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A closed-loop behavior of ternary polymer blends composed of three miscible binaries

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Abstract

Poly (methyl methacrylate) (PMMA) was known to be miscible with poly (vinyl phenol) (PVPh). According to literature, poly (vinyl cinnamate) (PVCN) was also miscible with PVPh. The miscibility between PMMA and PVCN was corroborated on the basis of preliminary experiments. Is a ternary blend consisting of PMMA, PVPh and PVCN miscible in all the blend compositions? To answer this question, the miscibility of this ternary was examined in different blend compositions mainly based on calorimetry data in this investigation. The results using two different molecular weights of PVPh demonstrated an interestingly closed-loop behavior of immiscibility. The reason is likely because of the "$\Delta\chi$ effect".

Keywords: Closed-loop behavior; Ternary blends

1. Introduction

With the increasing application of multicomponent polymers [1,2], much interest has been directed toward ternary polymer blends recently. Since the early works of Scott and Tompa [3,4], most studies on the ternary polymer blends have been centered on the concept that polymer A, which is miscible with both polymers B and C, can compatibilize the immiscible binary pair B and C [5–8]. When all three binary pairs are miscible, a completely homogeneous ternary is possible [9]. However, differences in the interaction parameters of the binary system, the so-called "$\Delta\chi$ effect", can result in phase separation.

The phase relationships for ternary mixture where one component is solvent and the other two polymers have been described by Scott and Tompa [3,4] using the lattice theory of Flory and Huggins. Robard and Patterson [10] have demonstrated the existence of the $\Delta\chi$ effect in a ternary mixture of poly(styrene), poly (vinyl methyl ether) and chloroform. A distinguished feature in this ternary is the closed-loop region of immiscibility. The extension of the Flory–Huggins theory to ternary polymer blends has been conducted by Hsu and Prausnitz [11]. The effect of the asymmetry in the interaction parameters as well as the difference in molecular weight of the coexistence curves has been simulated. Su and Fried [12] also used the Flory–Huggins theory to compute spinodal curves and critical points for different interaction parameters, thus providing useful predictions in the phase diagrams of ternary systems.

Jo et al. [13] have reported in their work, ternary PMMA, poly(ethylene oxide) and poly(hydroxy ether of bisphenol-A) (composed of three miscible binaries) shows a closed loop of phase separated region in the phase diagram. Ternary polystyrene/poly(2-chlorostyrene)/poly(cyclohexylacrylate) consisting of three miscible binaries was demonstrated by Rabeony et al. [14] to show a closed-loop immiscibility. Recently Chang [15] also reported that ternary polymer blends of phenolic resin, poly(ethylene oxide) and poly (ε-caprolactone) with three miscible binaries also exhibited a closed immiscibility loop in the phase diagram.

Poly (methyl methacrylate) (PMMA) was known to be miscible with poly (vinyl phenol) (PVPh) [16]. Infrared characterization of poly (vinyl cinnamate) (PVCN) and its blends with PVPh before and after UV exposure was investigated by Coleman [17] and coworkers. PVCN was determined to be miscible with PVPh. PMMA was found to be miscible with PVCN on the basis of preliminary results in this lab. Therefore a ternary polymer blend consisting of PMMA, PVPh and PVCN with three miscible binaries is worthwhile for study and was pursued in this investigation. A closed-loop behavior of immiscibility

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was corroborated on the basis of calorimetry data in this report. FTIR spectra were used to elucidate the interaction existing in the binaries and are also included in discussion.

2. Experimental

2.1. Materials

PMMA and PVPh were purchased from Polysciences, Inc., Warrington, PA. According to manufacturer information, the molecular weight of PMMA was 100,000 g/mol. The M_w values for PVPh were 1500–7000 g/mol (designated as PVPh1) and 9000–11,000 g/mol (designated as PVPh2), respectively. PVCN obtained from Scientific Polymer Products, Inc. (Ontario, NY) had a M_w value of 200,000 g/mol.

2.2. Film preparation

Thin films of the following binary and ternary polymer blends were made by solution casting from tetrahydrofuran (THF) onto glass plates. The actual compositions of the binary and ternary blends are shown later in corresponding tables and figures. THF is reagent grade purchased from Riedel-deHaën, Germany. The final drying step for all the films took place in a vacuum oven at ca. 70 °C for about 24 h. The temperature at 70 °C was chosen to prevent PVCN from undergoing thermal cross-linking. 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.

