

Miscibility Enhancement on the Immiscible Poly (vinyl pyrrolidone) and Poly (ethyl methacrylate) with Poly (vinyl phenol)

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ABSTRACT: The miscibility behavior of ternary blends of poly (vinyl phenol) (PVPh)/poly (vinyl pyrrolidone) (PVP)/poly (ethyl methacrylate) (PEMA) was investigated mainly with calorimetry. PVPh is miscible with both PVP and PEMA on the basis of the single T_g observed over the entire composition range. FTIR was used to study the hydrogen bonding interaction between the hydroxyl group of PVPh and the carbonyl group of PVP and PEMA at various com-

positions. Furthermore, the addition of PVPh is able to enhance the miscibility of the immiscible PVP/PEMA and eventually transforms it into a miscible blend, especially when the ratio between PVP/PEMA is 3:1, probably because of favorable physical interaction. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1205–1213, 2006

Key words: ternary blends; miscibility, PEMA; PVPh

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) (PVDF) to the immiscible pair poly (methyl methacrylate) (PMMA)/poly (ethyl methacrylate) (PEMA) was studied and the pair was found to be miscible. The list of investigated ternary has been enlarged considerably since then.^{2–8} Nearly, in 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.

Zhang et al.⁹ 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 strong specific interactions (hydrogen bonds) are present, one might reasonably presume that immiscible binary blends might be well “homogenized” 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.

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TABLE I
Glass-Transition Temperatures of PVP/PEMA Blends

PVP/PEMA	T_g (°C)	ΔT_g (°C)
(100/0)	180.8	25
(75.0/25.0)	79.8, 168.9	9, 19
(50.0/50.0)	76.4, 176.0	10, 13
(25.1/74.9)	77.1, 176.3	15, 12
(0/100)	77.0	15

an M_w value of 55,000 g/mol. In this study, PEMA, instead of PMMA, was used to blend with PVP. The preliminary results indicated that PEMA and PVP were not miscible. The results were not unexpected, since PEMA is highly hydrophobic and PVP is highly hydrophilic. Poly (vinyl phenol) (PVPh) was known to be miscible with PEMA^{11,12} and PVP.^{13,14} The second part of this investigation was focused on using PVPh as a potential cosolvent to homogenize PEMA/PVP mixture. A ternary blend composed of PEMA, PVP, and PVPh was prepared and measured calorimetrically. Fourier transform infrared spectroscopy (FTIR) was used to study the interhydrogen bonding between PVPh and PEMA (or PVP). Factors influencing the miscibility of a ternary blend such as the ratio between PEMA and PVP and the amount of PVPh were investigated and discussed in terms of physical ($\Delta\chi$) and chemical (ΔK) interactions between the component polymers.

EXPERIMENTAL

Materials

PEMA and PVP used for this study were obtained from Aldrich Chemical Company, Inc., Milwaukee, WI. According to the supplier information, the number-average molecular weight (M_n) and weight-average molecular weight (M_w) of PEMA were 126,000 and 340,000 g/mol, respectively. PVP had an M_w value of 55,000 g/mol. PVPh with an M_w value of 30,000 g/mol was purchased from Polysciences, Inc., Warrington, PA.

Film preparation

Thin films of binary blends in different weight ratios (~3/1, 1/1, and 1/3) were made by solution casting onto glass plates. *N,N*-Dimethyl formamide (DMF) was used as the solvent for all the blend compositions. DMF is of reagent grade, purchased from Riedel-de Haën Germany Laboratory Chemicals. Thin films of ternary blends of PEMA, PVP, and PVPh were made in several weight ratios. The weight ratios were designed in such a way that the ratios between PEMA and PVP were fixed at 3/1, 1/1, and 1/3. Then, the amount of PVPh was added increasingly from 25% to

75% at a 25% interval. PVPh is known to form complex with PVP. In this study, PEMA was first blended with PVPh. Then, the following day, PVP was added to minimize the effect of complexation. The final drying step for all the films took place in a vacuum oven at 131–137°C for 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) study.

Differential scanning calorimetry

Glass-transition temperatures (T_g 's) of the polymer blends were determined with a DuPont 2000 thermal analyzer coupled with a mechanical cooling system. The experiments were performed in two consecutive scans from 30°C to 300°C in the ambient environment of nitrogen gas at a flow rate of 90–110 mL/min. At the end of the first thermal scan, the samples were kept at 300°C for 1 min. The samples were then cooled to 30°C at a cooling rate of 20°C/min and were scanned the second time. A heating rate of 20°C/min was used in each scan. 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 T_g .

Fourier transform infrared spectroscopy

The samples were prepared in two different methods. One is that the polymer was ground with KBr powder to make a disk-like sample. The other method is to cast the samples directly onto KBr windows. Then, all the prepared samples were subjected to thermal treatments similar to those for the DSC samples. Spectra were obtained on the aforementioned prepared samples with 64 scans at a resolution of 4 cm⁻¹ at room temperature with a Perkin-Elmer FTIR 2000. The wave-number range was 400–4000 cm⁻¹.

RESULTS AND DISCUSSION

For brevity, the thermal scans of the binary and ternary polymer blends are omitted in this presentation.

