

# Phase Behavior of Ternary Polymer Blends with Favorable Interactions

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**ABSTRACT:** Atactic poly(methyl methacrylate) (aPMMA) and poly(vinyl pyrrolidone) (PVP) with a weight-average molecular weight of 360,000 g/mol were found to be immiscible on the basis of preliminary studies. Poly(styrene-co-vinyl phenol) (MPS) with a certain concentration of vinyl phenol groups is known to be miscible with both aPMMA and PVP. Is it possible to homogenize an immiscible aPMMA/PVP pair by the addition of MPS? For this question to be answered, a ternary blend consisting of aPMMA, PVP, and MPS was prepared and measured calorimetrically. The

role of MPS between aPMMA and PVP and the effects of different concentrations of vinyl phenol groups on the miscibility of the ternary blends were investigated. According to experimental results, increasing the vinyl phenol contents of MPS has an adverse effect on the miscibility of the ternary blends. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 2064–2070, 2005

**Key words:** ternary blends; favorable interactions

## 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.<sup>1</sup> in 1977. In their study, poly(vinylidene fluoride) was added to the immiscible pair poly(methyl methacrylate) (PMMA)/poly(ethyl methacrylate) (PEMA) and was found to be miscible. The list of investigated ternaries has been considerably enlarged since then.<sup>2–8</sup> 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<sup>9</sup> 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 the 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.

Painter et al.<sup>10</sup> reported an interesting review on the effect of hydrogen bonding on the phase behavior of ternary polymer blends. They asked in their article the following questions: "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)?" "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, we 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  $\Delta K$  effect (by analogy to the commonly known  $\Delta\chi$  effect) was proposed by them. The  $\Delta K$  effect reflects the difference in the chemical interactions between the self-association polymer and the other polymers in the mixture. They concluded from their simulations the following:

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TABLE I  
 $T_g$ 's of aPMMA/PVP Blends

aPMMA/PVP	$T_g$ (°C)	$\Delta T_g$ (°C)
1. 100/0	105.7	11
2. 75.0/25.0	104.1,178.0	12,16
3. 49.7/50.3	104.7,183.5	12,10
4. 24.9/75.1	104.3,181.7	10,11
5. 0/100	186.0	10

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 ( $\Delta K$ ) 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 addition of a small amount of a third polymer (compatibilizer).
3. Although the presence of a specific intermolecular interaction enhances the probability of forming a homogeneous ternary polymer blend, they can concurrently exacerbate the situation through the  $\Delta K$  effect, which promotes phase separation.

In a previous study of ours,<sup>11</sup> weakly self-associated poly(styrene-*co*-vinyl phenol) (MPS; previously abbreviated PSVPh) with 5 or 15 mol % vinyl phenol (VPh) units (MPS5 or MPS15) was added to immiscible

PEMA/PMMA pairs. MPS formed inter-hydrogen bonds with both PEMA and PMMA. The results showed that the miscibility region of the ternary blends consisting of MPS5, PEMA, and PMMA was larger than that of similar ternaries containing MPS15. The reason may be that the MPS15 ternaries had a strong  $\Delta K$  effect.

Now we turn our attention to atactic poly(methyl methacrylate) (aPMMA), poly(vinyl pyrrolidone) (PVP), and MPS. aPMMA and PVP with a weight-average molecular weight ( $M_w$ ) of 360,000 g/mol were found to be immiscible in preliminary studies. However, in a previous study,<sup>12</sup> aPMMA was miscible with PVP with a lower  $M_w$  value of 10,000–55,000 g/mol. MPS with about 4–5% VPh is known to be miscible with both aPMMA<sup>13</sup> and PVP.<sup>14</sup> Therefore, MPS is a potential candidate for cosolubilizing the immiscible aPMMA/PVP pair. aPMMA is a hydrophobic polymer, but PVP is quite hydrophilic. Blending them through the addition of MPS is a worthwhile study. Therefore, in this investigation, MPS containing 5 or 15 mol % VPh groups was used to homogenize the immiscible pair aPMMA/PVP.  $T_g$ '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 effects of using different hydroxyl group concentrations of the copolymer and blend compositions on the ternary phase diagram were examined and are presented in this article.

