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Miscibility enhancement on the immiscible binary blend of poly(vinyl acetate) and poly(vinyl pyrrolidone) with bisphenol A

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Abstract

The miscibility behavior and hydrogen bonding of ternary blends of bisphenol A (BPA)/poly(vinyl acetate) (PVAc)/poly(vinyl pyrrolidone) (PVP) were investigated by using differential scanning calorimetry and Fourier transform infrared spectroscopy (FTIR). The BPA is miscible with both PVAc and PVP based on the observed single T_g over the entire composition range. FTIR was used to study the hydrogen-bonding interaction between the hydroxyl group of BPA and the carbonyl group of PVAc and PVP at various compositions. Furthermore, the addition of BPA is able to enhance the miscibility of the immiscible PVAc/PVP binary blend and eventually transforms into miscible blend with single T_g, when a sufficiently quantity of the BPA is present due to the significant $\Delta\chi$ and the ΔK effect. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Bisphenol A; Ternary blend; Hydrogen bonding

1. Introduction

It is well known that most polymer blends are immiscible due to a high degree of polymerization. Therefore, the entropy term becomes vanishingly small and the miscibility is increasingly dependent on the nature of the enthalpic term contribution. During last 20 years, the miscibility and phase behavior of binary polymer blends have been extensively studied [1–5]. Many well known binary pairs of polymers have been found to be miscible and these miscible binary polymer blends, in general, possess specific interaction including inter-molecular hydrogen bonding [6–8], ionic interaction [9–11], charge transfer complex, and copolymer repulsion effect [12–14]. On the contrary, ternary polymer blends have received substantially less attention due to complexity in calculating phase diagram and problems of experimental accuracy. Nonetheless, the phase behavior of ternary polymer blends has received great attention in polymer science due to its significant industrial importance. Increasing the number of polymer components in a polymer blend make the system much more complicated; however, it does provide enhanced design flexibility for the control of multiple properties. Many prior studies of ternary polymer blends have paid their attention primarily on two pairs of miscible polymers. Since the early works of Scott and Tompa [15,16], the ternary polymer blends have been developed with the concept that polymer B, which is miscible with both polymers A and C, can compatibilize the immiscible binary pair of A and C. Classical examples are the ternary blends of poly(vinylidene fluoride) (PVDF)/poly(methyl methacrylate) (PMMA)/poly(ethyl methacrylate) [17], poly(vinyl phenol) (PVPh)/PMMA/PEMA [18], and SAN/PMMA/PEMA [19]. While PMMA and PEAM are immiscible with each other, the addition of a large amount of PVDF, PVPh or SAN leads to miscible ternary polymer blend due to the significant $\Delta\chi$ or the ΔK effect in these ternary blend systems [20,21]. This is analogous to a good solvent to enhance miscibility of two immiscible polymers.

In addition to the high molecular weight polymer, compatibilization of an immiscible binary polymer blend also can be achieved using a suitable low molecular weight compound due to its significantly greater entropy change than the high molecular weight polymer [22]. Based on our knowledge, only few studies have been reported on polymer blends by using low molecular weight compounds through hydrogen-bonding interaction [23–27]. Recently, He et al. have reported that several bifunctional low molecular weight compounds are miscible with poly(ϵ-carprolactone) (PCL) due to the existence of hydrogen bonding between the hydroxyl group of these dihydric phenols and the carbonyl group of PCL. In these studies [24–27], they also proposed that these dihydric phenols are able to act as

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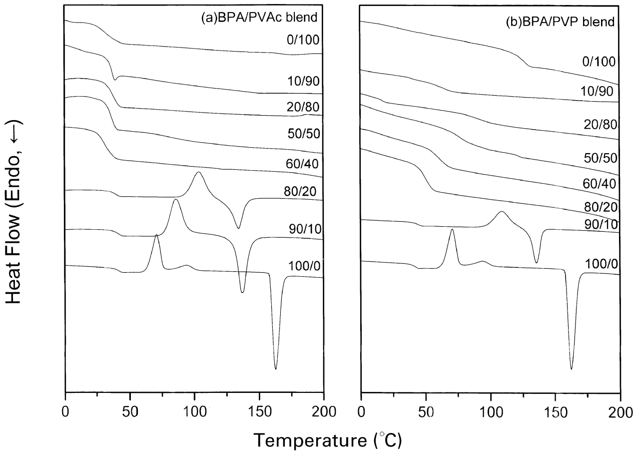

Fig. 1. The DSC thermograms of BPA/PVAc (a) and BPA/PVP (b) blends with different composition.

compatibilizers to improve the miscibility between two hydrogen bonding acceptor polymers.