TABLE II
Phase Compositions of PVP/PEMA Blends

PVP/PEMA	w_1' (W) (%)	w_1'' (W) (%)
W_{1T}/W_{2T} (%)		
75.0/25.0	94.8 (77.7)	6.1 (22.3)
50.0/50.0	100 (50.0)	0 (50.0)
25.1/74.9	98.1 (25.3)	0.2 (74.7)

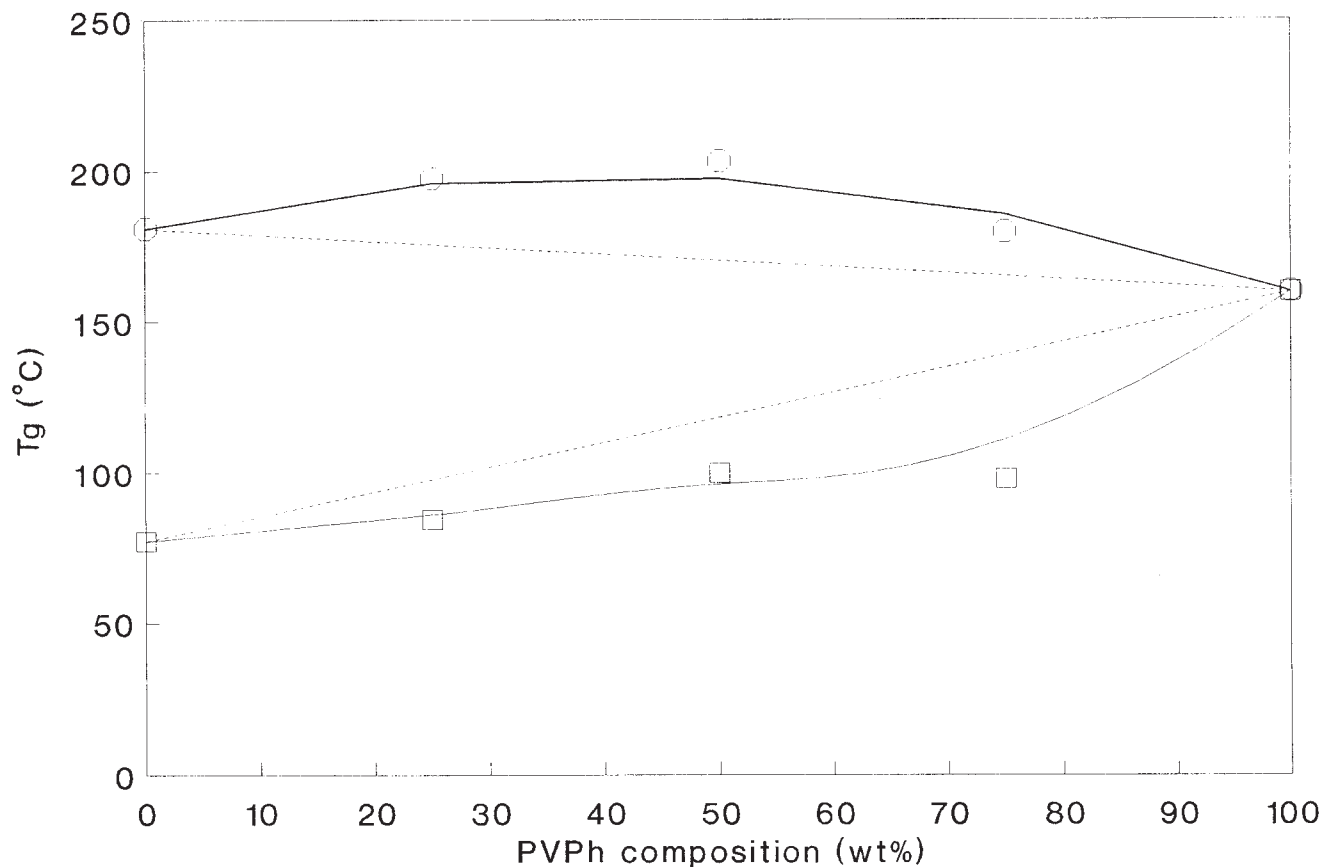


Figure 1 Glass-transition temperatures of PVPh binary blends. (○), PVP/PVPh; (□), PEMA/PVPh; (—), the Kwei equation.