2.3. Differential scanning calorimetry (DSC)

Glass transition temperatures (T_gs) of the polymer blends were determined by a DuPont DSC Q1000 thermal analyzer. The scanning range for temperature was from 30 to 220 °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 220 °C for 2 min. Then the samples were cooled to 30 °C using a cooling rate of 20 °C/min. The mid-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.

2.4. Fourier transform infrared spectroscopy (FTIR)

Most of the binary polymers were ground with KBr powder to make samples for FTIR studies. For some brittle binary polymers, the polymers were cast directly onto KBr windows. All the aforementioned samples were subjected to thermal treatments similar to those for the DSC samples. Spectra were obtained with a Perkin-Elmer FTIR 2000 spectrometer at room temperature. Sixty-four scans at a resolution of 2 cm^{-1} was signal averaged. The wave-number range was 400–4000 cm^{-1}.

Table 1
Glass transition temperatures of PVCN/PMMA blends

PVCN/PMMA	T_g (°C)	ΔT_g (°C)	T_{gF} (°C)
1. 100/0	75.0	8	–
2. 75.0/25.0	72.2	6	79.1
3. 50.0/50.0	85.0	7	83.3
4. 25.0/75.0	84.8	6	87.6
5. 0/100	92.0	11	–

3. Results and discussion

Thermal scans of calorimetry were not shown for brevity. The calculated glass transition temperature data are presented in the following section.

3.1. PVCN/PMMA blends

Table 1 presents the glass transition temperatures (T_gs) of PVCN/PMMA blends. Single composition dependent T_g was detected in the blends indicating possibility of miscibility. Since component T_gs are only 17 °C apart therefore film transparency is used to ensure the miscibility. All the prepared films were transparent, therefore PVCN and PMMA are determined to be miscible. ΔT_g values of the PVCN/PMMA blends are also listed in Table 1 for reference. The T_{gF} values tabulated in the third column of Table 1 represent the Fox prediction. The Fox equation [18] is shown below as

$$\frac{1}{T_g} = \frac{w_1}{T_{g_1}} + \frac{w_2}{T_{g_2}} \tag{1}$$

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 Fox estimation seemed to describe the experimental T_g approximately good.

Coleman et al. [17] reported that PVCN is actually a copolymer of vinyl alcohol and vinyl cinnamate. According to their estimation of the same product, mole fraction of vinyl alcohol is about 0.24. FTIR spectra of PVCN in our study (shown later in Fig. 2) also indicated the existence of vinyl alcohol. The spectra of PVCN/PMMA is not presented here because of no marked observation of interaction. However, the possibility of some degree of hydrogen bonding between C=O of PMMA and OH of PVCN cannot be ruled out.

3.2. Binary blends with PVPh

Table 2 presents the glass transition temperatures of PVPh/PMMA blends. Single composition dependent T_g was detected in the blends indicating miscibility in agreement with literature. Regardless of PVPh1 or PVPh2, the blends showed positive deviation from Fox prediction (represented as T_{gF}). The deviation is more enhanced at 25% and 75% PVPh compositions. Based on the magnitude of deviation, PVPh2 seems to form slightly more favorable interactions with PMMA than PVPh1 in spite of its higher molecular weight. ΔT_g values of the PVPh/PMMA blends are also listed in Table 2 for reference.

Table 2
Glass transition temperatures of PVPh/PMMA blends

	T_g (°C)	ΔT_g (°C)	T_{gF} (°C)
PVPh1/PMMA			
1. 100/0	133.1	10	–
2. 75.0/25.0	124.0	10	122.0
3. 50.0/50.0	111.0	10	111.5
4. 25.0/75.0	104.3	12	101.5
5. 0/100	92.0	11	–
PVPh2/PMMA			
1. 100/0	137.8	11	–
2. 75.0/25.0	131.2	14	125.3
3. 50.0/50.0	114.3	13	113.5
4. 25.0/75.0	108.9	13	102.5
5. 0/100	92.0	11	–