In this present study, hydrogen bonding acceptor polymers, such as poly(vinyl acetate) (PVAc) and poly(vinyl pyrrolidone) (PVP) are immiscible with each other due to weak interaction and large solubility parameter difference. In our previous study [28,29], we have found that blends of phenolic/PVAc and PVPh/PVP are miscible, because of hydrogen bonding existing in these binary polymer blends. Therefore, we expected that a bifunctional hydrogen bonding donor polymers may interact with these hydrogen bonding acceptor polymers and act as a compatibilizer to improve their miscibility. The purpose of this work is to study of the miscibility behavior and its hydrogen bonding of the ternary blend of BPA/PVAc/PVP system. The effect of hydrogen bonding on the miscibility will be investigated using differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR).

2. Experimental

2.1. Materials and blend preparation

The bisphenol A (BPA) with molecular weight 228.29 was supplied by the Showa Chemical Company, Japan. The PVAc with a $M_w = 58\,000$ and PVP with a $M_w = 10\,000$ were purchased from Aldrich Chemical Company of USA. They were used as received without further purification. The ternary blends of BPA/PVAc/PVP with various compositions were prepared by solution blend. The DMF solvent containing 5 wt% of these three components was stirred for 6–8 h, and the solution was allowed to evaporate slowly at room 50 °C for 1 day. The film of the blend was then dried at 100 °C for 2 days to ensure total elimination of the solvent.

2.2. Characterizations

Thermal properties were characterized using a TA instruments 2920 Differential Scanning Calorimeter with mechanical cooling accessory. Each sample was first heated to 200 °C and maintained at that temperature for 5 min and then quickly quenched to -20 °C. The glass transition temperature was obtained as the inflection point of the jump heat capacity with scan rate of 20 °C/min and temperature range of -20 to 200 °C. Infrared spectra of polymer blend films were determined by using the conventional NaCl disk method. The DMF solution containing the blend was cast onto NaCl disk and dried under condition similar to that used in the bulk preparation. The film used in this study was sufficiently thin to obey the Beer–Lambert law. FTIR measurement was recorded on a Nicolet Avatar 320 FT-IR spectrophotometer and 32 scans were collected with a spectral resolution 1 cm^{-1}. Samples containing hydroxyl groups are water sensitive; a pure nitrogen gas was used to purge the IR optical box in order to maintain sample film dry.

3. Result and discussion

3.1. Analyses of binary blend of BPA/polymer

DSC analysis is extensively used to investigate the miscibility behavior in polymer blends. Fig. 1 shows the DSC thermograms of BPA/PVAc and BPA/PVP blends with various compositions recorded during the second heating scan. Both PVAc and PVP amorphous polymers exhibit a single T_g at 32.1 and 126.7 °C, respectively. Interestingly, even though the molar mass of BPA is only 228, it also shows a single T_g behavior at 42.5 °C during the second heating scan. BPA contains a high density of hydroxyl groups, which probably forms a weakly physical cross-linking network, a pseudo supramolecule. Meanwhile, the pure BPA also has a melting temperature at 162.3 °C. It is well known that hydrogen bonding plays an important role in determining thermal properties of polymers. Formation of hydrogen bonding has a profound effect on various physical properties; including melting temperature, glass transition temperature, and crystal structure. Therefore, the BPA with its high density of hydrogen bonding has the glass transition behavior similar to high molecular weight polymer and a melting temperature. However, in this study, the thermal property and morphology of the blend are not our main concerning. Our interest is the effect of hydrogen bond formation on the miscibility behavior of the polymer blend. Clearly, the binary blends of BPA/PVAc and BPA/PVP are totally miscible in the amorphous phase due to only single T_g based on DSC analyses as shown in Fig. 1 and their thermal properties are summarized in Table 1. Compared with Fig. 1(a) and (b), we have found that the binary blend of BPA/PVAc = 80/20 has the crystallization and melting