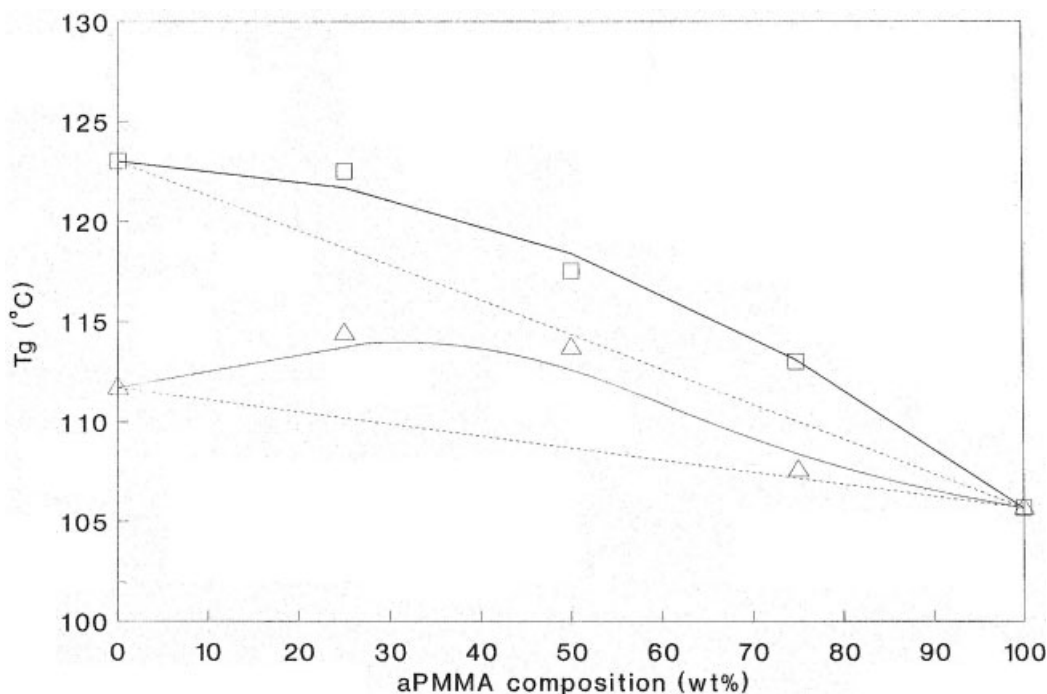


Figure 1  $T_g$ 's of aPMMA/MPS blends: (Δ) MPS5 and (□) MPS15.