Table 3
Glass transition temperatures of PVPh1/PVCN/PMMA blends

PVPh1/PVCN/PMMA	T_g (°C)	ΔT_g (°C)	T_{gF} (°C)
1. 75.0/18.7/6.3	124.9	17	118.1
2. 75.0/12.5/12.5	124.8	17	119.4
3. 75.0/6.3/18.7	126.5	18	120.7
4. 50.0/37.5/12.5	101.8, 119.3	14, 6	
5. 50.0/25.0/25.0	104.5	25	106.6
6. 50.0/12.5/37.5	118.8	18	109.0
7. 25.0/56.2/18.8	88.7	17	91.2
8. 25.0/37.5/37.5	84.8, 103.8	11, 11	
9. 25.0/18.8/56.2	103.9	11	98.0

The glass transition temperatures of PVCN/PVPh blends are illustrated in Fig. 1. For PVCN/PVPh1 and PVCN/PVPh2 blends, miscibility was detected on the basis of single T_g observation. This finding is in accordance with the results of Coleman et al. [17]. For PVCN/PVPh1 blends, one blend composition showed negative deviation from the weight average and the other two compositions demonstrated positive deviation. However, a positive deviation from weight average was observed in all the studied PVCN/PVPh2 blends. The possible reason for PVPh2 to have more interactions with PVCN at 75% PVPh than PVPh1 is lower degree of PVPh self-association resulting from higher molecular weight. A simplified Kwei equation [19] is used to describe the T_g of PVCN/PVPh2 blends and shown as below

$$T_g = w_1 T_{g_1} + w_2 T_{g_2} + q w_1 w_2 \qquad (2)$$

where all the symbols except q have the same definitions as in Eq. (1). And q is a parameter that depends on the net polymer–polymer interaction. A q value of 11.8 was obtained to describe the parabolic T_g dependence of the PVCN/PVPh2 blends relatively well.

FTIR spectra of all the blends with PVPh2 are similar to those of the blends with PVPh1. Therefore in the following, PVPh1 blends are used as a representation. Fig. 2(a) presents the FTIR spectra of PVPh1/PVCN blends in the carbonyl absorption region. The carbonyl absorption region is used to demonstrate difference in interaction between PVPh/PVCN and PVPh/PMMA blends. The free C=O absorption of PVCN was observed as a peak at 1715 cm^{-1} in Fig. 2(a). There is likely a shoulder detected at ca. 1690 cm^{-1} which is attributed to carbonyl groups hydrogen bonded aliphatic hydroxyls (i.e. vinyl alcohol) in the pure PVCN sample. When PVPh is added to PVCN, a prominent peak at 1695–1696 cm^{-1} was observed due to hydrogen bonding between hydroxyl groups of PVPh and carbonyl groups of PVCN. The hydrogen-bonded peak shift is ca. 20 cm^{-1} compared favorably with 22 cm^{-1} reported in reference 17. The spectra of PVPh1/PMMA are given in Fig. 2(b). Absorptions at 1732 and 1716 cm^{-1} are assigned to free C=O groups and hydrogen-bonded C=O groups, respectively. The peak shift of 16 cm^{-1} in PVPh/PMMA blends is similar to that of PVPh/PVCN blends. This indicates that the interaction in PVPh1/PVCN blends is likely in similar strength to that in PVPh1/PMMA blends. However, the C=O group of PVCN is less accessible to PVPh compared to PMMA because of steric hindrance and low concentration (mole fraction of VCN about 0.76). Therefore the probable binary interaction order is as the following:

PVPh–PMMA > PVPh–PVCN > PMMA–PVCN

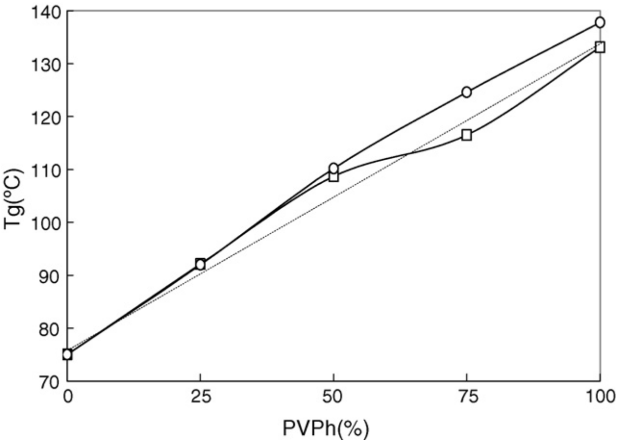

Fig. 1. Glass transition temperatures of miscible PVPh/PVCN polymer blends: (□) PVPh1 and (○) PVPh2.

