVAc phases. ΔT_g values of the PEMA/PVAc blends are listed in Table I for reference.

Binary blends with PVPh by DSC

Figure 1 presents the results of PEMA/PVPh1 and PEMA/PVPh2 blends. For these two blends, a single composition-dependent T_g was detected, indicating miscibility. A positive T_g deviation from the weight average is likely due to hydrogen bonding existing between PEMA and PVPh.

Several empirical equations in the literature have been proposed to describe the composition dependence of T_g of miscible blends that involve strong specific interactions. Because there are only a few data points, the following equation has been chosen to

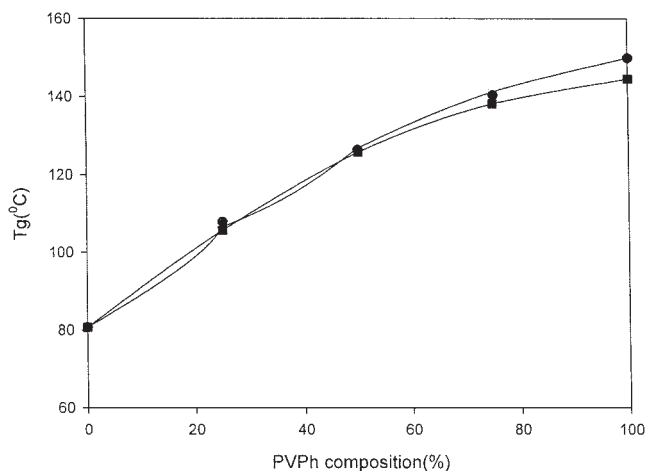


Figure 1 T_g 's of miscible PEMA/PVPh polymer blends: (■) PVPh1 and (●) PVPh2.

describe the experimental data. The simplified Kwei equation is¹⁴

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

where T_g is the glass-transition temperature of a blend and T_{gi} and w_i are the glass-transition temperature and weight fraction of polymer i , respectively ($i = 1$ or 2). q is a parameter that depends on the net polymer-polymer interaction. q values of 50.5 and 45.8 were obtained to describe the parabolic T_g dependence of the PEMA/PVPh1 and PEMA/PVPh2 blends, respectively. Lower molecular weight PVPh1 has a lower T_g than PVPh2 (145°C vs 150°C). According to the magnitude of q , PVPh1 forms stronger hydrogen bonds with PEMA than PVPh2. The result is quite natural because lower molecular weight PVPh has a higher probability for forming hydrogen bonds and thus larger q values.

Figure 2 presents the results of PVAc/PVPh blends. For these two blends (PVAc/PVPh1 and PVAc/PVPh2), a single composition-dependent T_g was also observed, indicating miscibility. The lines shown in Figure 2 represent the weight-average prediction. The weight-average equation is shown as follows:

$$T_g = w_1 T_{g1} + w_2 T_{g2} \quad (2)$$

where T_{gi} , T_{gi} , and w_i have the same meanings as in eq. (1). The T_g 's of the PVAc/PVPh1 and PVAc/PVPh2 blends can be approximately described by the weight-average prediction with some slight deviation.

Binary blends by FTIR

To understand the role of hydrogen bonding operating in the binary blends, FTIR spectra of all the pre-

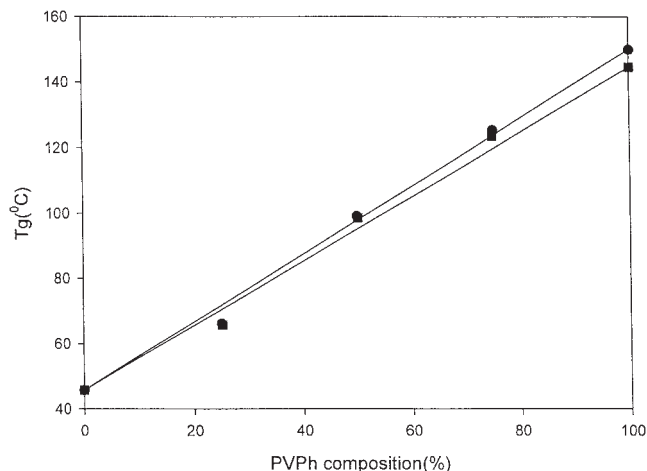


Figure 2 T_g 's of miscible PVAc/PVPh polymer blends: (■) PVPh1 and (●) PVPh2.