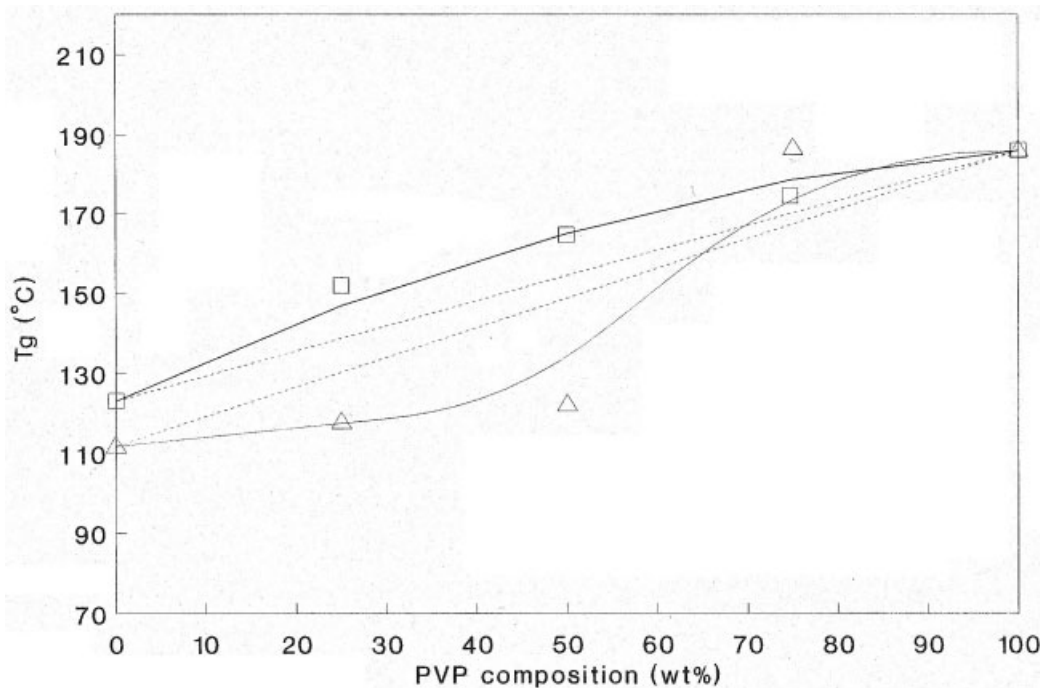


Figure 2  $T_g$ 's of MPS/PVP blends: ( $\Delta$ ) MPS5 and ( $\square$ ) MPS15.

## EXPERIMENTAL

### Materials

aPMMA was purchased from Polysciences, Inc. (War-rington, PA). The  $M_w$  value for aPMMA was approximately 100,000 g/mol. PVP, obtained from Scientific Polymer Products, Inc. (Ontario, NY), had an  $M_w$  value of 360,000 g/mol. The MPS used for this study contained 5 or 15 mol % VPh units (designated MPS5 and MPS15, respectively) and was synthesized with a procedure described previously.<sup>15</sup> The number-average molecular weight ( $M_n$ ) and  $M_w$  of MPS5 were determined by gel permeation chromatography to be 84,900 and 144,300 g/mol, respectively. MPS15 had an  $M_n$  value of 85,600 g/mol and an  $M_w$  value of 125,800 g/mol.

TABLE II  
 $T_g$ 's of aPMMA/PVP/MPS5 Blends

aPMMA/PVP/MPS5	$T_g$ (°C)	$\Delta T_g$ (°C)
a. 75.0/6.3/18.7	106.8	11
b. 74.7/12.5/12.8	104.8	12
c. 75.0/18.8/6.2	105.7	12
d. 50.2/12.2/37.6	107.3	12
e. 49.6/25.3/25.1	106.3	11
f. 49.8/37.5/12.7	106.6	11
g. 25.1/18.7/56.2	120.6	23
h. 25.0/37.4/37.6	105.9	14
i. 25.0/56.2/18.8	105.7,187.4	13,12

### Film preparation

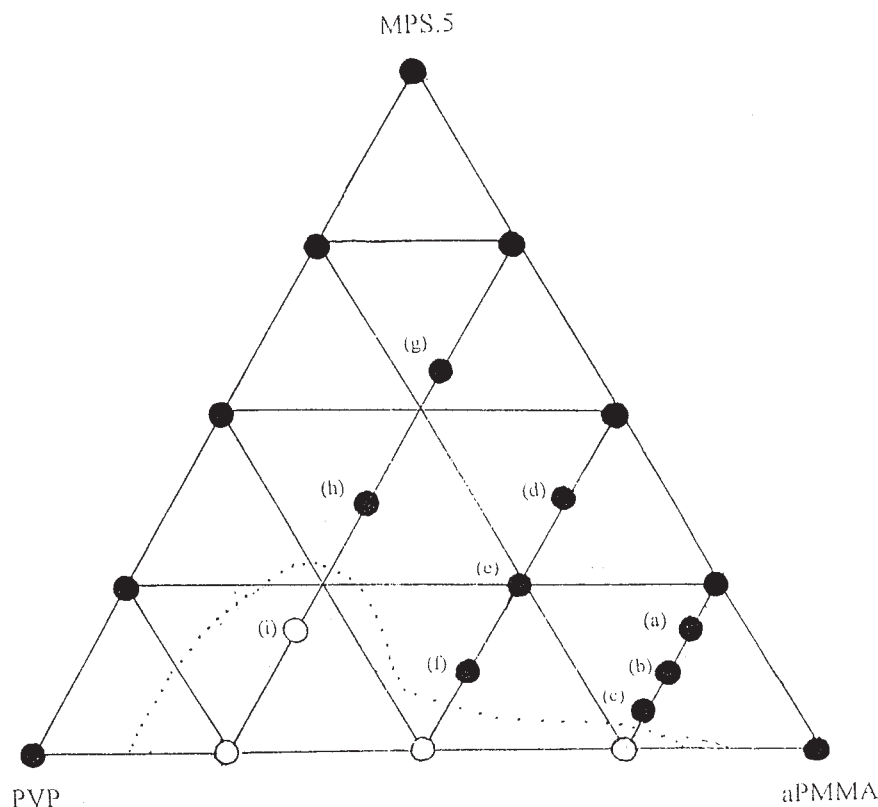
Thin films of the following binary and ternary polymer blends were made via solution casting onto glass plates:

1. aPMMA/PVP.
2. aPMMA/MPS5 and aPMMA/MPS15.
3. MPS5/PVP and MPS15/PVP.
4. aPMMA/PVP/MPS5 and aPMMA/PVP/MPS15.

