Phase Behavior of Hydrogen-Bonded Ternary Polymer Blends

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ABSTRACT: Although poly(ethyl methacrylate) (PEMA) and poly(methyl methacrylate) (PMMA) are only slightly different in structure, they are known to be immiscible. Polystyrene is not miscible with PEMA or PMMA. However, when polystyrene is modified to contain certain vinyl phenol groups to become poly(styrene-*co*-vinyl phenol) (PSVPh), it can be miscible with both PEMA and PMMA. What is the miscibility of a ternary blend consisting of PEMA, PMMA, and PSVPh? For this question to be answered, binary blends of PEMA (or PMMA) were first made with PSVPh. Their miscibility was examined. Then, ternary blends composed of PEMA, PMMA, and PSVPh were prepared and measured calorimetrically. The role of PSVPh between PEMA and PMMA and the effect of different contents of vinyl phenol groups on the miscibility of the ternary blends were investigated. On the basis of experimental results, increasing the vinyl phenol contents of PSVPh seemed to have an adverse effect on the miscibility of the ternary blends. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 2088–2094, 2003

Key words: phase behavior; blends

INTRODUCTION

Ternary blends have been gaining importance in the field of polymer science through the years. The first systematic study of 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 investigated ternaries has considerably been enlarged since then.[2–8] In nearly all these blends, a third component, either a homopolymer or a copolymer, is added to homogenize an immiscible pair. Miscibility is often achieved in cases in which this third component is miscible with the other polymers.

Recently, Bicakci and Cakmak[9] investigated the phase behavior of binary and ternary blends of poly-(ethylene naphthalate) (PEN), poly(ether imide) (PEI), and poly(ether ether ketone) (PEEK) with differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) techniques. The PEN/PEI and PEI/PEEK binary blends exhibited single glass-transition temperatures (T_g's) over the full composition range, and PEN and PEEK were immiscible, particularly at middle concentrations. When PEI was added to the immiscible PEN/PEEK system, the blends formed two separated PEN-rich and PEEK-rich phases below a PEI concentration of about 40%; above this concentration, the three homopolymers formed a miscible phase in the amorphous state exhibiting a single T_g. An approximate ternary phase diagram was established that was based on the DSC and DMTA results.

PEMA and PMMA are known to be immiscible. According to Coleman et al.,[10] poly(styrene-*co*-vinyl phenol) (PSVPh) with less than 1% vinyl phenol (VPh) was determined to be miscible with both PEMA and PMMA. Additionally, PMMA and PSVPh formed a phase-separated structure when cast from tetrahydrofuran (THF) but were miscible when cast from 2-butanone.[11] Therefore, in this investigation, 2-butanone was used to mix the polymers. PSVPh containing 5 or 15 mol % VPh groups was used to homogenize the immiscible pair PEMA/PMMA. T_g's of the ternary mixtures were determined calorimetrically. An approximate phase diagram of the ternary blends was established on the basis of calorimetry data, and a single T_g was used as the criterion for determining miscibility. The effect of using different hydroxyl group contents of the copolymer and blend composition on the ternary phase diagram was examined and is presented in this article.

EXPERIMENTAL

Materials

PEMA and PMMA of secondary standards were purchased from Aldrich Chemical Company, Inc. (Mil-

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TABLE I
T_g **Values of PEMA/PMMA Blends**

	T_g (°C)	ΔT_g (°C)
PEMA/PMMA		
1. (100/0)	83.4	14
2. (75.0/25.0)	87.6, 122.6	13, 13
3. (50.0/50.0)	85.3, 117.8	12, 12
4. (25.0/75.0)	84.0, 117.3	14, 12
5. (0/100)	118.6	11

The solvent was THF.

waukee, 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. The M_n and M_w values of PMMA were 48,300 and 102,600 g/mol, respectively. The PSVPh used for this study contained 5 or 15 mol % VPh units (designated PSVPh5 and PSVPh 15) and was synthesized with a procedure described previously.[12] M_n and M_w of PSVPh5 were determined by gel permeation chromatography to be 84,900 and 144,300 g/mol, respectively. PSVPh15 had an M_n value of 85,600 g/mol and an M_w value of 125,800 g/mol.