pared binary blends were taken. Figure 3 presents the spectra of PEMA/PVAc blends. The free carbonyl absorption peaks of PEMA and PVAc are located at 1727 and 1737 cm^{-1} , respectively. The blends (as represented in Fig. 3) did not indicate any interaction between PEMA and PVAc. Because the results for the PVPh2 blends are similar to those for the PVPh1 blends, the spectra of PVPh1/PEMA and PVPh1/PVAc are used as representations. PVPh did not show any observable feature in this region and is therefore

not included in Figures 4 and 5. A hydrogen-bonded carbonyl peak was detected at 1705 and 1714 cm^{-1} in Figures 4 and 5, respectively, for the two studied blends. This indicates that PVPh1 formed hydrogen bonds with PEMA and PVAc, respectively. On the basis of approximately the same peak shift between free and hydrogen-bonded carbonyl groups observed in PEMA/PVPh and PVAc/PVPh blends (22 vs 23 cm^{-1}), the strength of inter-hydrogen bonding between PVAc and PVPh is similar to that between PEMA and PVPh. These findings are in agreement with the literature.⁹ Zhang et al.⁹ reported that the interassociation constant between PEMA and PVPh is 37.5 (ca. the same as that between PMMA and PVPh). For PVAc and PVPh, the estimated interassociation constant is 57.5. The magnitude of this constant symbolizes the strength of inter-hydrogen bonding. On the basis of the magnitude of these constants, the inter-hydrogen bonding between PVAc and PVPh is stronger but similar in strength to that between PEMA and PVPh. The hydroxyl group absorption of the FTIR spectra is not shown here. PVPh1 and PVPh2 showed almost the same broad peak, which indicated that the degree of self-association of PVPh segments was about the same. It is observed here that the effect of self-association is minimal in the blends and the dominant factor in the blends is inter-hydrogen bonding.

Because PVPh forms hydrogen bonds with both PVAc and PEMA, PVPh can be used as a cosolvent to