3.3. *Ternary blends*

The glass transition temperatures of the PVPh1/PVCN/PMMA blends are tabulated in Table 3. For PVPh1 ternaries, the blends showed a single T_g except for two compositions. These two blend compositions demonstrated two T_g values indicating immiscibility. ΔT_g values of the aforementioned blends are also tabulated in Table 3 for reference. For the purpose of illustrating the effect of PVPh addition, the T_g values of the ternaries with PVCN/PMMA weight ratios of (3/1, 1/1 and 1/3) taken from Table 3 were plotted in Fig. 3(a–c). Results of the corresponding binaries (PVPh1/PMMA and PVPh1/PVCN blends) were also included in Fig. 3 for comparison. The single T_g criterion for miscibility is used in our ternary system. The detection of single T_g is believed to encompass a domain size on the order of 2–15 nm [1]. For PVCN/PMMA(weight ratios 3/1) ternaries (in Fig. 3(a)), the 50% PVPh blend showed two T_g values indicating immiscibility. The other two blend compositions exhibited sin-

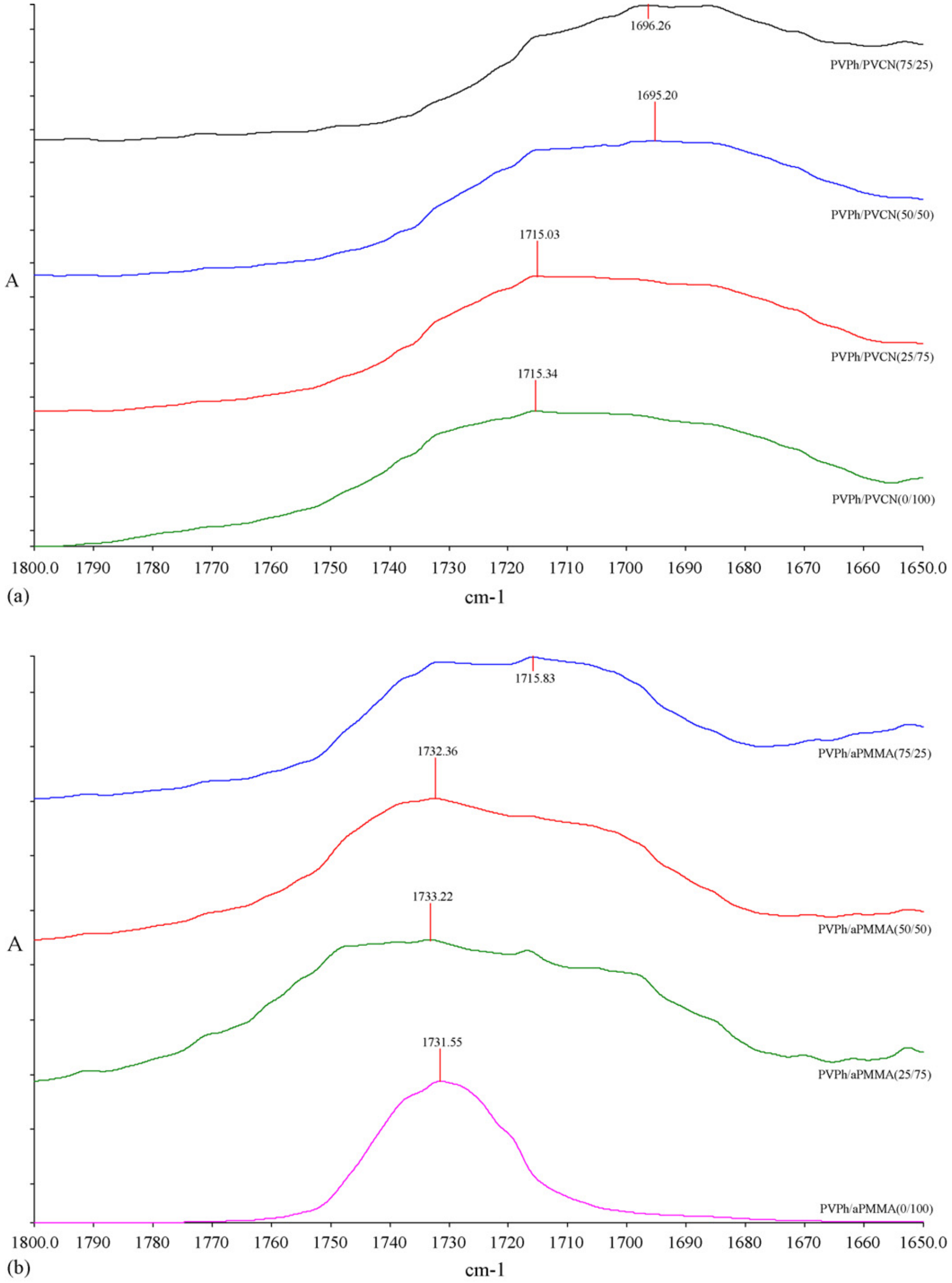

Fig. 2. (a) FTIR spectra of PVPh1/PVCN blends and (b) FTIR spectra of PVPh1/PMMA.