Table 1
Thermal properties of BPA/PVAc and BPA/PVP binary blends

	T_g (°C)	T_m (°C)	ΔH_f (J/g)	T_c (°C)	ΔH_c (J/g)
BPA/PVAc					
100/0	42.5	162.3	112.9	71.6 94.3	46.7 9.5
90/10	42.0	136.8	54.8	85.9	45.4
80/20	39.9	134.4	36.3	104.2	34.5
60/40	38.3				
50/50	37.8				
30/70	37.2				
20/80	37.8				
10/90	37.6				
0/100	32.1				
BPA/PVP					
90/10	44.9	136.0	46.9	109.1	40.7
80/20	50.2				
65/35	58.9				
60/40	60.3				
50/50	77.7				
20/80	92.8				
10/90	64.4				
0/100	126.7				

temperatures of BPA component. Nonetheless, crystallization and melting temperatures of BPA are missing of the binary blend of BPA/PVP = 80/20, revealing that the inter-association hydrogen bonding of BPA/PVP blend is greater than that of the BPA/PVAc blend. Stronger inter-association hydrogen bonding of BPA/PVP = 80/20 blend inhibits BPA component aggregation to crystallize during heating scanning. In order to support this claim, we turn our attention on FTIR analyses.

Figs. 2 and 3 show the FTIR spectra of BPA/PVAc and BPA/PVP blends in the hydroxyl and carbonyl vibration regions by varying BPA fractions at room temperature. In Fig. 2(a), the pure BPA shows a broad band centered at 3325 cm^{-1} that can be attributed to the wide distribution of the hydrogen bonded hydroxyl group. A small and narrow band at 3525 cm^{-1} is caused by the free hydroxyl group. For pure PVAc, only a very weak band centered at 3455 cm^{-1} was observed in this region, and it should be attributed the overtone of the carbonyl group in the PVAc polymer chain. Meanwhile, this broad hydrogen bonded hydroxyl band shifts into higher wavenumber with increasing PVAc content (50 wt%) at 3430 cm^{-1}. This shift reflects a new distribution of hydrogen bonds between hydroxyl–hydroxyl and hydroxyl–carbonyl specific interactions. All these observed changes have come from the switching of the strong self-association of hydroxyl–hydroxyl bond into the relatively weaker inter-molecular hydroxyl–carbonyl bond.

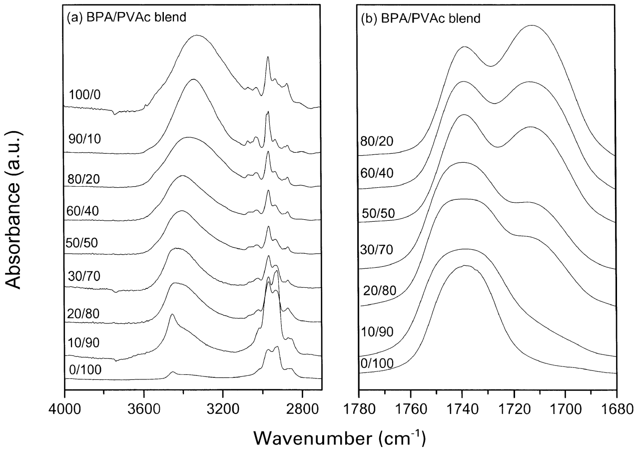

Fig. 2. Infrared spectra of blend of BPA/PVAc at room temperature in the hydroxyl stretching region (a) and carbonyl stretching region (b).

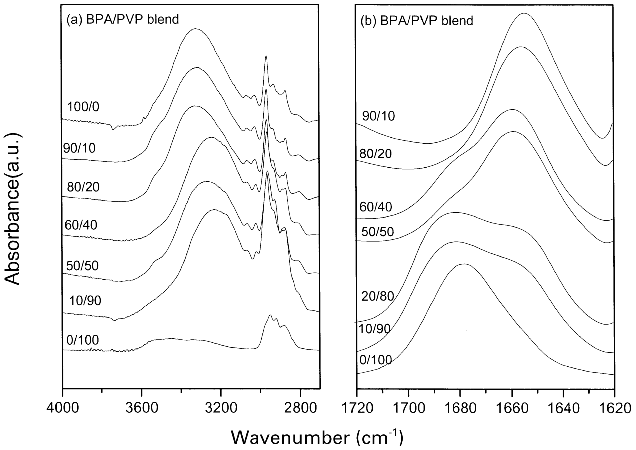

Fig. 3. Infrared spectra of blend of BPA/PVP at room temperature in the hydroxyl stretching region (a) and carbonyl stretching region (b).