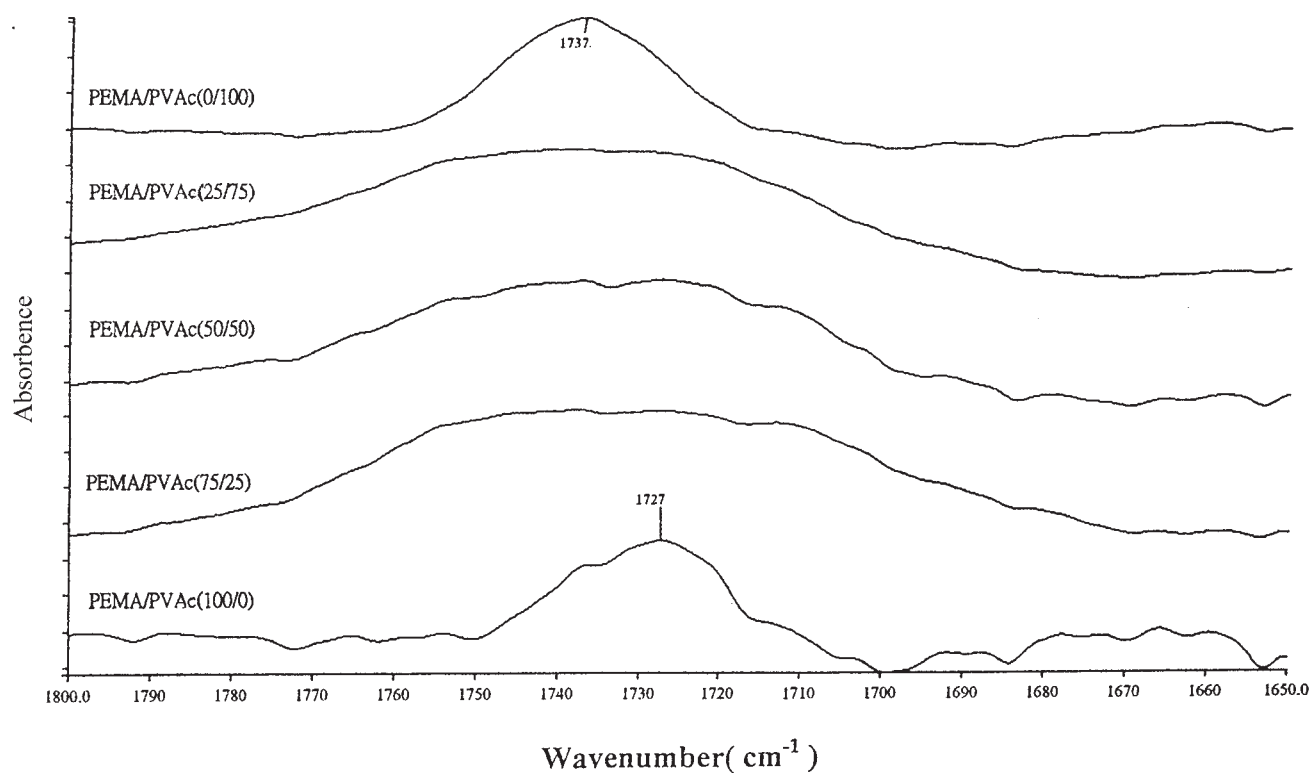


Figure 3 FTIR spectra of PEMA/PVAc blends in the carbonyl absorption region (1650–1800 cm^{-1}).