gle T_g close to low T_g of corresponding binary and therefore are miscible. In Fig. 3(b), the ternaries with PVCN/PMMA weight ratio 1/1 demonstrated two T_gs at 25% PVPh indicating immiscibility. The PVCN/PMMA (1/3) ternaries in Fig. 3(c) all showed single T_g near high T_g of corresponding binary demonstrating miscible behavior.

The glass transition temperatures of the PVPh2/PVCN/PMMA blends are tabulated in Table 4. For PVPh2 ternaries, the results are similar to those of PVPh1 ternaries. Two of nine studied blend compositions exhibited two T_g values indicating immiscibility. However, one composition occurs at 50% PVPh2 with PVCN/PMMA weight ratio of 1/1 different from PVPh1 ternaries. ΔT_g values of the aforementioned blends are also tabulated in Table 4 for reference. For the purpose of illustrating the effect of PVPh addition, the T_g values of the ternaries with PVCN/PMMA weight ratios of (3/1, 1/1 and 1/3) taken from Table 4 were plotted in Fig. 4(a–c). Results of the corresponding binaries (PVPh2/PMMA and PVPh2/PVCN blends) were also included in Fig. 4 for reference. The results showed similarity to those of PVPh1 ternaries. On the basis of observations in Fig. 4(a and b), the blends with 50% exhibited two T_g values indicating immiscibility. Interestingly, the high T_g of these