The actual compositions of the binary and ternary blends are shown later in the tables and figures. Chloroform, an American Chemical Society reagent, was purchased from Fisher Scientific (Fair Lawn, NJ). The final drying step for all the films took place in a vacuum oven at 124–125°C for 15–16 h. Then, the films were cooled to room temperature slowly with air, and this resulted in the 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 (Wilmington, DE) coupled with a mechanical cooling system. The scanning range was 10–220°C, and a heating rate of 20°C/min was used for every measurement. The experiments were performed in two consecutive scans in an ambient environment of nitrogen gas at a flow rate of 90–110 mL/min. In the first thermal scan, the samples



**Figure 3** Phase diagram of aPMMA/PVP/MPS5 blends: (●) miscible region, (○) immiscible region, and (---) estimated immiscible region. The letters indicate the compositions listed in Table III.

were kept at 220°C for 1 min. Then, the samples were cooled to 10°C at a cooling rate of 20°C/min. The inflection point of the specific heat jump of a second thermal scan was taken to be  $T_g$ . The cooling rate was proven to be fast enough to produce virtually the same results as quenching.  $\Delta T_g$  was calculated as the difference between the onset and end points of  $T_g$ .

## RESULTS AND DISCUSSION

### aPMMA/PVP blends

Table I presents  $T_g$ 's of aPMMA/PVP blends. aPMMA and PVP were obviously not miscible because of the observation of two  $T_g$ 's. With the error in the  $T_g$  determination, we found that the blends phase-separated into highly pure aPMMA and PVP-rich phases. The  $\Delta T_g$  values of the aPMMA/PVP blends are listed in Table I for reference.

### Binary blends

Figure 1 presents the results for aPMMA/MPS5 and aPMMA/MPS15 blends. A single  $T_g$  behavior was observed for the two studied blends. For the aPMMA/MPS5 blends, the  $T_g$  values showed a complex composition dependence. However, the  $T_g$  values of the

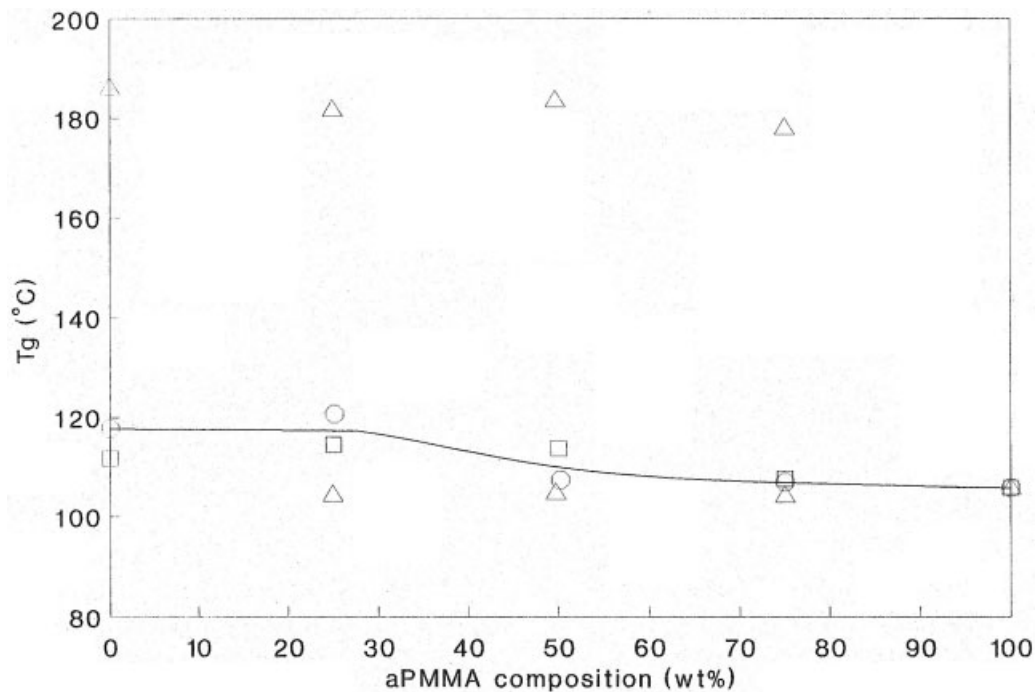
aPMMA/MPS15 blends displayed an approximately parabolic dependence on the composition. aPMMA formed miscible blends with both MPS5 and MPS15 because of inter-hydrogen bonding.