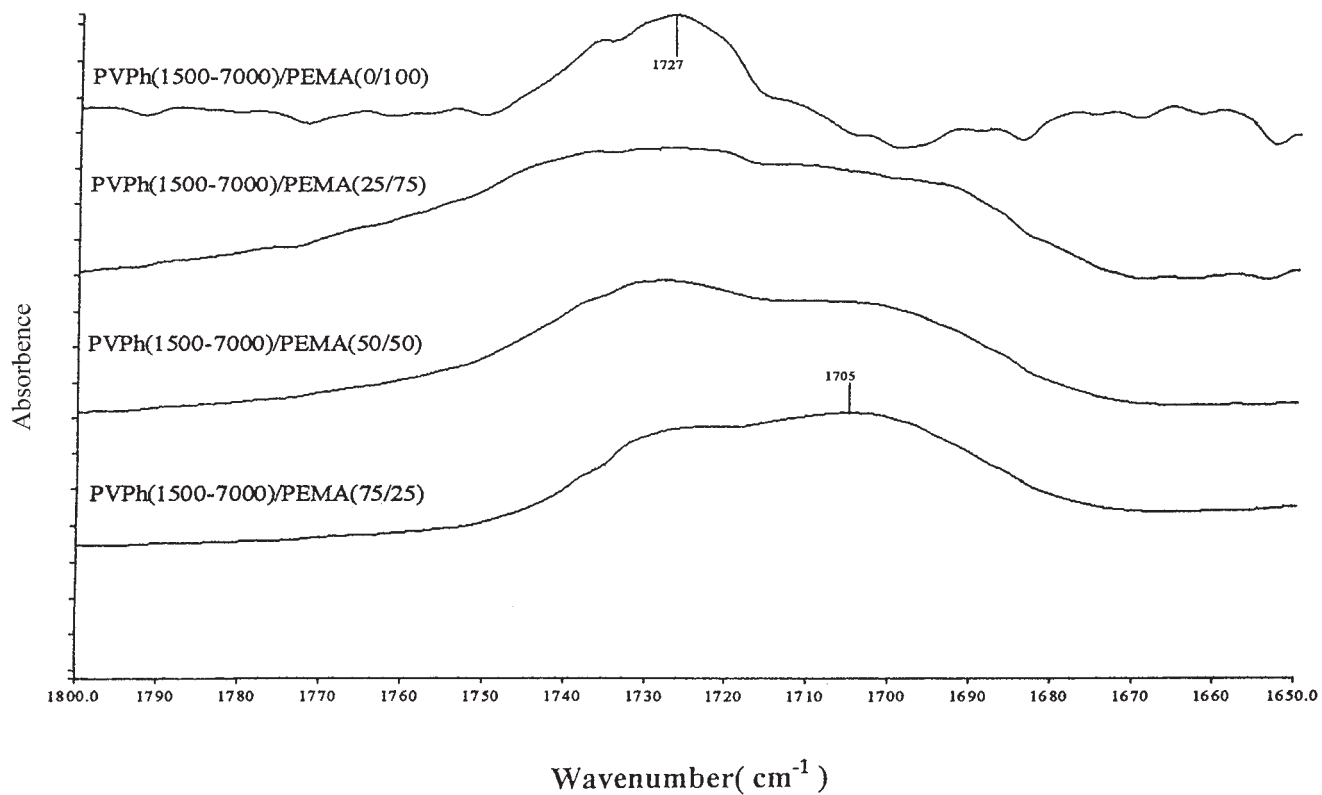


Figure 4 FTIR spectra of PEMA/PVPh1 blends in the carbonyl absorption region (1650–1800 cm⁻¹).