Film preparation

Thin films of the following binary and ternary polymer blends were made via solution casting onto glass plates:

1. PEMA/PMMA by THF.
2. PEMA/PSVPh5 and PEMA/PSVPh15 by 2-butanone.
3. PMMA/PSVPh5 and PMMA/PSVPh15 by 2-butanone.
4. PEMA/PMMA/PSVPh5 and PEMA/PMMA/PSVPh15 by 2-butanone.

The actual compositions of the binary and ternary blends are shown later in Tables I–III. THF and 2-bu-

TABLE II
T_g **Values of 2-Butanone-cast PEMA/PMMA/PSVPh5 Blends**

	T_g (°C)	T_{gF} (°C)	ΔT_g (°C)
PEMA/PMMA/PSVPh5			
1. (12.5/75.0/12.5)	118.5	113.2	12
2. (43.4/43.7/12.9)	115.5	101.9	13
3. (75.0/12.5/12.5)	118.8	91.0	13
4. (37.7/37.6/24.7)	117.1	103.3	15
5. (12.8/49.8/37.4)	111.0	111.8	14
6. (50.0/12.6/37.4)	112.6	98.4	13
7. (25.1/25.1/49.8)	108.0	106.6	15
8. (12.8/12.6/74.6)	110.9	109.9	9

The solvent was 2-butanone.

TABLE III
T_g **Values of 2-Butanone-cast PEMA/PMMA/PSVPh15 Blends**

	T_g (°C)	T_{gF} (°C)	ΔT_g (°C)
PEMA/PMMA/PSVPh15			
1. (12.7/74.5/12.8)	118.8	114.4	10
2. (43.8/43.7/12.5)	92.6, 120.4	—	14, 11
3. (74.9/12.6/12.5)	115.2	92.2	12
4. (37.6/37.5/24.9)	120.3	105.7	10
5. (12.5/50.2/37.3)	121.0	115.7	12
6. (50.0/12.7/37.3)	101.1, 122.5	—	14, 9
7. (24.9/25.1/50.0)	111.0	111.6	27
8. (12.4/12.6/75.0)	119.8	117.6	11

The solvent was 2-butanone.

tanone were American Chemical Society (ACS) reagents purchased from Aldrich Chemical. The final drying step for all the films took place in a vacuum oven at 113–128°C for 15–23 h. Then, the films were cooled to room temperature slowly with air, and this resulted in as-cast samples. The as-cast samples were later used for DSC studies.

DSC

T_g's of the polymer blends were determined with a DuPont 2000 thermal analyzer (Taipei, Taiwan) coupled to a mechanical cooling system. The temperature scanning range was 30–200°C, and a heating rate of 20°C/min was used in every measurement. The experiments were performed in two consecutive scans in the ambient environment of nitrogen gas at a flow rate of 100–110 mL/min. In the first thermal scan, the samples stayed at 200°C for 1 min. Then, the samples were cooled to 30°C at 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. Occasionally, a third thermal scan was performed to confirm the data in the second scan. The cooling rate was proven to be fast enough to produce virtually the same results as quenching.

RESULTS AND DISCUSSION

PEMA/PMMA blends

Table I presents T_g's of PEMA/PMMA blends. It is obvious that PEMA and PMMA were not miscible because of the observation of two T_g's, in agreement with the literature.[1] With the error in T_g determination taken into consideration, it was found that the blends phase-separated into highly pure PEMA and PMMA phases. ΔT_g was calculated as the difference between the onset and end points of the T_g region. The ΔT_g values of the PEMA/PMMA blends are listed in Table I for reference. As mentioned previously, PSVPh with sufficient hydroxyl groups could be miscible with both PEMA and PMMA. Binary
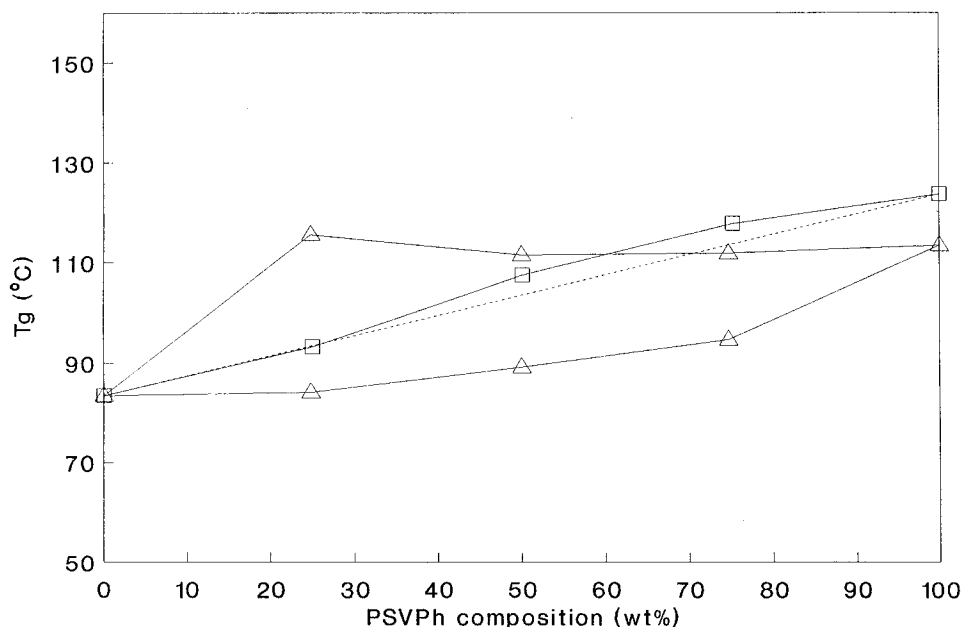
Figure 1 T_g's of 2-butanone-cast PEMA/PSVPh blends: (△) PSVPh5 and (□) PSVPh15.