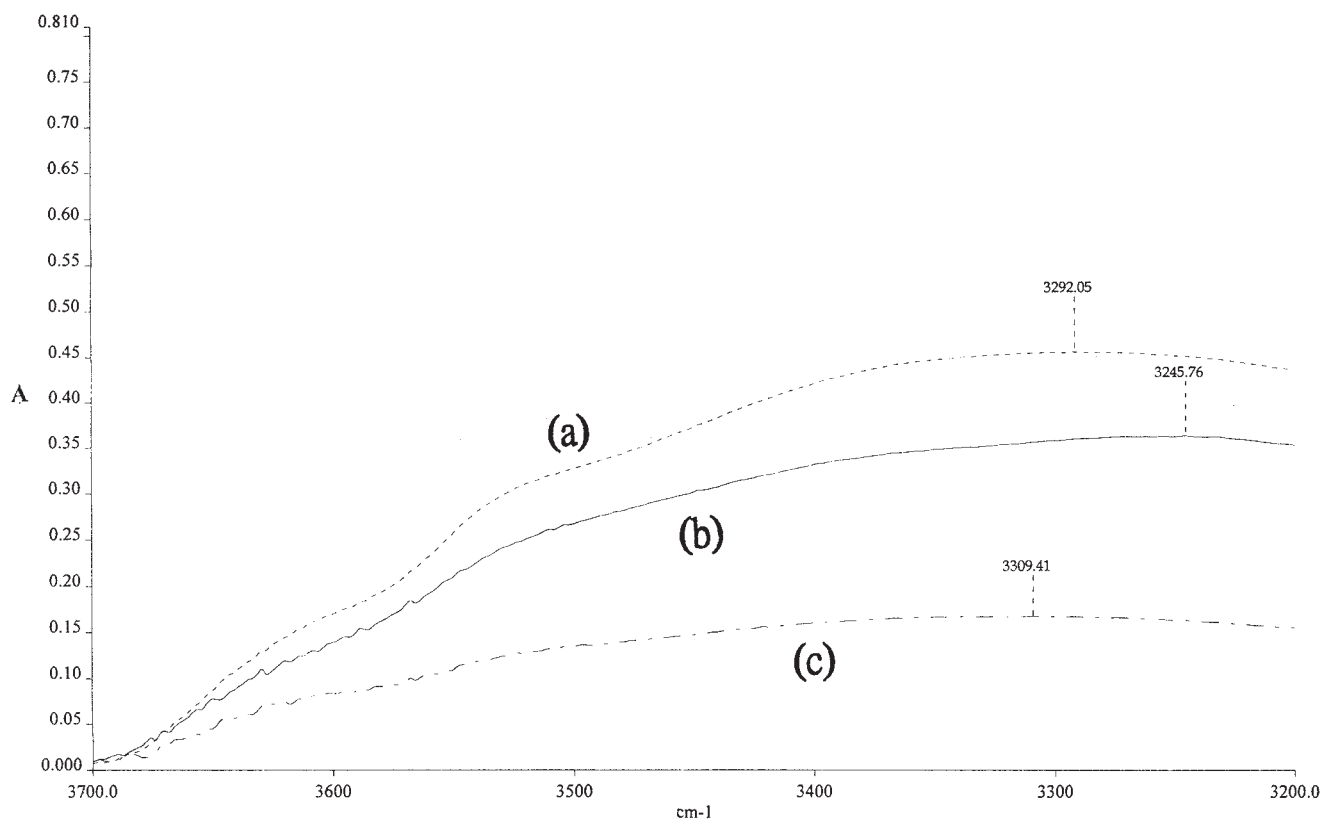


Figure 2 FTIR spectra of PVP/PVPh blends at the 3200–3700 cm^{-1} region. PVP/PVPh ratio: (a) 50.0/50.0; (b) 25.1/74.9; and (c) 0/100.

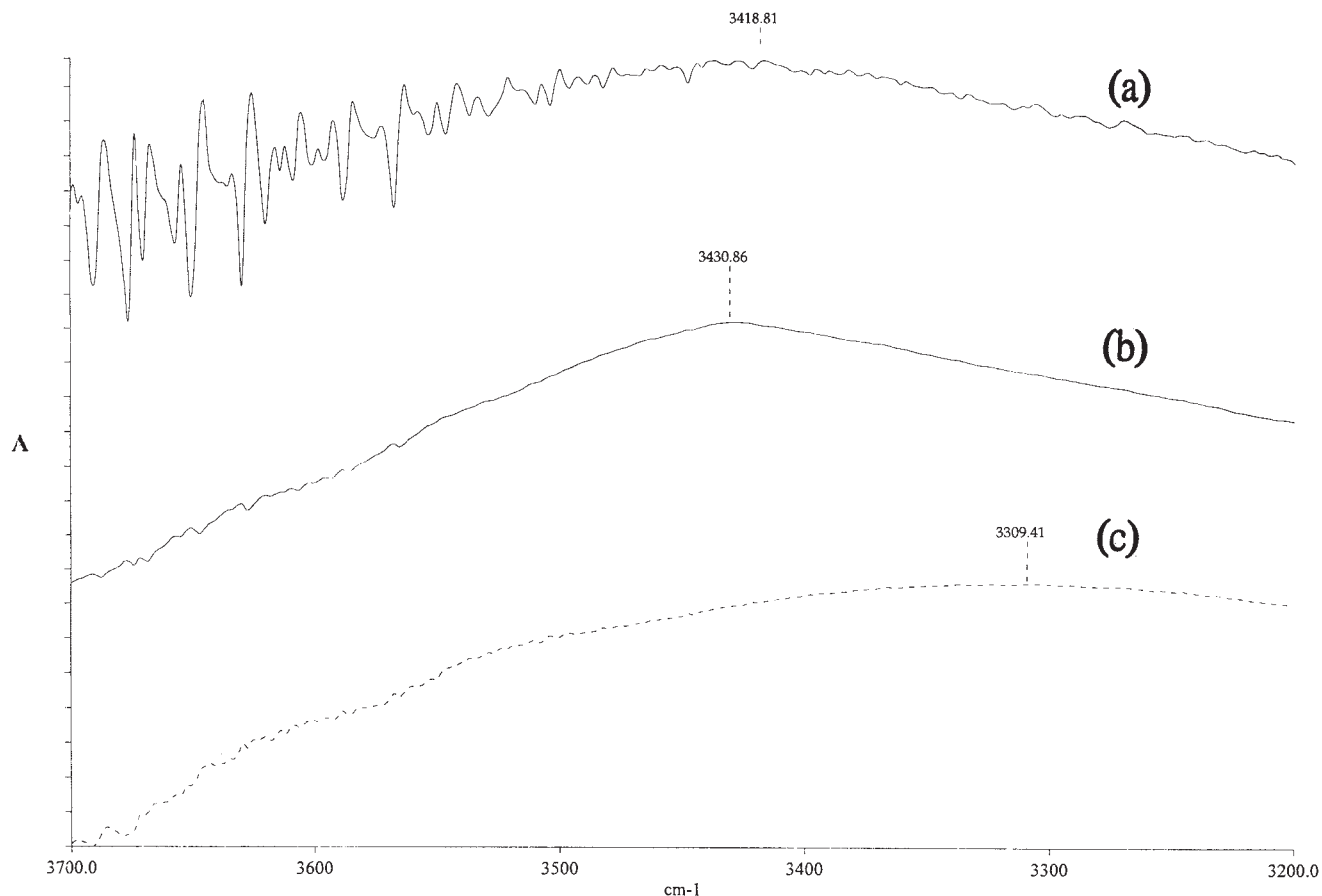


Figure 3 FTIR spectra of PEMA/PVPh blends at the 3200–3700 cm^{-1} region. PEMA/PVPh ratio: (a) 75.0/25.0; (b) 25.1/74.9; and (c) 0/100.