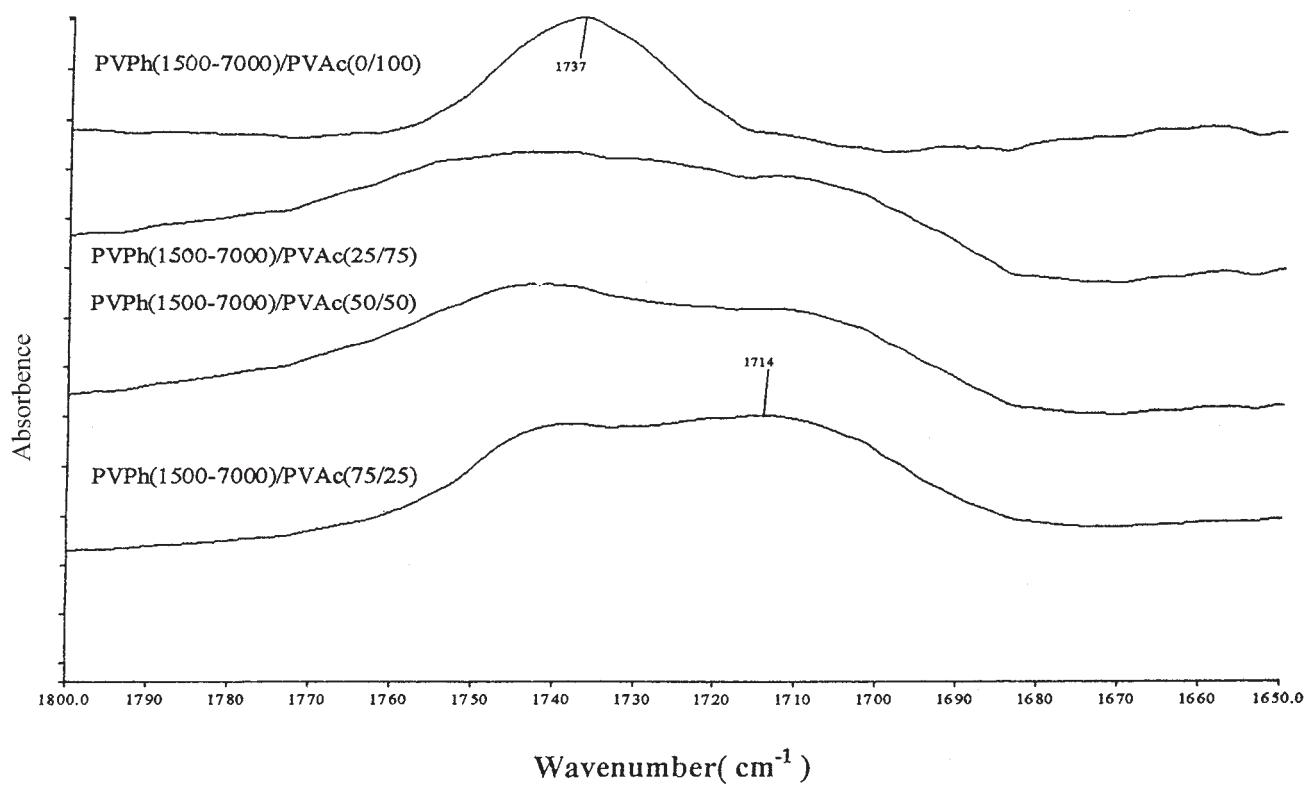


Figure 5 FTIR spectra of PVAc/PVPh1 blends in the carbonyl absorption region (1650–1800 cm⁻¹).

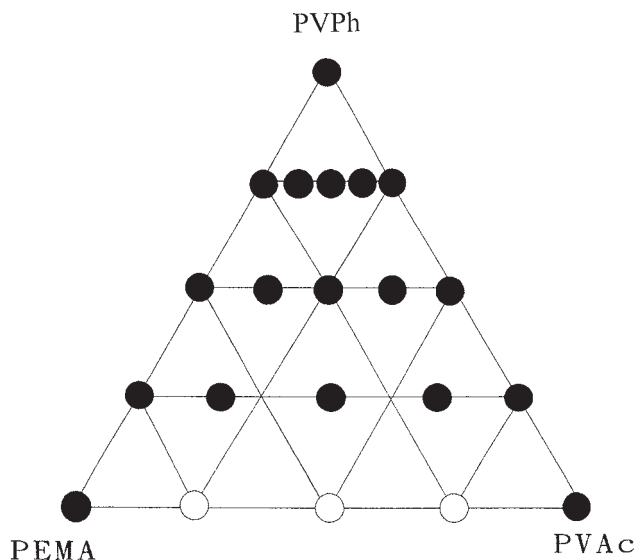


Figure 6 Phase diagram of ternary polymer blends: (●) one T_g and (○) two T_g 's. The numbers in the figure indicate approximately the same compositions as those in Tables II and III.

cosolubilize PEMA/PVAc. In the ternary, PVPh can simultaneously interact with both PVAc and PEMA, enhancing the miscibility of PVPh/PVAc/PEMA blends.

Ternary blends

T_g 's of the PEMA/PVAc/PVPh blends are tabulated in Tables II and III in the order of PVPh1 and PVPh2, respectively. All nine studied blend compositions in the two ternaries showed a single T_g indicating miscibility. ΔT_g values of the aforementioned blends are also tabulated in Tables II and III for reference. There is a slight ΔT_g broadening phenomenon observed, and this occurs quite often in multicomponent systems. However, there is no ΔT_g broadening phenomenon detected in previously studied PMMA/PVAc/PVPh blends. With a single T_g as the criterion for miscibility, the phase diagram composed of PEMA, PVAc, and PVPh was established and is shown in Figure 6. The solid and empty circles represent a single T_g and two T_g 's, respectively. Miscibility is encountered in all the studied ternary blends. However, a small immiscibility region encompassing three two- T_g points cannot be ruled out. It is quite possible that at low PVPh concentrations (<25%), the ternary is immiscible. Adopting explanations from the previous study, we find that weak $\Delta\chi$ and ΔK effects are the reasons for the observed miscibility in the PEMA/PVAc/PVPh blends. Because PEMA has a structure similar to that of PVAc, the $\Delta\chi$ effect is not significant. The weak $\Delta\chi$ effect can be reflected by not sizable differences in the polymer solubility parameters. The solubility parameters of

PEMA and PVAc have been reported to be 8.9 and 9.6 $\text{cal}^{1/2} \text{cm}^{-3/2}$, respectively.⁹ A weak ΔK effect is substantiated by the similar magnitude of interaction observed in both PEMA/PVPh and PVAc/PVPh blends on the basis of FTIR spectra.