blends of PEMA (or PMMA) with PSVPh5 (or PS-VPh15) and ternary blends consisting of PEMA, PMMA, and PSVPh were prepared through casting from 2-butanone, and the results are presented in the following section.

Binary and ternary blends

Figure 1 presents the results of PEMA/PSVPh5 and PEMA/PSVPh15 blends. For PEMA/PSVPh5 blends, two T_g's were detected in the studied composition.

Therefore, PEMA and PSVPh5 were still not miscible; this result is different from the prediction of Coleman et al.[10] The reason might be the differences in the molecular weights. However, PEMA and PSVPh15 were found to be miscible on account of the observation of a single T_g. The T_g values of the same blends were mostly above the weight average, indicating strong interhydrogen bonding. For the PMMA/PSVPh blends shown in Figure 2, PMMA formed miscible blends with both PSVPh5 and PSVPh15 because the blends showed single T_g's.
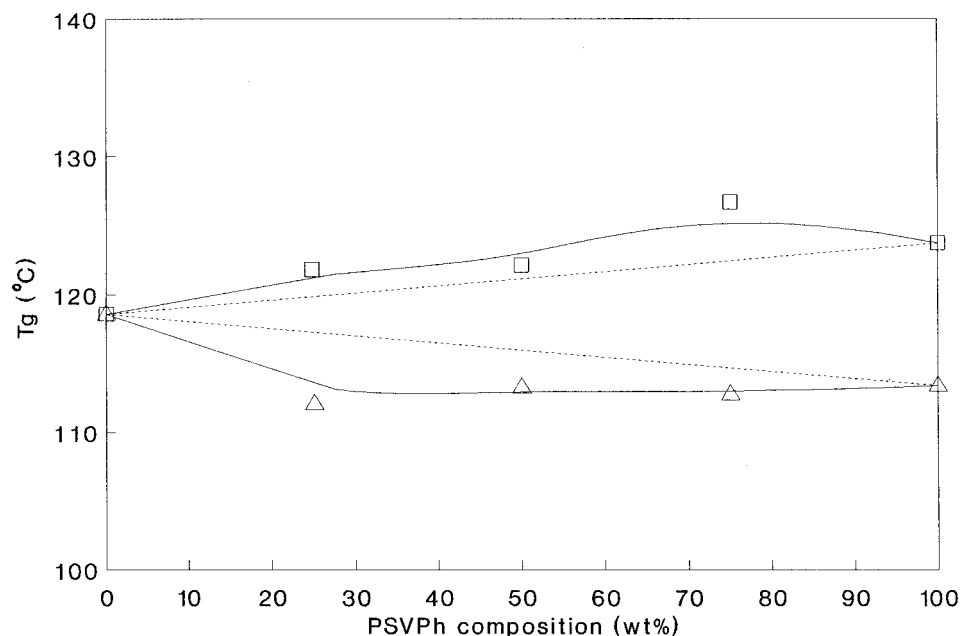