PVP/PEMA blends

Table I presents the glass-transition temperatures (T_g 's) of PVP/PEMA blends. As two T_g 's were observed, it is obvious that PVP and PEMA are not miscible. With the error in T_g determination, it was found that the blends phase separated into PVP-rich and PEMA-rich phases. The solubility parameters of PEMA⁹ and PVP¹⁵ are reported to be 8.9 and 11.0 $\text{cal}^{1/2} \text{cm}^{-3/2}$, respectively. The $\Delta\chi$ effect is strong between PEMA and PVP because of significant differ-

ence in solubility parameters. ΔT_g values of the PVP/PEMA blends are listed in Table I for reference.

Estimations of the compositions of these two phases of the PVP/PEMA blends were attempted and illustrated as the following. If the T_g of PEMA-rich phase is equal to or slightly lower than that of PEMA, the phase is considered to be 100% PEMA. If T_g is located between PVP and PEMA, its composition was estimated from the Fox equation¹⁶ shown below as in eq. (1)

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

where w_1 and w_2 represent the weight fractions of the components, and T_g , T_{g1} and T_{g2} are the T_g 's of the blend and components 1 and 2, respectively. Although the Fox equation was derived for and is often used in miscible blends, attempts made here for immiscible blends were a qualitative estimation. Equation (1) can be rearranged to

$$w_1' = T_{g1}(T_{g1,b} - T_{g2}) / (T_{g1,b}(T_{g1} - T_{g2})) \quad (2)$$

where w_1' is the apparent weight fraction of PVP in the PVP-rich phase, $T_{g1,b}$ is the observed T_g of PVP-rich phase. Similarly, eq. (1) can also be rearranged to

TABLE III
Glass-Transition Temperatures of Ternary Blends

PVPh/PVP/PEMA	T_g ($^{\circ}\text{C}$)	ΔT_g ($^{\circ}\text{C}$)
25.0/56.2/18.8	204.3	19
25.0/37.5/37.5	81.7, 214.5	5, 15
25.0/18.8/56.2	85.2, 219.9	9, 7
50.0/37.5/12.5	205.1	21
50.0/25.0/25.0	78.2, 191.6	12, 12
50.0/12.5/37.5	82.1, 203.6	10, 9
75.0/18.8/6.2	178.6	19
75.0/12.5/12.5	113.8, 177.1	21, 21
75.0/6.2/18.8	127.3, 165.4	27, 15