Several empirical equations have been proposed in the literature to describe the composition dependence of  $T_g$  of miscible blends that involve strong specific interactions. Three articles<sup>16–18</sup> offer theoretical insight into the underlying reason for the experimental observations. In the limiting case, these equations can be reduced to a simple expression:<sup>19</sup>

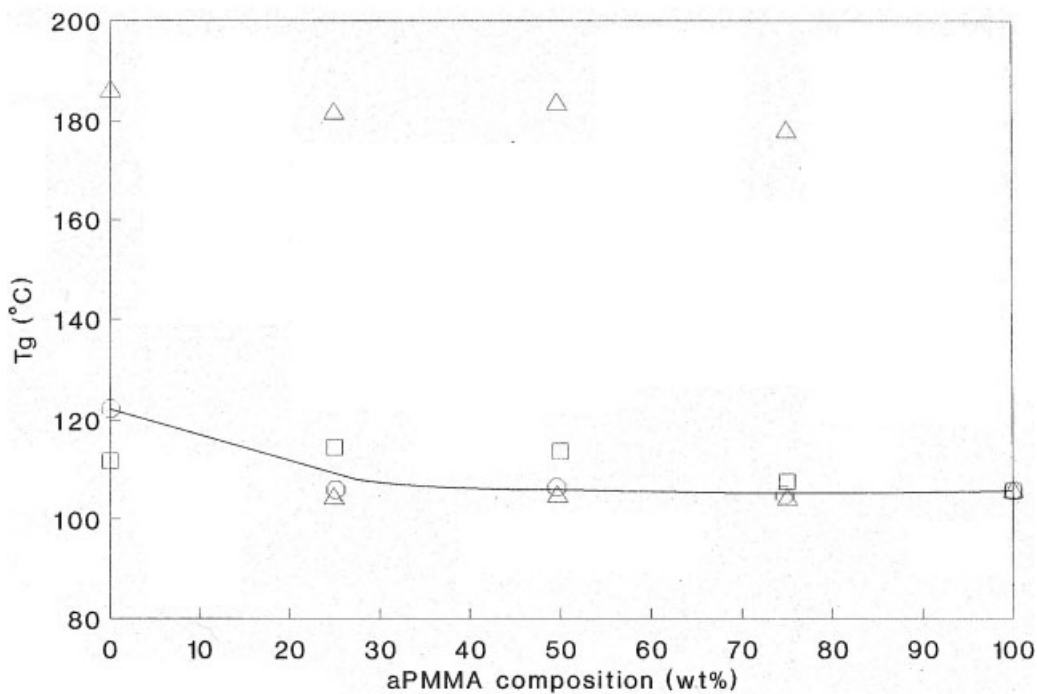
$$T_g = w_1 T_{g1} + w_2 T_{g2} + q w_1 w_2 \quad (1)$$

where  $w_1$  and  $w_2$  represent the weight fractions of the components and  $T_g$ ,  $T_{g1}$ , and  $T_{g2}$  are the glass-transition temperatures of the blend and components 1 and 2, respectively.  $q$  is a parameter corresponding to the strength of the interaction between polymers 1 and 2. A  $q$  value of 16.2 (shown as a dark, solid line in Fig. 1) describes the experimental  $T_g$  values of the aPMMA/MPS15 blends approximately well. A large  $q$  value indicates a strong interaction between aPMMA and MPS15.