Figure 2 T_g's of 2-butanone-cast PMMA/PSVPh blends: (△) PSVPh5 and (□) PSVPh15.
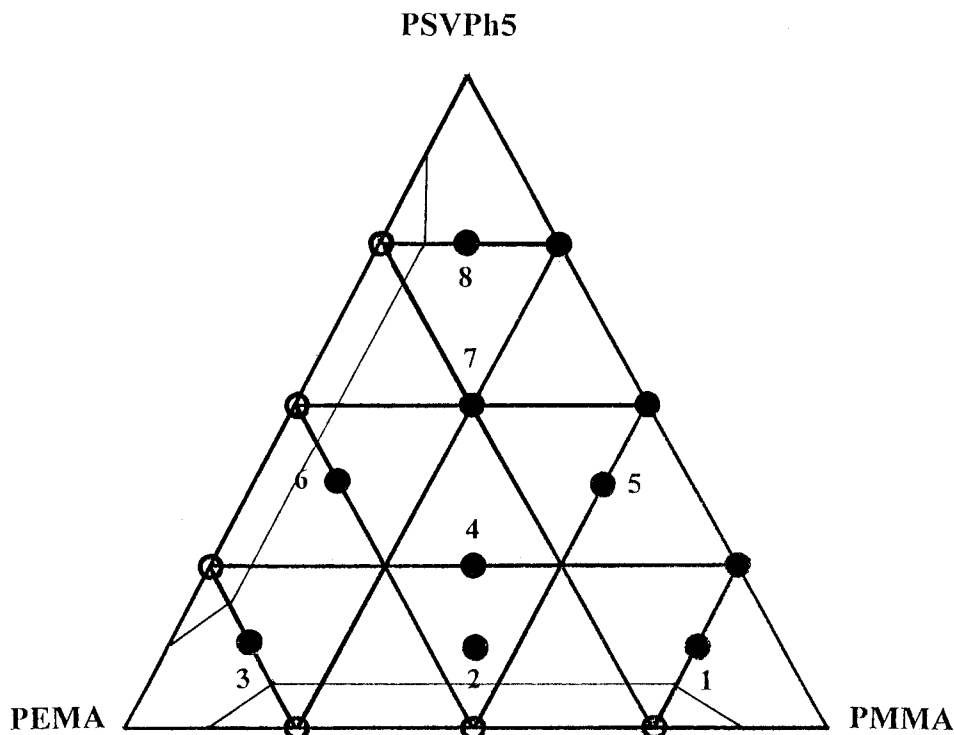
Figure 3 Phase diagram of 2-butanone-cast PEMA/PMMA/PSVPh5 blends: (●) miscible, (○) immiscible, and (—) estimated immiscible regions. The numbers indicate the same compositions listed in Table II.

The T_g's of the PEMA/PMMA/PSVPh5 blends are tabulated in Table II. The eight studied blend compositions all showed a single T_g, which indicated miscibility. However, two of the eight studied compositions of PEMA/PMMA/PSVPh15 blends (as presented in Table III) showed two T_g's; therefore, these two compositions lacked miscibility. The ΔT_g values of the aforementioned blends are tabulated in Tables II and III. For the PEMA/PMMA/PSVPh15 (24.9/25.1/50.0) blends, there was a broadening phenomenon observed that indicated possible microheterogeneity.

With a single T_g as the criterion for miscibility, phase diagrams composed of PEMA, PMMA, and PSVPh5 (or PSVPh15) were established and are shown in Figures 3 and 4. The solid and empty circles represent single T_g's and two T_g's, respectively. Miscibility was encountered in the majority of the studied ternary blends. A postulated phase boundary (shown as solid lines in Figs. 3 and 4) was established for reference by a connection through middle points between miscibility and immiscibility data. Two small immiscibility regions were observed in PEMA/PMMA/PSVPh5 blends. For PEMA/PMMA/PSVPh15 blends, immiscibility often occurred in the blends with a high PEMA content. The reason for this observation is that PSVPh15 formed stronger hydrogen bonds with PMMA than with PEMA. Therefore, when the PEMA concentration in the ternaries was high, phase separation probably easily occurred because of a greater