In Fig. 2(b), pure PVAc shows the carbonyl vibration band centered at 1740 cm^{-1}, which is attributed to the free carbonyl group. By increasing BPA content, a second band appeared at a lower wavenumber (1710 cm^{-1}) that can be attributed to the hydrogen bonded carbonyl vibration, indicating that the hydrogen bonding existing between the hydroxyl group of BPA and the carbonyl group of PVAc. These two carbonyl bands can be fitted well to the Gaussian function. The fraction of the hydrogen-bonded carbonyl group can be calculated by the following equation [6]

$$f_b^{C=O} = \frac{A_b/a}{A_b/a + A_f} \qquad (1)$$

A_f and A_b denote peak areas corresponding to the free and the hydrogen-bonded carbonyl groups, respectively. In this study, the ratio of these two absorptivities ($a = a_2/a_1$) is equal to 1.5 according to previous infrared studies in the hydroxyl–carbonyl inter-association [28]. Table 2 summarizes results from curve fitting, indicating that the hydrogen bonded fraction of the carbonyl group increases with the increase of the BPA content.

In Fig. 3(a), this broad hydrogen bonded hydroxyl band shifts into lower wavenumber with increasing PVP content (50 wt%) at 3250 cm^{-1}, revealing that the inter-molecular hydroxyl–carbonyl group of BPA/PVP is stronger than the self-association of hydroxyl–hydroxyl bond. Coleman et

Table 2
Curve fitting results of binary blends of BPA/PVAc and BPA/PVP blend at room temperature

	Free C=O			H-bonded C=O			fb (%)[a]
	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	A_f (%)	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	A_b (%)	
BPA/PVAc							
10/90	1741.4	25.3	68.93	1719.7	31.2	31.06	23.10
20/80	1740.9	22.9	63.80	1712.8	25.0	36.20	27.44
30/70	1740.3	21.8	61.75	1711.8	23.4	38.25	29.23
50/50	1739.7	16.8	42.25	1712.0	24.0	57.75	47.68
60/40	1740.0	17.2	37.84	1711.9	25.3	62.16	52.27
80/20	1739.6	16.2	32.20	1711.7	24.7	67.80	58.40
BPA/PVP							
10/90	1684.9	24.0	52.87	1656.8	25.0	47.13	40.68
20/80	1685.6	24.6	52.32	1658.1	26.8	47.68	41.21
50/50	1687.9	17.3	23.51	1658.5	26.7	76.49	71.45
60/40	1683.1	19.5	12.24	1658.5	24.4	87.75	84.64
80/20	1685.8	4.4	0.18	1658.9	26.0	99.81	99.76

[a] fb: fraction of hydrogen bonding.

al. [30] have used the frequency difference ($\Delta\nu$) between the hydrogen bonded hydroxyl absorption and the free hydroxyl absorption to investigate the average strength of the inter-molecular interaction. Compared with Figs. 2(a) and 3(a), we found that the frequency difference from the inter-association hydrogen bonding of BPA/PVP ($\Delta\nu = 275$ cm^{-1}) is stronger than that of the BPA/PVAc ($\Delta\nu = 100$ cm^{-1}), which is consistent with previous DSC results. In Fig. 3(b), the carbonyl stretching absorption splits into two bands at 1680 and 1654 cm^{-1}, corresponding to the free and the hydrogen-bonded carbonyl groups, which also can be fitted well to the Gaussian function. The fraction of the hydrogen-bonded carbonyl group can be calculated based on Eq. (1) by using an appropriate absorptivity ratio ($a = 1.3$) that has been discussed in our previous study [29]. The results from curve fitting are also summarized in Table 2, indicating that the hydrogen bonded fraction of the carbonyl group increases with the increase of the BPA content.