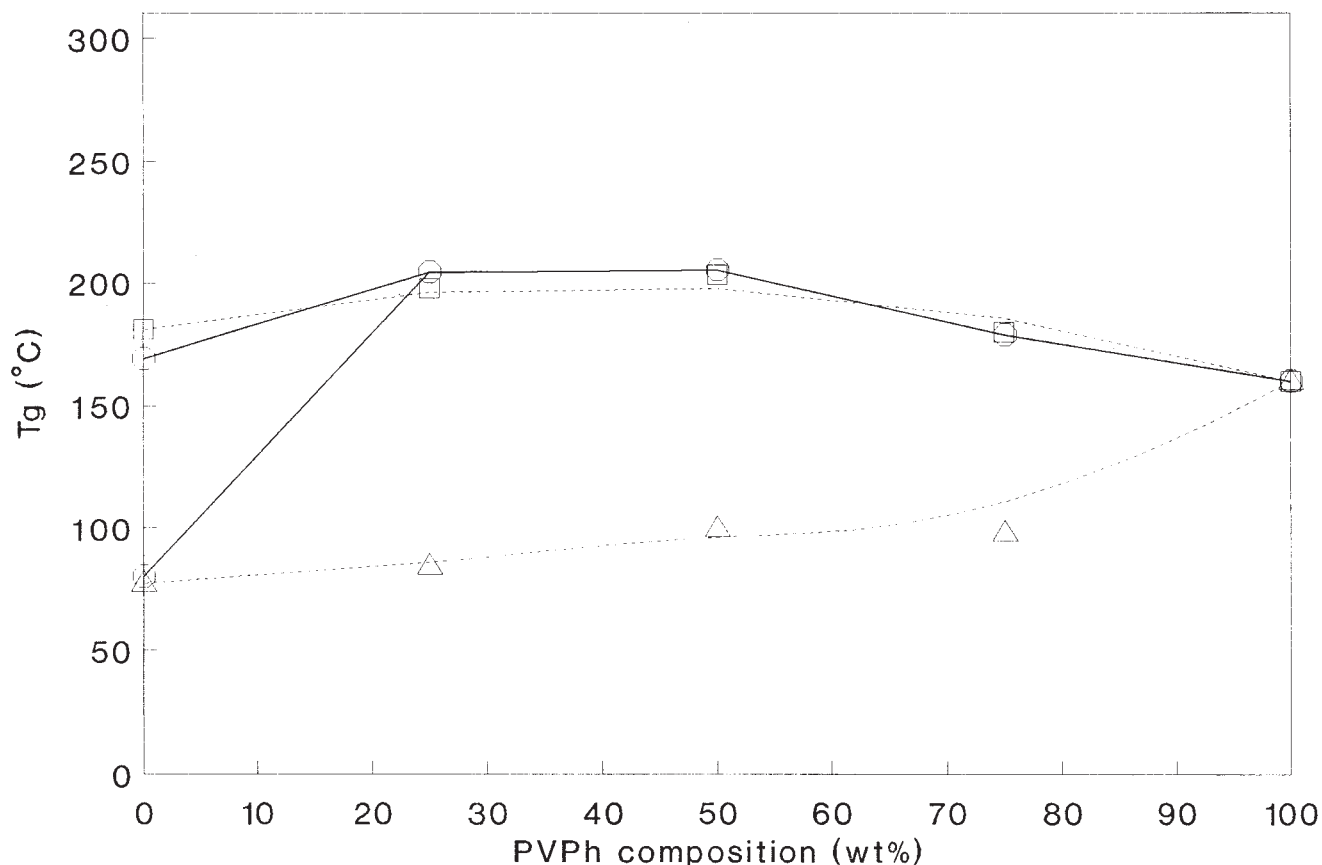


Figure 4 Change of T_g of the ternary blends with PVPh composition (PVP/PEMA weight ratio = 3/1). (○), data point; (△), PEMA/PVPh; (□), PVP/PVPh (curves drawn for viewing).

$$w_1'' = T_{g1}(T_{g2,b} - T_{g2}) / (T_{g2,b}(T_{g1} - T_{g2})) \quad (3)$$

where w_1'' is the apparent weight fraction of PVP in the PEMA-rich phase, $T_{g2,b}$ is the observed T_g of PEMA-rich phase.

By applying eqs. (2) and (3) to the T_g values of PVP/PEMA blends, the apparent weight fractions of PVP in the PVP-rich phase (w_1') and in the PEMA-rich phase (w_1'') were calculated. The results are tabulated in Table II. All the three blends behave similarly and phase separate into PVP-rich phase with PVP composition of 94.8–100% and PEMA-rich phase with 0–6.1% PVP composition. If the estimated value is taken literally, the mutual solubility between PVP and PEMA is the highest when PVP/PEMA ratio is 3/1.

The overall weight fraction of PVP-rich phase (W') and PEMA-rich phase (W'') is calculated by the following material balance equations:

$$W_{1T} = w_1'W' + w_1''W'' \quad (4)$$

$$W_{2T} = w_2'W' + w_2''W'' \quad (5)$$

where W_{1T} and W_{2T} are the overall weight fractions of PVP and PEMA for blending, respectively, and w_1'

and w_2' are obtained from eqs. (2) and (3), respectively. The W' and W'' values were calculated and are also listed in Table II for reference. When the PVP concentration is increased, higher W' (PVP-rich phase) and lower W'' values (PEMA-rich phase) were observed as expected. The W' value of 77.7% is also an indication of the highest mutual solubility between PVP and PEMA when PVP/PEMA ratio is 3/1.

Binary blends

Figure 1 presents the results of PEMA/PVPh and PVP/PVPh blends. A single T_g behavior was observed in the two studied blends. The T_g values of the PEMA/PVPh blends showed negative deviation from weight average. However, the T_g values of the PVP/PVPh blends displayed an approximately parabolic dependence on composition. PVPh forms miscible blends with PEMA and PVP because of interhydrogen bonding.

Several empirical equations in literature have been proposed to describe the composition dependence of T_g of miscible blends that involve strong specific interactions. Three articles^{17–19} offer theoretical insight into the underlying reason for the experimental obser-