amount of the not-hydrogen-bonded fraction of PEMA. Pomposo et al.[13] studied a similar ternary blend composed of PEMA, PMMA, and poly(vinyl phenol) (PVPh). PVPh was miscible with both PEMA and PMMA. An approximate ternary phase diagram was established, and a very large immiscibility region was observed. Recently, Coleman et al.[14] also predicted a largely immiscible region in the same ternary with their association model. They concluded that although the presence of intermolecular interactions enhances the probability of forming a homogeneous ternary polymer blend, they can concurrently exacerbate the situation through the ΔK effects working in concert with the $\Delta\chi$ effects, which promote phase separation. The presence of ΔK effects is caused by differences in interassociation equilibrium constants. In our case, the interassociation happened between PEMA (or PMMA) and PSVPh. Because PEMA/PMMA/PSVPh15 had a larger immiscibility region than the PSVPh5 ternary, it was concluded that stronger ΔK effects were likely observed in the PEMA/PMMA/PSVPh15 blends than in the PEMA/PMMA/PSVPh5 blends. The differences in the interactions between PMMA and PSVPh15 and PEMA and PSVPh15 were probably greater than those between PMMA and PSVPh5 and PEMA and PSVPh5.

For the purpose of illustrating the cosolvent effect of PSVPh5 (or PSVPh15), the T_g values of the ternary blends with a PEMA/PMMA weight ratio of about 1
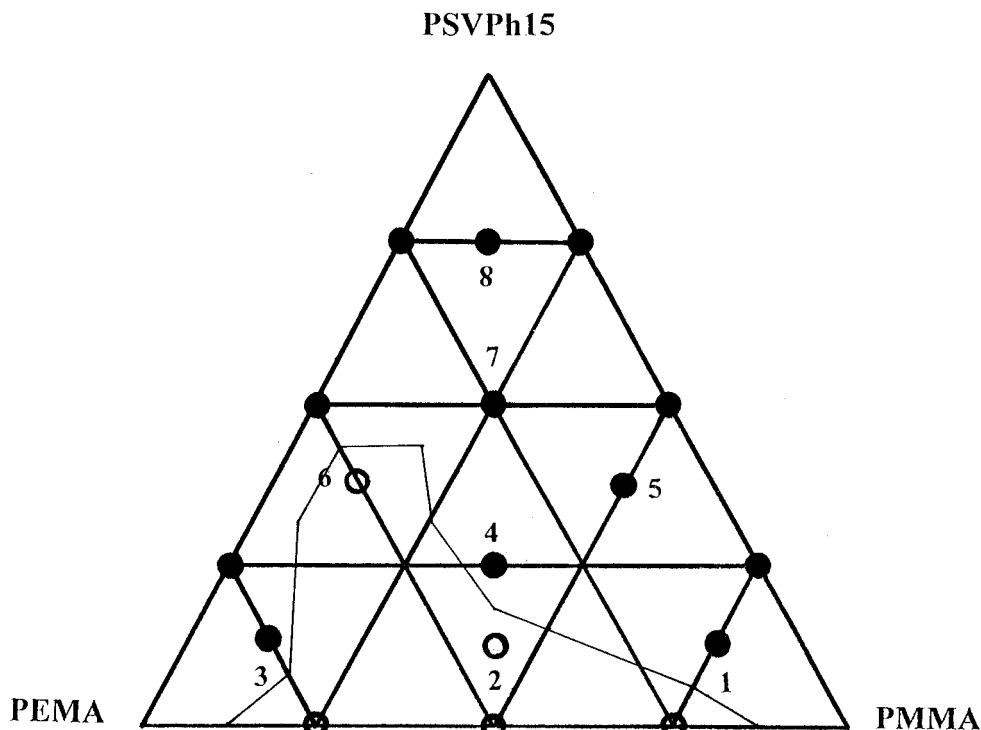
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Figure 4 Phase diagram of 2-butanone-cast PEMA/PMMA/PSVPh15 blends: (●) miscible, (○) immiscible, and (—) estimated immiscible regions. The numbers indicate the same compositions listed in Table III.