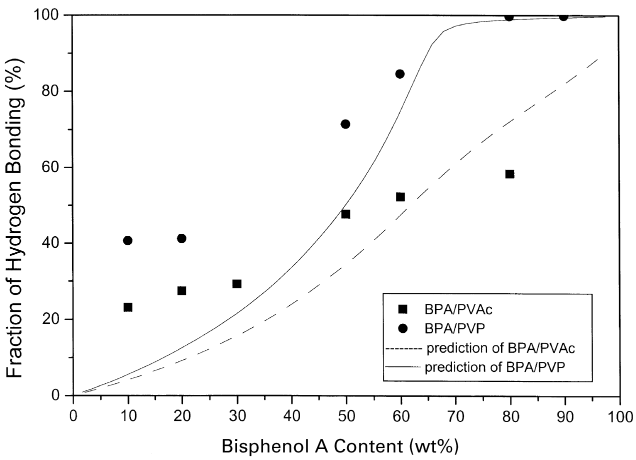

Fig. 4. Fraction of the hydrogen-bonded carbonyl group versus composition: (■) carbonyl group of PVAc, (●) carbonyl group of PVP, (- - -) theoretical values of PVAc and (—) of PVP at 25 °C.

In general, the half-width and wavenumber of carbonyl vibration depends on its specific interaction and transitional dipole coupling between neighboring molecules or polymer segments, especially in the pure PVP homopolymer [31]. In our previous studies [32,33], we have found that the carbonyl vibration of PVP is strongly depended on the chemical environment. For example, the half-width of the pure PVP at 1680 cm^{-1} is decreased and the peak shifts to higher wavenumber at 1682 cm^{-1} with the incorporation of the acetoxystyrene monomer (inert diluent segment) into the PVP chain (PAS-*co*-PVP copolymer). However, after deacetylation of the PAS-*co*-PVP into PVPh-*co*-PVP copolymer, the carbonyl absorption shifts from 1682 to 1651 cm^{-1}. At the same time, the same carbonyl stretching frequency of the PVPh/PVP blend shifts only to 1660 cm^{-1}. In this present work, the carbonyl vibration of PVP shifts to 1654 cm^{-1} with increasing the BPA content, indicating that the hydrogen bonding strength of low molar mass of BPA is stronger than that of the high molecular weight PVPh, but is weaker than the PVPh-*co*-PVP copolymer. In addition, the $W_{1/2}$ of the free carbonyl band from Table 2 increases with increasing PVP content, indicating that the pure PVP has strong transition dipole coupling between neighboring molecules or polymer segment and the observed result is similar to that of our previous study on PVPh/PVP blend [29]. Compared with Fig. 2(b) and Fig. 3(b), the fraction of hydrogen-bonded carbonyl groups of PVAc and PVP are generally increased with increasing BPA content and their relationships are summarized in Fig. 4. Clearly, the fraction of hydrogen-bonded group of PVP is greater than that of the PVAc and this result is also consistent with previous DSC analyses and hydroxyl group analyses by infrared spectra.

Table 3
Summary of the self-association and inter-association equilibrium constants and thermodynamic parameter of BPA/PVAc/PVP ternary blends at room temperature (the molar volume, molecular weight and solubility parameter is estimated by using a group contribution method proposed by Coleman et al. [6])

Polymer	Molar volume (ml/mol)	Molecular weight (g/mol)	Solubility parameter $(cal/ml)^{0.5}$	Self-association equilibrium constant		Inter-association equilibrium constant	
				K_2	K_B	K_A	K_C
Bisphenol A	176.6	228.3	10.38	21.0	66.8		
PVAc	69.8	86.1	9.61			172	
PVP	73.6	115.1	11.0				6000