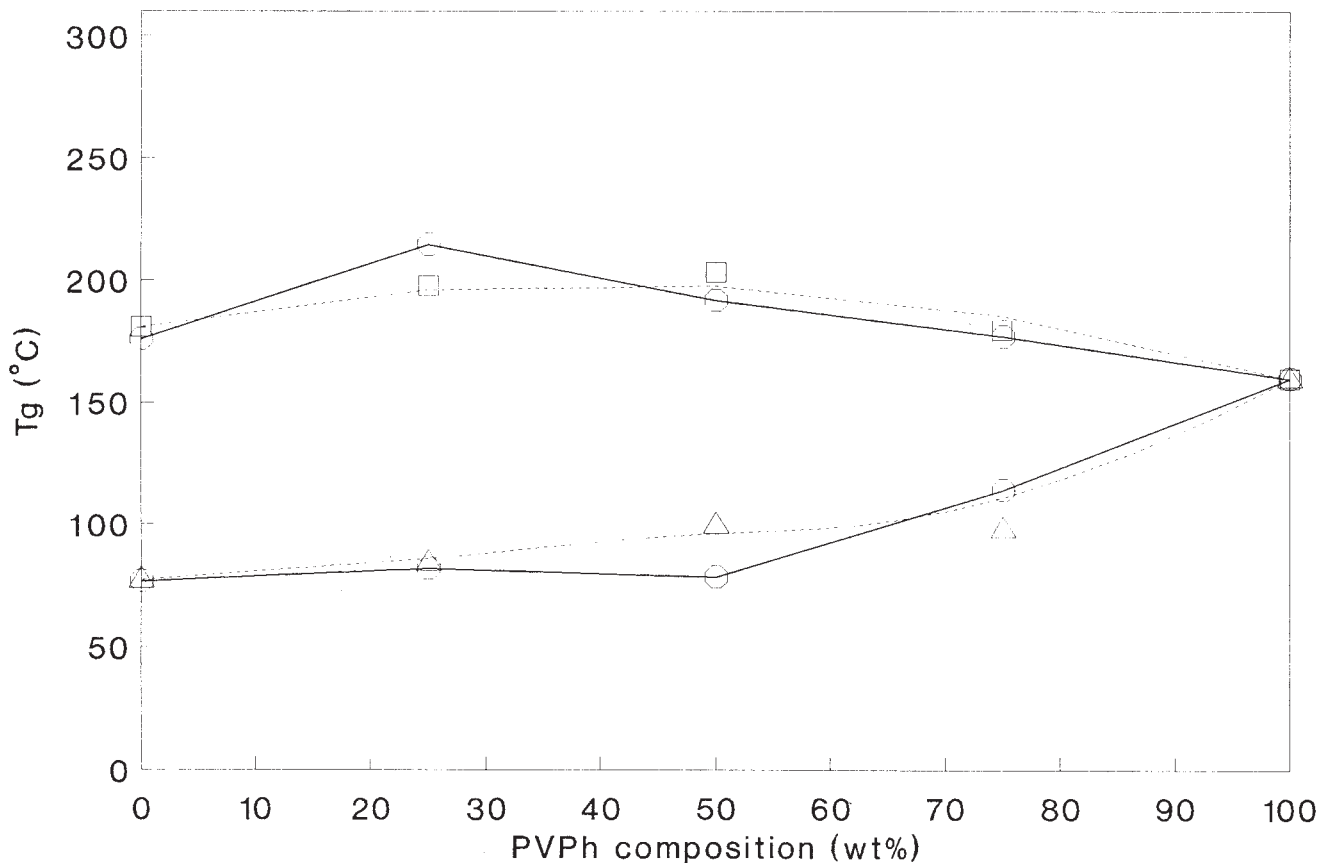


Figure 5 Change of T_g of the ternary blends with PVPh composition (PVP/PEMA weight ratio = 1/1). (○), data point; (△), PEMA/PVPh; (□), PVP/PVPh (curves drawn for viewing).

variations. In the limiting case, these equations reduce to a simple expression²⁰

$$T_g = w_1 T_{g1} + w_2 T_{g2} + qw_1 w_2 \quad (6)$$

where w_1 , w_2 , T_{g1} , T_{g2} , and T_{g2} have the same meaning as in eq. (1) and q is a parameter corresponding to the strength of interaction between polymers 1 and 2. A q value of 109.1 (shown as solid line in Fig. 1) was found to describe the experimental T_g values of the PVP/PVPh blends reasonably well. A very large q value indicates extremely strong interaction between PVP and PVPh. Actually, PVP formed complexes with PVPh.

On the basis of T_g deviation from weight average and large q value, the interaction between PVP and PVPh is much stronger than that between PEMA and PVPh.

FTIR spectra

FTIR spectra of the binary blends were carried out to detect possible interaction existing between the polymers. In the following spectra, A in the ordinate axis represents absorbance. The spectra of PVP/PEMA

blends at their carbonyl absorption region were not presented here. The carbonyl absorption peaks of PEMA were at 1716–1727 cm^{-1} , indicating a very weak interaction between PEMA and PVP. PVP carbonyl absorption peak was lower than 1682 cm^{-1} reported by Moskala et al.¹⁴ because of water absorption.

The FTIR spectra of PVP/PVPh blends in the hydroxyl absorption are shown in Figure 2. For PVPh, there is one broad peak centered at 3309 cm^{-1} indicative of extensively hydrogen-bonded hydroxyl groups. This is entirely consistent with self-association of the polymer chains through intermolecular hydrogen bonding of the hydroxyl groups. There should likely be some unassociated (free) hydroxyl groups present in the PVPh shown as a shoulder at higher frequencies ($>3500 \text{ cm}^{-1}$) but not clearly observed here. When PVP is added to PVPh, the carbonyl group of PVP also will form hydrogen bonds with the hydroxyl groups of PVPh. Therefore, in the blends of PVP and PVPh, hydrogen bonds have two types of interaction, i.e., OH—OH and OH—O=C interactions. Actually, OH—O=C interactions play a major role in making the blends miscible. Figure 2 shows