For polymer blends with weak or no interaction, the Fox equation seems to predict T_g quite well. The T_g values of the ternary blends (designated T_{gF}) were estimated with PEMA, PVAc, and PVPh T_g 's in an extended equation for the ternary¹⁵ (i.e., $1/T_g = w_1/T_{g1} + w_2/T_{g2} + w_3/T_{g3}$). The outcome is shown in Tables II and III. For 25% PVPh1 (or PVPh2), the experimental T_g values ($T_g < 100^\circ\text{C}$) are close to the Fox prediction. However, for 50% or more PVPh, the experimental T_g values are higher than Fox predictions. The reason may be the ternary with 50% or more PVPh tends to have a higher degree of hydrogen bonding. This high degree of hydrogen bonding likely contributes to a large experimentally observed T_g value. Although the molecular weight of PVPh1 is lower than that of PVPh2, their T_g difference is only 5°C . Regardless of the difference in the T_g values of PVPh, the observed T_g values of the PVPh1 (or PVPh2) ternary are quite consistent. The reason is probably that PVPh1 has a more favorable interaction with PEMA (or PVAc) than PVPh2 compensating the T_g lowering effect caused by a smaller molecular weight.

Attempts were made in a previous study¹³ to predict the miscible ternary T_g values. A similar approach is adopted here. A miscible ternary consisting of a pseudobinary mixture of PEMA/PVPh and PVAc/PVPh entities is assumed. Therefore, the contribution from PEMA/PVAc is neglected because PVPh is acting as a compatibilizer between PEMA and PVAc. The Kwei equation is modified as shown for the ternary:

$$T_g = w_1 T_{g1} + w_2 T_{g2} + w_3 T_{g3} + q_{12} w_1' w_2 + q_{13} w_1'' w_3 \quad (3)$$

where T_g is the glass-transition temperature of a blend and T_{gi} and w_i are the glass-transition temperature and weight fraction of polymers i , respectively ($i = 1, 2, \text{ or } 3$). $w_1' + w_1''$ is equal to w_1 , and q_{12} and q_{13} represent the binary interaction parameters between different corresponding components. Components 1, 2, and 3 denote PVPh, PEMA, and PVAc, respectively. The q_{12} values obtained previously in binary blends are 50.5 and 45.8 for PVPh1/PEMA and PVPh2/PEMA, respectively. Because T_g of PVAc/PVPh blends showed little deviation from the weight average, $q_{13} \approx 0$. Therefore, the contribution of the last term in eq. (3) is neglected. w_1'/w_1'' is likely a function of w_2 , w_3 , q_{12} , and q_{13} . The tentative simplification is to set w_1'/w_1'' equal to w_2/w_3 because the PEMA/PVPh interaction and the PVAc/PVPh interaction are not very different. The modified Kwei glass-transition temperature (T_{gk})