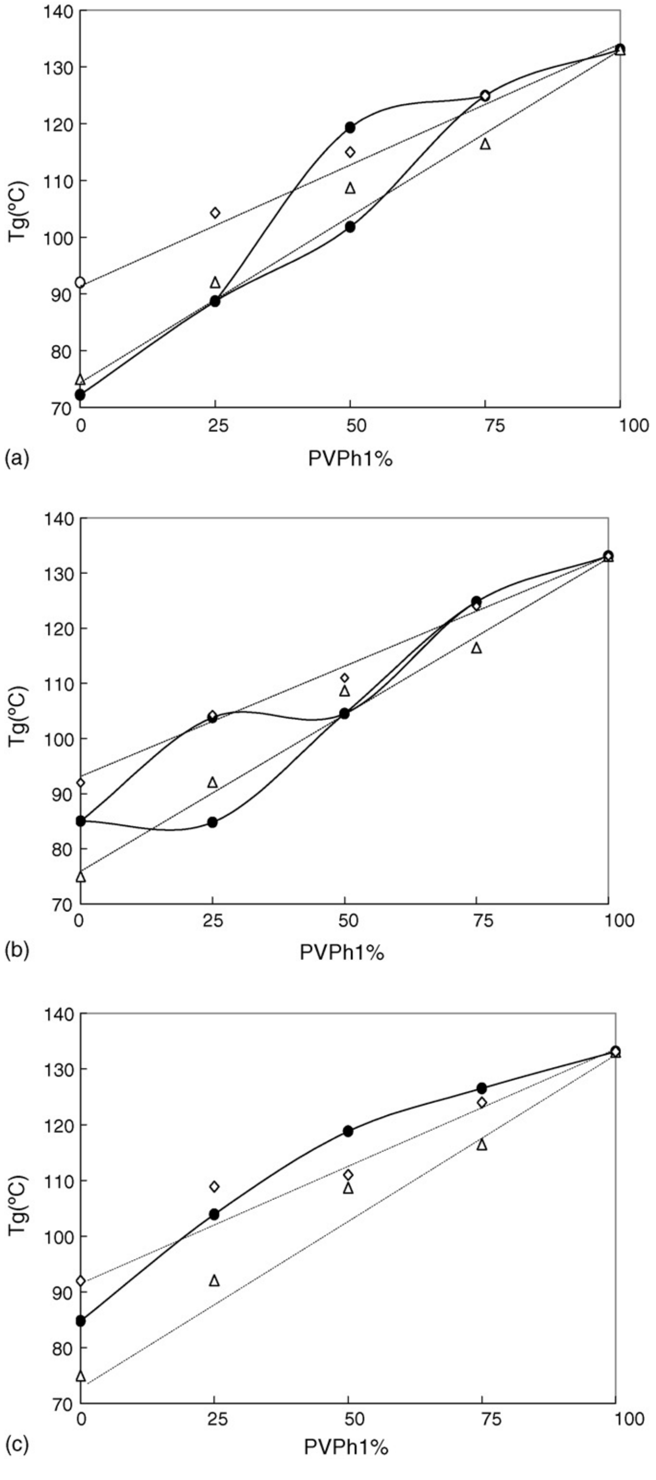

Fig. 3. (a) Change of T_g of the ternary blends with PVPh1 composition (PVCN/PMMA weight ratio = 3/1): (●) data point, (△) PVCN/PVPh blends and (◊) PMMA/PVPh blends (curves drawn for viewing). (b) Change of T_g of the ternary blends with PVPh1 composition (PVCN/PMMA weight ratio = 1/1): (●) data point, (△) PVCN/PVPh blends and (◊) PMMA/PVPh blends (curves drawn for viewing). (c) Change of T_g of the ternary blends with PVPh1 composition (PVCN/PMMA weight ratio = 1/3): (●) data point, (△) PVCN/PVPh blends and (◊) PMMA/PVPh blends (curves drawn for viewing).