are plotted in Figures 5 and 6. In strict terms, PSVPh5 was not a cosolvent between PEMA and PMMA because it was not miscible with PEMA but was miscible with PMMA. The results of the corresponding binaries (PEMA/PSVPh and PMMA/PSVPh blends) are also included in Figures 5 and 6 for comparison. As already shown in Table II, the addition of a small amount of PSVPh5 (Fig. 5) seemed to be enough to cause PEMA and PMMA to be miscible. For PSVPh15 ternaries, adding about 25 wt % PSVPh15 to the PEMA/PMMA binaries was sufficient to cause miscibility (Fig. 6). The ternary T_g values were always lo-
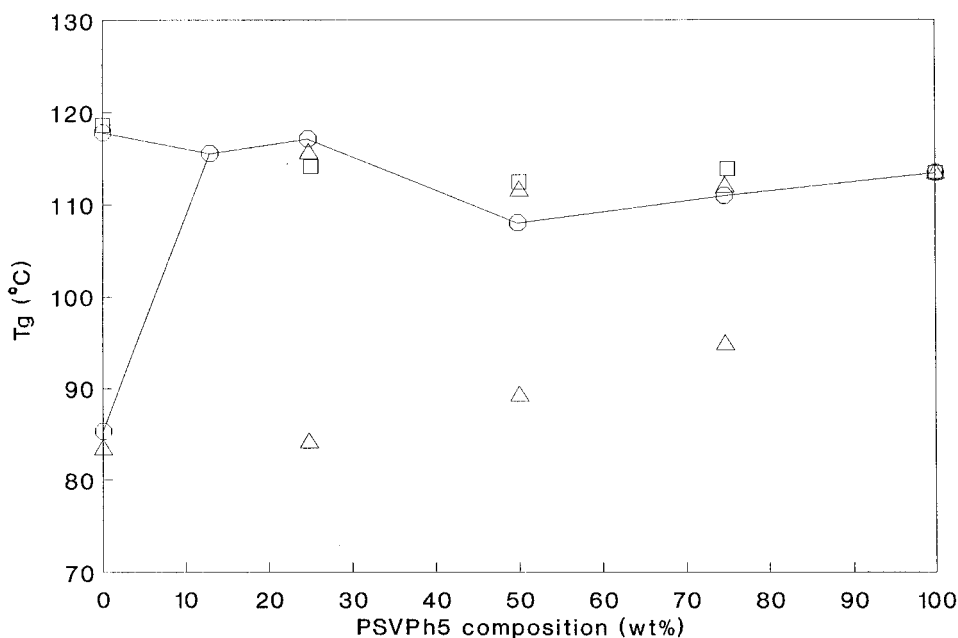

Figure 5 Changes in T_g's of the ternary blends with the PSVPh5 composition (PEMA/PMMA weight ratio ~ 1): (○) data points, (△) PEMA/PSVPh5 blends, and (□) PMMA/PSVPh5 blends.
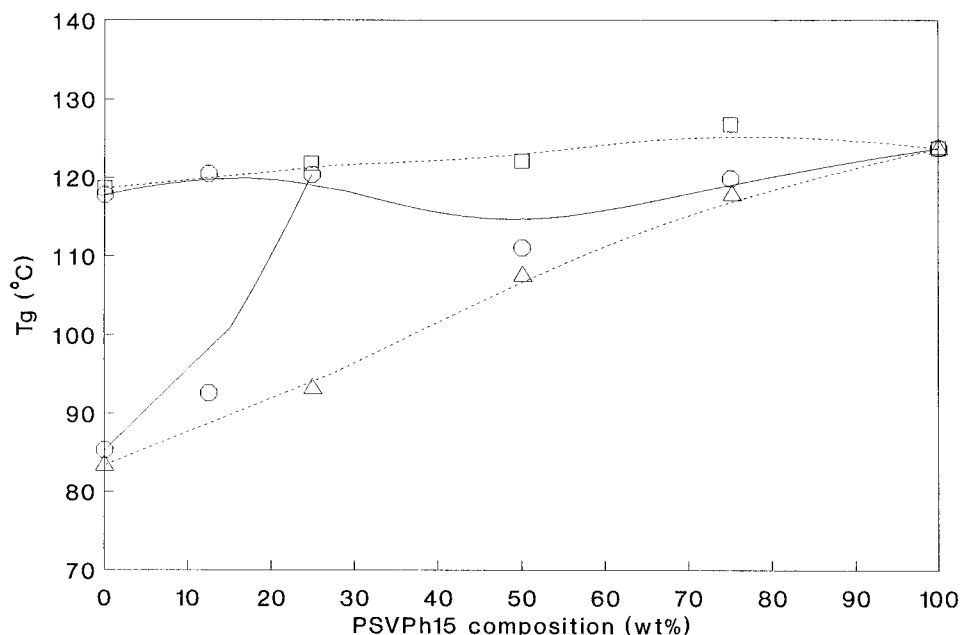
Figure 6 Changes in T_g's of the ternary blends with the PSVPh15 composition (PEMA/PMMA weight ratio ~ 1): (○) data points, (△) PEMA/PSVPh15 blends, and (□) PMMA/PSVPh15 blends.

cated between those of the binaries with the same PSVPh15 composition.