For the MPS/PVP blends shown in Figure 2, PVP formed miscible blends with both MPS5 and MPS15



(a)



(b)

**Figure 4** Changes in  $T_g$  of the ternary blends with the aPMMA composition: (○) data points, (Δ) aPMMA/PVP blends, and (□) aPMMA/MPS5 blends. The PVP/MPS5 weight ratios were approximately (a) 1/3, (b) 1/1, and (c) 3/1.

because the blends showed a single  $T_g$ . According to the literature,<sup>14</sup> when polystyrene is modified to contain 1.4% VPh units, it is immiscible with PVP. However, when MPS contains more than 4% VPh, it is miscible with PVP. Therefore, our results correspond

well to those of the literature. For the MPS5/PVP blends, the  $T_g$  values showed an S-shape composition dependence. However, the  $T_g$ 's of the MPS15/PVP blends manifested a parabolic dependence on the composition. The Kwei equation [eq. (1)] was again

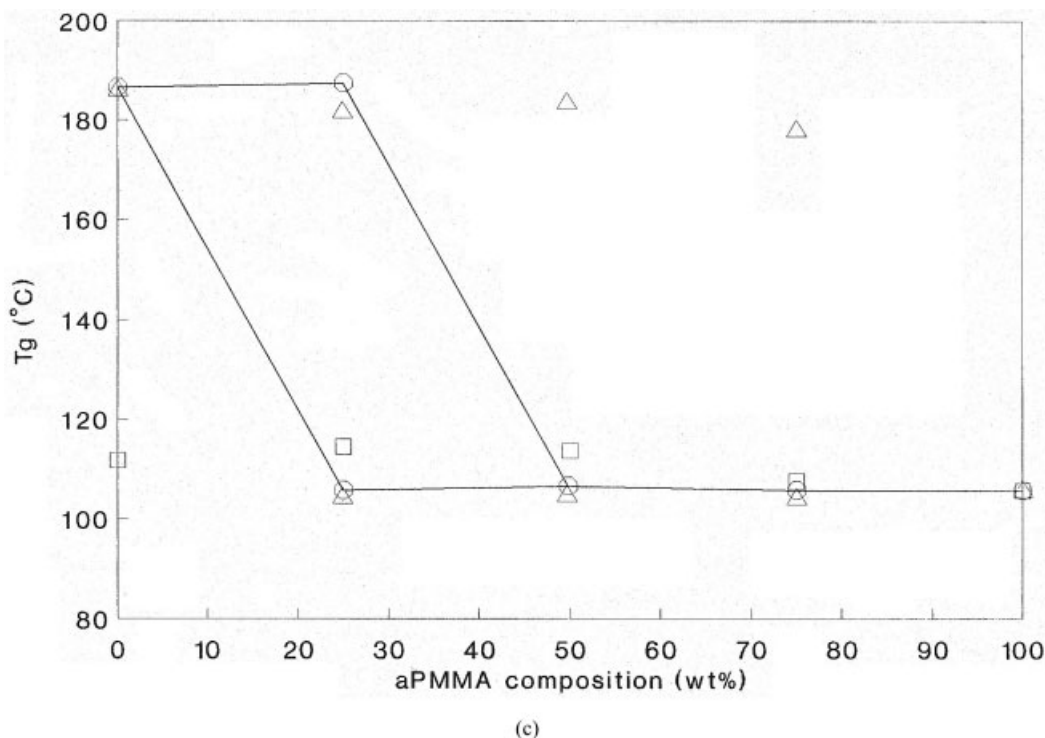


Figure 4 (Continued from the previous page)

used in describing the  $T_g$  data of the aforementioned blends. The  $T_g$  values of the MPS15/PVP blends were approximately fitted by a  $q$  value of 44.9 (the Kwei equation is shown as a dark, solid line in Fig. 2), which was much larger than that of the MPS15/aPMMA system. This indicates that MPS15 formed stronger hydrogen bonding with PVP than aPMMA.

### Ternary blends

The  $T_g$ 's of the aPMMA/PVP/MPS5 blends are listed in Table II. Eight of the nine studied blends showed a single  $T_g$ , which indicated miscibility. One blend exhibited two  $T_g$ 's and was, therefore, not miscible. The reason for the observed immiscibility is likely as follows. When the PVP concentration is high, MPS5 forms a stronger interaction with PVP than with aPMMA, and this results in phase separation. The  $\Delta T_g$  values of the aforementioned blends are listed in Table II for reference.