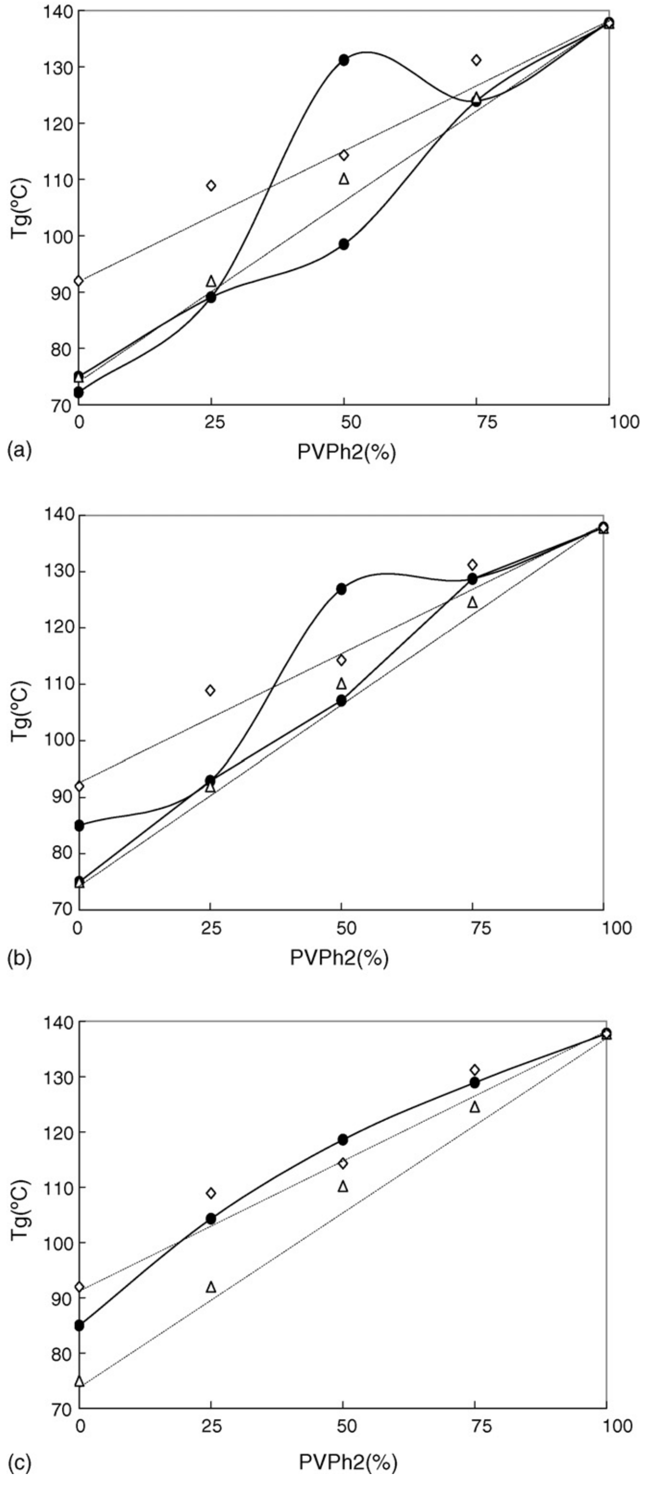

Fig. 4. (a) Change of T_g of the ternary blends with PVPh2 composition (PVCN/PMMA weight ratio = 3/1): (●) data point, (△) PVCN/PVPh blends and (◊) PMMA/PVPh blends (curves drawn for viewing). (b) Change of T_g of the ternary blends with PVPh2 composition (PVCN/PMMA weight ratio = 1/1): (●) data point, (△) PVCN/PVPh blends and (◊) PMMA/PVPh blends (curves drawn for viewing). (c) Change of T_g of the ternary blends with PVPh2 composition (PVCN/PMMA weight ratio = 1/3): (●) data point, (△) PVCN/PVPh blends and (◊) PMMA/PVPh blends (curves drawn for viewing).

Table 4
Glass transition temperatures of PVPh2/PVCN/PMMA blends

PVPh2/PVCN/PMMA	T_g (°C)	ΔT_g (°C)	T_{gF} (°C)
1. 75.0/18.7/6.3	123.9	20	121.4
2. 75.0/12.5/12.5	128.7	21	122.7
3. 75.0/6.3/18.7	128.9	17	124.0
4. 50.0/37.5/12.5	98.5, 131.2	12, 9	
5. 50.0/25.0/25.0	107.1, 126.9	10, 22	
6. 50.0/12.5/37.5	118.6	30	111.1
7. 25.0/56.2/18.8	89.1	17	92.0
8. 25.0/37.5/37.5	92.9	20	95.5
9. 25.0/18.8/56.2	104.3	19	99.0

two T_gs is higher than high T_g of corresponding binary and the low T_g lower than low T_g of corresponding binary. The behavior is more pronounced when the ratio of PVCN/PMMA is larger. The PVCN/PMMA (1/3) ternaries in Fig. 4(c) showed miscible behavior similar to the findings in Fig. 3(c).

Two T_g values observed in Figs. 3(a and b) and 4(a and b) were likely composed of two phases. The films with two T_g values exhibited some turbidity. The high T_g phase contains mostly PVPh and PMMA. PVCN is the major component of the low T_g phase. The reason for this observation is likely the interaction between PMMA and PVPh is much larger than that between PMMA and PVCN. At these immiscible ternary compositions when PVCN/PVPh weight ratio larger than or equal to 1/1, PMMA interacts favorably with PVPh than PVCN causing phase separation.