For polymer blends with weak interactions or none, the Fox equation[15] seems to predict T_g quite well. The Fox equation extended for a ternary mixture is as follows:

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} + w_3/T_{g3} \quad (1)$$

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 ($i = 1, 2,$ or 3). The T_g values of the ternary blends (designated T_{gF}) were estimated with PEMA, PMMA, and PSVPh T_g' in eq. (1). Only the blends with a single T_g, as listed in Tables II and III, were taken and attempted. The outcome is shown in Figure 7 (T_{gF} vs experimental T_g). The data can be divided into three groups. The first groups (containing eight data points) can be described qualitatively by the Fox equation. The second groups (with four data points in proximity) indicate that the
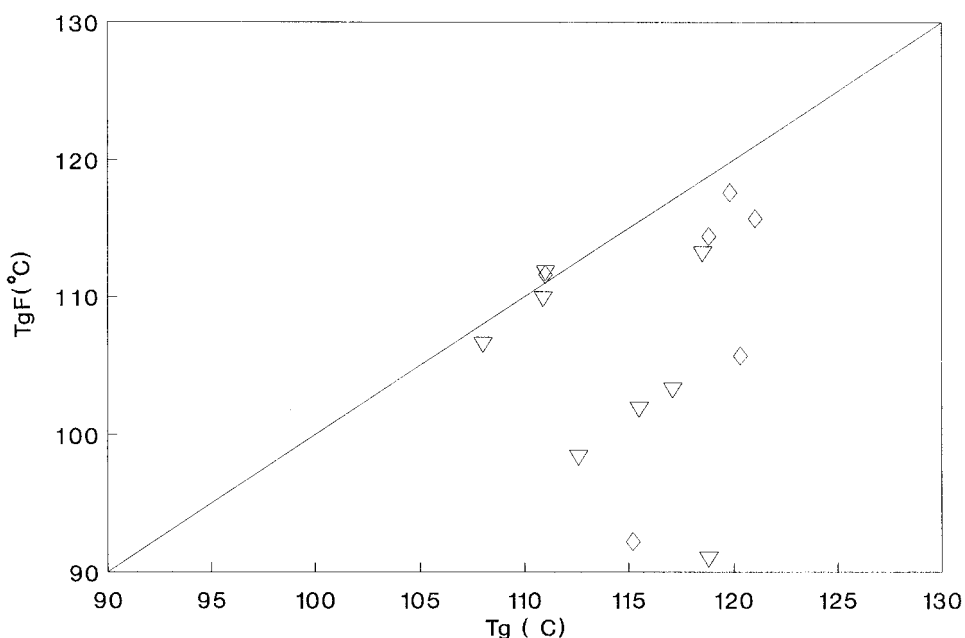

Figure 7 T_{gF} versus experimental T_g: (▽) ternary PSVPh5 blend and (◇) ternary PSVPh15 blend.

Fox prediction underestimated the experimental T_g values. However, the T_{gF} values still increased in proportion to the increase in the experimental T_g values. For the last groups with the remaining two data points, the Fox predicted values were much lower than the experimental values. In general, the predictions of the Fox equation are not satisfactory, as difficulties are often encountered in predicting T_g's of multicomponent polymers. Additionally, hydrogen bonding that existed in these ternaries obviously contradicted the assumption of weak interactions or no interactions in the polymers. Attempts to apply other well-known equations used for blends with specific interactions, such as the Kwei equation,[16] to the ternary blends were not successful and, therefore, are not reported here.

CONCLUSIONS

For the PEMA/PSVPh blends, PEMA was not miscible with PSVPh5 but was miscible with PSVPh15. However, for the PMMA/PSVPh blends, the situation was different. PMMA was miscible with both PSVPh5 and PSVPh15.

Although PSVPh5 (not like PSVPh15) was not miscible with PEMA, the miscibility region of the ternary blends consisting of PSVPh5, PEMA, and PMMA was determined to be larger than that of similar ternaries containing PSVPh15. The reason may be that the PSVPh15 ternaries exhibited strong ΔK effects. The ΔK effects were likely caused by stronger interactions between PMMA and PSVPh15 than those between PEMA and PSVPh15.

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