With a single  $T_g$  as the criterion for miscibility, a phase diagram composed of aPMMA, PVP, and MPS5 was established and is shown in Figure 3. The solid and empty circles represent single  $T_g$ 's and two  $T_g$ 's, respectively. We established a postulated phase boundary in Figure 3 as a reference by connecting through middle points between miscibility and immiscibility data. A small immiscibility region was observed for the aPMMA/PVP/MPS5 blends.

Figure 4(a–c) displays the  $T_g$  values of the ternary blends with different PVP/MPS5 ratios and increasing aPMMA concentration. The  $T_g$  values of the corresponding aPMMA binaries are included for comparison. For the ternary blends with 1:3 or 1:1 (w/w) PVP/MPS5, similar  $T_g$  behaviors were observed [Fig. 4(a,b)]. A single  $T_g$  value close to the low  $T_g$  value of the corresponding binary was observed. However, for the ternaries with a PVP/MPS5 ratio of 3:1 [Fig. 4(c)], only one composition (ca. 25% aPMMA) was immiscible, its two  $T_g$ 's approximately corresponding to those of the high and low  $T_g$ 's of aPMMA/PVP blends.

Table III presents the  $T_g$  values of the aPMMA/PVP/MPS15 blends. All the blends exhibited two  $T_g$  values, which indicated immiscibility. A large immis-

TABLE III  
 $T_g$ 's of aPMMA/PVP/MPS15 Blends

aPMMA/PVP/MPS15	$T_g$ (°C)	$\Delta T_g$ (°C)
a. 75.0/6.3/18.7	106.7, 154.3	12, 10
b. 75.0/12.5/12.5	103.8, 161.7	10, 14
c. 74.8/18.9/6.3	105.6, 171.4	12, 12
d. 50.0/12.6/37.4	106.5, 152.6	12, 11
e. 50.0/24.9/25.1	105.2, 164.4	10, 12
f. 50.0/37.5/12.5	105.7, 174.2	11, 10
g. 25.0/18.8/56.2	106.6, 152.8	9, 13
h. 24.9/37.4/37.7	105.1, 165.0	11, 11
i. 24.3/57.5/18.2	106.6, 175.1	11, 9

cibility region was obviously observed for the aPMMA/PVP/MPS15 blends. The  $\Delta T_g$  values of the aforementioned blends are also listed in Table III for reference.

A similar investigation<sup>11</sup> was reported by this laboratory in which the same MPS was used to cosolubilize aPMMA and PEMA. Although PEMA is slightly different from aPMMA in structure, they are immiscible like aPMMA and PVP in this study. MPS5 was not miscible with PEMA, but MPS15 was found to be miscible with PEMA. Both MPS5 and MPS15 were miscible with aPMMA. The immiscibility region of the ternary blends consisting of MPS15, PEMA, and PMMA was determined to be larger than that of similar ternaries containing MPS5. The reason may be that the MPS15 ternaries exhibited strong  $\Delta K$  effects. The  $\Delta K$  effects were likely caused by interactions between PMMA and MPS15 that were stronger than those between PEMA and MPS15. Because the aPMMA/PVP/MPS15 blends exhibited a larger immiscibility region than the MPS5 ternaries, we concluded that the  $\Delta K$  effects that occurred in the MPS15 ternaries were likely stronger than those in the MPS5 blends. Adopting previous explanations, we believe that the differences in the interactions between aPMMA and MPS15 and between PVP and MPS15 are probably stronger than those between aPMMA and MPS5 and between PVP and MPS5.

### CONCLUSIONS

aPMMA and PVP were not miscible according to the observation of two  $T_g$ 's. MPS5 was found to be miscible with both aPMMA and PVP because the prepared blends exhibited single  $T_g$ 's. MPS15 also formed miscible blends with both aPMMA and PVP.

The miscibility region of the ternary blends consisting of aPMMA, PVP, and MPS5 was determined to be larger than that of similar ternaries containing MPS15. The reason may be that the MPS15 ternaries exhibited strong  $\Delta K$  effects. The  $\Delta K$  effects were likely caused by interactions between PVP and MPS15 stronger than those between aPMMA and MPS15.

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