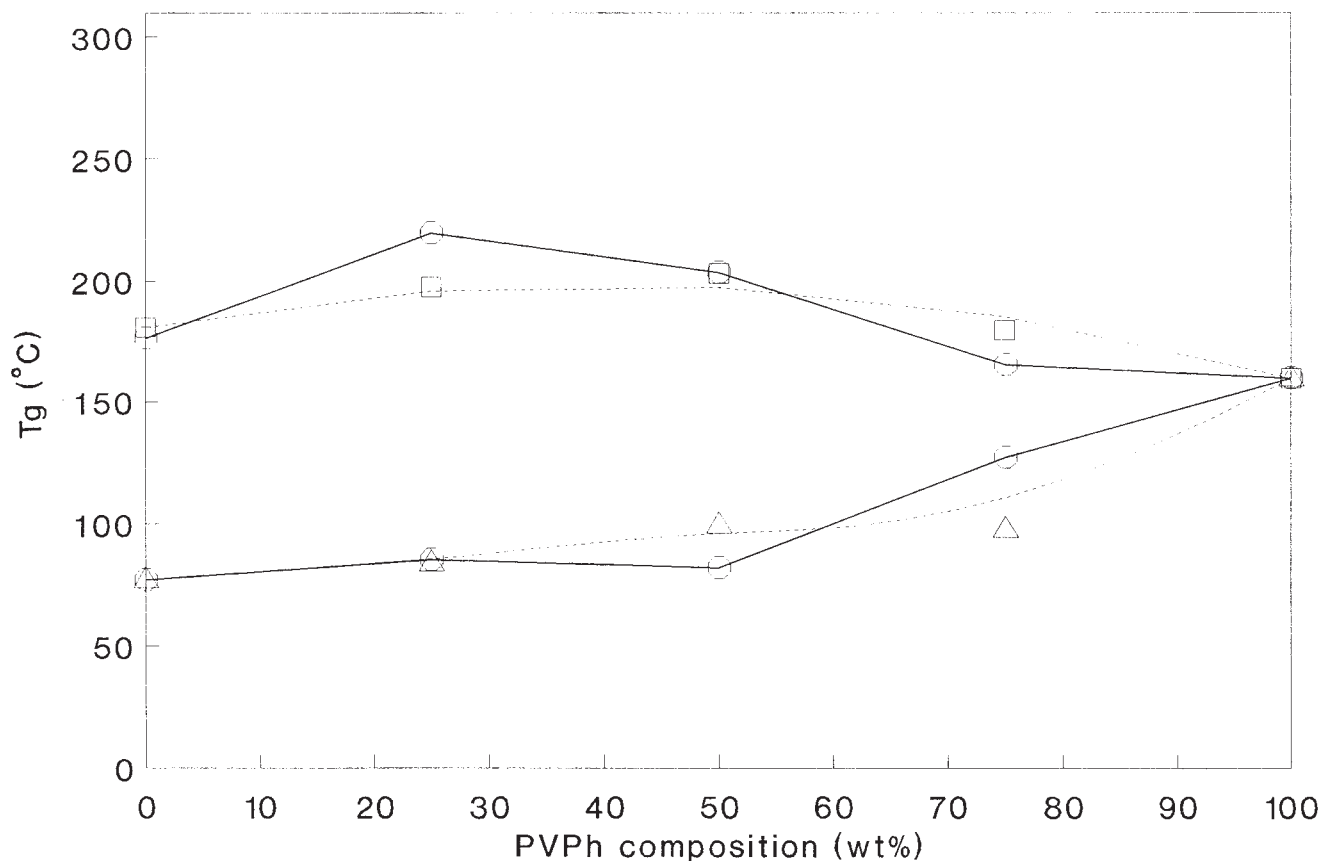


Figure 6 Change of T_g of the ternary blends with PVPh composition (PVP/PEMA weight ratio = 1/3). (○), data point, (△), PEMA/PVPh; (□), PVP/PVPh (curves drawn for viewing).

that, upon mixing with PVP, the broad hydrogen-bonded hydroxyl band of the PVPh (the major peak) was observed to be shifted to lower frequencies mostly. The spectra of ~75% PVP binary was not included because of likely strong water absorption. Judging from the peak shift, interhydrogen bonding (PVP-PVPh) is likely to be generally stronger than self-association (PVPh-PVPh). This finding is more or less in agreement with literature.¹⁴ Moskala et al.¹⁴ demonstrated clearly in their FTIR spectra on PVP/PVPh blends that the frequency of the hydrogen-bonded PVPh hydroxyl occurs at lower frequency (3230 cm^{-1}) than that ascribed to pure PVPh (3360 cm^{-1}). They also could not exclude the effect of moisture. However, on the basis of frequency difference, they concluded that the intermolecular interaction in PVP/PVPh blends is considerably stronger than the self-association of hydroxyl groups in PVPh.

Figure 3 shows the FTIR spectra of hydroxyl absorption of the PEMA/PVPh blends. The absorption peak of PVPh was as aforementioned. Although there were some scatterings in data, the general trend was observed clearly. When PEMA is added to PVPh, the carbonyl groups of PEMA will form hydrogen bonds with hydroxyl groups of PVPh. Similar to PVP, there

are also two types of hydrogen bonds. Figure 3 shows that, upon mixing with PEMA, the broad hydrogen-bonded hydroxyl band of the PVPh (the major peak) was observed to be shifted to higher frequencies as a function of increasing PEMA concentration. On the basis of observation, the interhydrogen bonding (PEMA-PVPh) is weaker than self-association (PVPh-PVPh). However, the interhydrogen bonding still plays a major role in making the blends miscible.

Since PVP-PVPh interaction is stronger than PVPh-PVPh interaction and PEMA-PVPh interaction is weaker than PVPh-PVPh interaction, it can be concluded that the PVP-PVPh interaction is stronger than the PEMA-PVPh interaction. Moskala et al.¹⁴ also observed that the intermolecular interaction in PVP/PVPh blends is considerably stronger than the interaction in PVPh/polyester- and PVPh/acetate-containing polymers.

Ternary polymer blends and phase diagram

Table III presents the glass-transition temperatures of the ternary blends. Three out of the nine studied blends showed single T_g , indicating miscibility. ΔT_g values are included in Table III for reference.