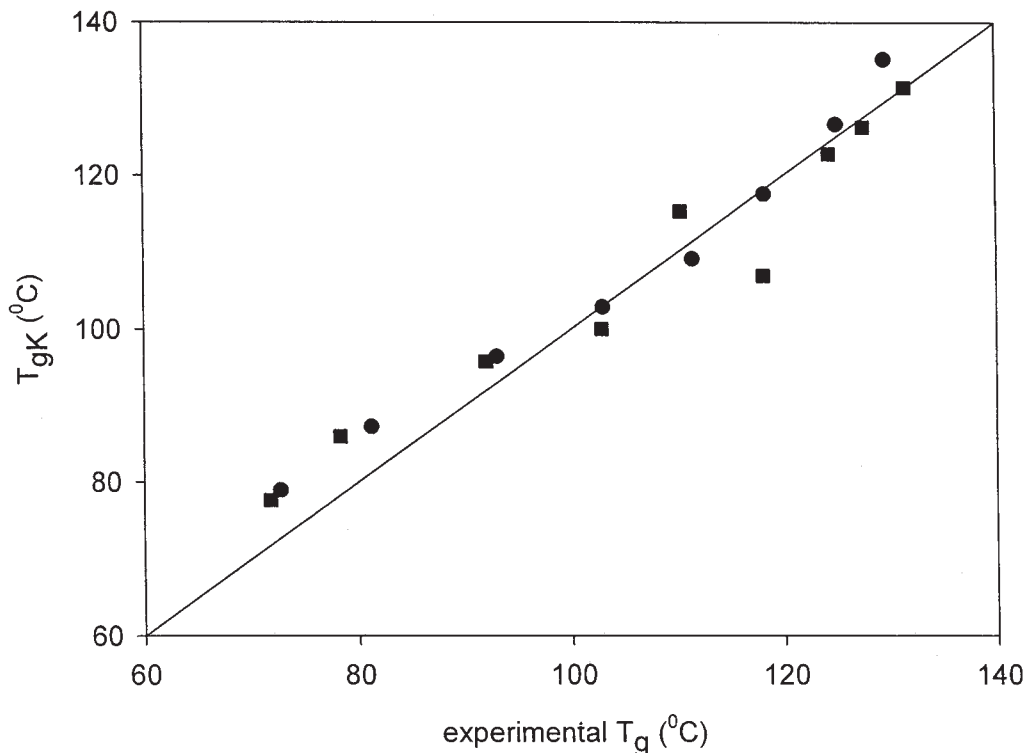


Figure 7 Predicted T_{gk} versus experimental T_g : (■) PVPh1 and (●) PVPh2.

values estimated through eq. (3) are tabulated in Tables II and III with estimated w_1' values. The T_{gk} values predicted by the modified Kwei equation were plotted versus experimental T_g values and are shown in Figure 7. The straight line represents when experimental T_g values are equal to T_{gk} . The agreement between the T_{gk} values and experimental results are almost quantitatively good and are much better than previous Fox predictions. The difference between the T_{gk} values and experimental results has been calculated to be $3.5 \pm 2.4^\circ\text{C}$, much smaller than $6.3 \pm 3.3^\circ\text{C}$ (i.e., the difference between the Fox predictions and data). The success of the modified Kwei equation provides additional proof for the assumption of a similar interaction in PEMA/PVPh and PVAc/PVPh blends.

CONCLUSIONS

PEMA and PVAc are immiscible. PVPh is miscible with both PEMA and PVAc on the basis of calorimetry data in accordance with the literature. The miscibility between PVAc (or PEMA) and PVPh, driven by inter-hydrogen bonding, has been substantiated by the observation of the hydrogen-bonded carbonyl group absorption in the FTIR spectra. The peak shifts between free and hydrogen-bonded carbonyl group absorption are approximately the same in PEMA/PVPh and PVAc/PVPh blends. Therefore, PVAc or PEMA forms hydrogen bonding of similar strength with PVPh. A ternary blend

consisting of PEMA, PVAc, and PVPh ($M_w = 1500$ – 7000 or 9000 – $11,000$ g/mol) was found to be completely miscible. The miscibility of the ternary was probably driven by the weak $\Delta\chi$ and ΔK effects in concert. The $\Delta\chi$ effect is insignificant because PEMA and PVAc have similar solubility parameters. The weak ΔK effect is caused by a similar magnitude of strength in the inter-hydrogen bonding between PEMA and PVPh and that between PVAc and PVPh. The experimentally observed T_g values of the two ternaries are quite consistent, regardless of differences in the molecular weight of PVPh. The reason is that a more favorable interaction forming between PVPh1 and PEMA (or PVAc) than between PVPh2 and PEMA (or PVAc) compensates the T_g lowering effect caused by the smaller molecular weight of PVPh1. For predicting the T_g values of the studied miscible ternary, a miscible ternary consisting of pseudobinary PEMA/PVPh and PVAc/PVPh entities has been assumed. Two incorporated binary interaction parameters (actually only q_{12} because $q_{13} \approx 0$) enable the Kwei equation to successfully predict the T_g 's of miscible ternaries. The assumption of a similar interaction existing in PEMA/PVPh and PVAc/PVPh seems approximately good as demonstrated by the success of the modified Kwei equation.

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