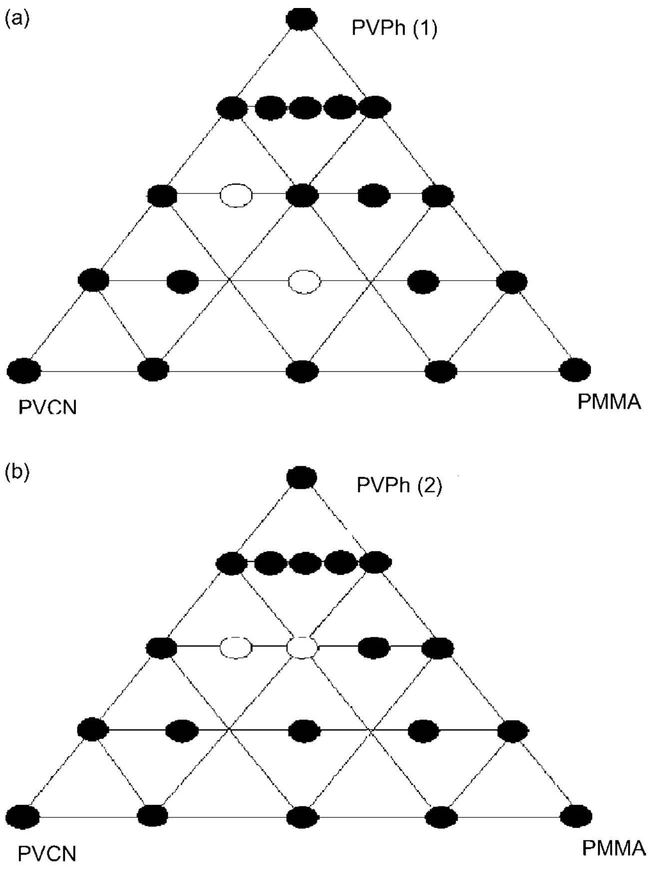

Fig. 5. (a) Phase diagram of PVPh1/PVCN/PMMA ternary blends: (●) one T_g and (○) two T_gs. (b) Phase diagram of PVPh2/PVCN/PMMA ternary blends: (●) one T_g and (○) two T_gs.

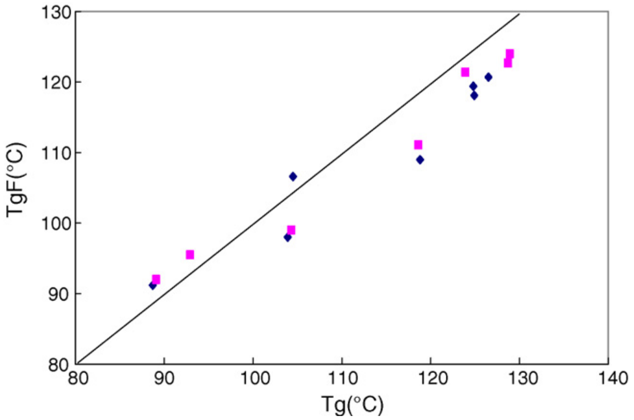

Fig. 6. Fox predicted T_g vs. experimental T_g: (■) PVPh1 and (♦) PVPh2.

Using single T_g as the criterion for miscibility, the phase diagram composed of PVPh, PVCN and PMMA was established and is shown in Fig. 5(a and b) in the order of PVPh1 and PVPh2, respectively. The solid and empty circles represent single T_g and two T_gs. Miscibility is encountered in most of the studied ternary blends. However, a small immiscibility region encompassing two empty circles was observed in Fig. 5(a and b). The composition range of immiscibility is slightly different in Fig. 5(a and b). The entropic effect is considered to be negligible. The possible cause is the "$\Delta\chi$ effect". The stronger interaction in PVPh/PMMA blends than that in PMMA/PVCN blends is probably the driving force for $\Delta\chi$ effect. The binary interaction parameters among the studied ternary blends are not available to the best of our knowledge. Therefore the attempts to explain the composition range of immiscibility region by using binary interaction parameters were not pursued.

For predicting the miscible ternary T_g, the Fox equation derived for weak or no interaction was used as a qualitative attempt and listed as below

$$\frac{1}{T_g} = \frac{w_1}{T_{g_1}} + \frac{w_2}{T_{g_2}} + \frac{w_3}{T_{g_3}} \qquad (3)$$

where all the symbols have the same meaning as in Eq. (1). The outcome is shown in Fig. 6 (T_{gF} versus experimental T_g). The T_{gF} values were estimated using the T_g values of PVPh, PVCN and PMMA in Eq. (3). The straight line in Fig. 6 depicts when T_g is equal to T_{gF}. All the 14 miscible T_g values of PVPh/PVCN/PMMA blends can be described by the Fox estimations semi-quantitatively. Most experimental T_g data of the blends with 50% or 75% PVPh are larger than Fox predictions likely because of high degree of hydrogen bonding in the blends.

4. Conclusion

PMMA and PVPh were found to be miscible in agreement with literature. PVCN and PVPh are known to be also miscible. PMMA and PVCN were determined to be miscible in this article on the basis of single T_g observation and film transparency. The miscibility of a ternary composed of PVPh (with two different molecular weights), PMMA and PVCN was investigated on the basis of calorimetry data. An immiscibilty loop encompassing two blend compositions was detected in both PVPh1 and PVPh2 ternaries. The reason for this observation is likely because of stronger PMMA/PVPh interaction than PMMA/PVCN interaction (the $\Delta\chi$ effect).

Acknowledgments

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