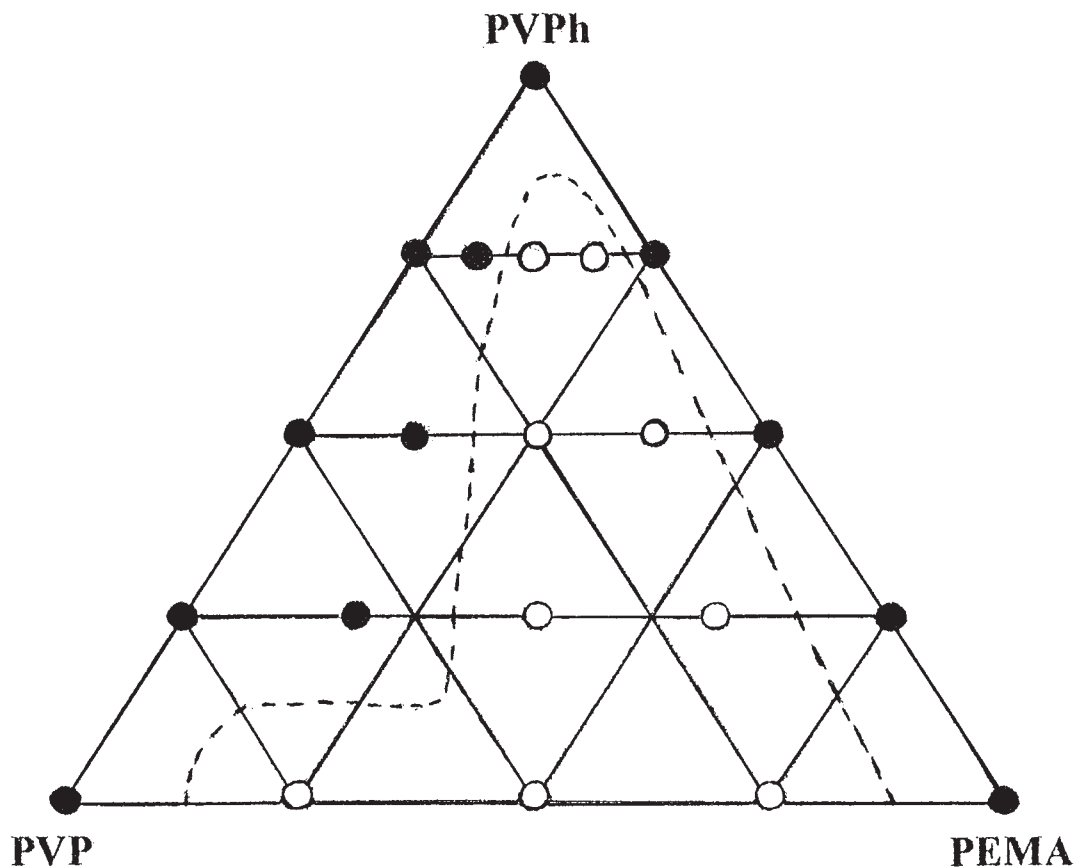


Figure 7 Phase diagram of ternary blends. (●), miscible; (○), immiscible, (—), estimated immiscible region.

For the purpose of illustrating cosolvent effect of PVPh, the T_g values of the ternaries with PVP/PEMA weight ratios of (1 : 3, 1 : 1, and 3 : 1) were plotted in Figures 4, 5, and 6, respectively. Results of the corresponding binaries with PVP and PEMA (taken from Fig. 1) were also presented for comparison. Since the T_g difference between PVP/PVPh and PEMA/PVPh blends with approximately the same PVPh composition is always greater than 60°C , the single T_g criterion for miscibility is justified in our ternary system. For PVP/PEMA (3/1) ternaries (as shown in Fig. 4), the addition of a small amount of PVPh (i.e., 25%) is sufficient to produce a miscible ternary. The T_g values of the miscible ternaries are more or less located between corresponding binaries with the same PVPh composition. For the ternaries with PVP/PEMA (weight ratio = 1/1 and 1/3) (as demonstrated in Figs. 5 and 6), two T_g values were always observed indicating immiscibility of the blends. Increasing PVPh composition in the ternaries and more PEMA content in PVP/PEMA cause the two T_g 's of the immiscible ternary to get closer. This indicates possible ternary miscibility when PVPh composition is higher than 75%. The reason for the observed miscibility in the ternaries with PVP/PEMA weight ratio of 3/1 is likely because of slightly better mutual solubility between PVP and PEMA.

By using the single T_g as the criterion for the miscibility, the phase diagram of the ternary blends composed of PVP, PEMA, and PVPh is presented in Figure 7. A postulated phase boundary (shown as the dash line) was established for reference by connecting through middle points between miscibility and immiscibility data. Inside the figure, the solid circles represent single T_g and the empty circles symbolize two T_g 's. An asymmetric immiscibility region is observed in Figure 7. The reason for the ternaries to exhibit immiscibility is likely due to the ΔK effect (stronger interaction between PVPh and PVP than that between PVPh and PEMA). This is in agreement with DSC and FTIR analyses that the interaction between PVPh and PVP is stronger than that between PVPh and PEMA. The ternary with high PVPh and PVP compositions are more likely to be miscible because of favorable physical ($\Delta\chi$) interaction. The favorable physical interaction is because the solubility parameter ($11.0 \text{ (cal/mL)}^{0.5}$) of PVP¹⁵ is close to that ($10.6 \text{ (cal/mL)}^{0.5}$) of PVPh²¹ not to that of PEMA ($8.9 \text{ (cal/mL)}^{0.5}$).²¹ Kuo et al.¹⁵ also observed the miscibility window shifted toward PVP-rich region in a similar ternary blend composed of bisphenol A (BPA)/poly(vinyl acetate) (PVAc)/PVP. In their study, the solubility parameter difference between BPA and PVP is smaller than that of BPA and PVAc. The interassocia-

tion constant in PEMA/PVPh blends is 37.5 according to Zhang et al.⁹ The K value (interassociation constant) between PVP and PVPh is not reported yet to the best of our knowledge. Kuo et al.¹⁵ estimated the interassociation constant between PVP and BPA to be 6000; much larger than that between PVAc and BPA (~ 172). Since PVPh is similar to BPA in structure and PEMA not so different from PVAc, their conclusion may be adopted here. In summary, the observed immiscibility window in our ternary is due to the strong ΔK effect and miscibility in the PVP-rich region is because of favorable $\Delta\chi$ effect.

CONCLUSIONS

The phase behaviors of the ternary blends of PVPh/PVP/PEMA have been investigated with mainly DSC analysis. The addition of PVPh is able to enhance the miscibility of the PVP/PEMA immiscible blend and eventually transforms it into a miscible blend with one single T_g , especially at the ternary with PVP/PEMA (3/1). The experimental results demonstrate the importance of both the effect of physical ($\Delta\chi$) and chemical (ΔK) interactions. The ΔK effect caused by stronger interaction PVPh and PVP than that between PEMA and PVPh is probably the reason for the observed large immiscibility region. In addition, the solubility parameter difference between PVPh and PVP is smaller than that of PVPh and PEMA, revealing that the physical ($\Delta\chi$) interaction is more favorable in the PVPh/PVP blend system. This probably causes the

miscibility window of ternary shifted toward the PVP-rich region.

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