3.2. Painter–Coleman association model analyses

We initially thought that the self-association equilibrium constant of the pure BPA can be determined directly based on the Whetsel and Lady (W&D) [34] methodology. Unfortunately, the pure BPA is insoluble in most inert diluent solvents, such as cyclohexane, benzene, toluene, and heptane. Therefore, the self-association equilibrium constants of PVPh ($K_2 = 21$ and $K_B = 66.8$) [6] are adopted in BPA in this study. In addition, the inter-association equilibrium constants of PVPh/PVAc ($K_A = 172$) [8] and PVPh/PVP ($K_C = 6000$) [31] from the model compound based on Coggesthall and Saier (C&S) [35] methodology are also adopted in BPA/PVAc and BPA/PVP blends, respectively. Here, we need to emphasize that the inter-association equilibrium constant obtained from model compounds is not exactly the same as that from the true polymer blend due to the intra-molecular screening and functional group accessibility effects [36–39], as well as the chain stiffness and connectivity in a miscible polymer blend. In this study, we intend to compare the inter-association equilibrium constants between BPA/PVAc and BPA/PVP blends based on the same method as employed in the polymer/polymer blend. Table 3 summarizes these equilibrium constants, molar volumes, molecular weights, and solubility parameters of BPA/PVAc and BPA/PVP blends. K_2 and K_B represent the hydrogen-bonded dimer and multimer of the self-association of BPA, respectively. The K_A reflects the extent of the hydrogen bonding in BPA/PVAc and BPA/PVP blends. As a result, the theoretical fractions of hydrogen-bonded carbonyl group of PVAc and PVP can be calculated by using MG&PC software [7] and obtained results are also shown in Fig. 4. Comparing the theoretical and the experimental fractions of hydrogen-bonded carbonyl groups of PVAc and PVP, a substantial deviation is noted, because some assumptions were made in this study as mentioned earlier. However, the trend of this result clearly shows that the strength of inter-association hydrogen bonding in the BPA/PVP blend is indeed greater than that of the BPA/PVAc blend from both theoretical prediction and experimental results.

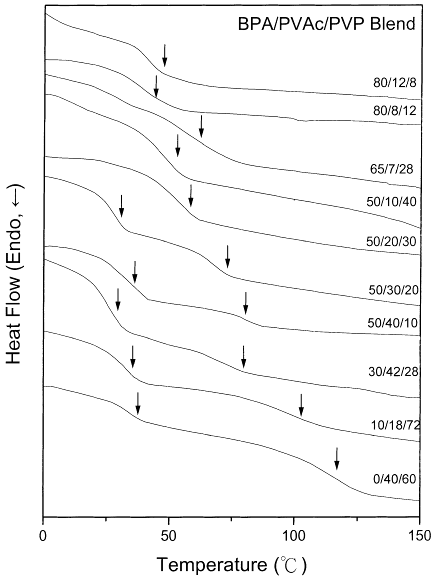

Fig. 5. DSC thermograms of BPA/PVAc/PVP ternary blend with various compositions.

3.3. Bisphenol A/PVAc/PVP ternary blend analyses

For brevity, Fig. 5 shows selected DSC curves of several ternary blends of BPA/PVAc/PVP with various compositions recorded during the second heating scan. The binary polymer blend of PVAc and PVP exhibits two glass transition temperatures located at the same temperatures of their respective pure polymers, revealing that this binary blend is completely immiscible. Substantially, larger solubility parameter difference between PVAc and PVP (1.39 $(cal/ml)^{0.5}$), shown in Table 3 reveals that this PVAc/PVP binary polymer blend is immiscible. However, the T_g shifts with increasing BPA content and the addition of a sufficiently large amount of BPA is able to enhance the immiscible PVAc/PVP binary blend in forming a miscible pair containing a single T_g, because the BPA is able to form hydrogen bonding with both PVAc and PVP and its solubility parameter is located at the interval region between pure PVAc and pure PVP homopolymers. Thermal properties of this ternary blend are summarized in Table 4. Interestingly, the different miscibility behavior is observed for these blends containing a constant composition (50 wt%) of BPA. In our previous study on the phenolic/PEO/PCL ternary blend system [40], we found that the hydroxyl–ether inter-association is more favorable than the

Table 4
Thermal properties of BPA/PVAc/PVP blends

BPA/PVAc/PVP	T_g (°C)		
10/18/72	31.9		98.8
10/36/54	26.7		76.9
10/54/36	40.9		116.8
10/72/18	41.6		116.7
30/14/56		67.9	
30/28/42	24.2		75.4
30/42/28	24.7		68.9
30/56/14	21.4		63.2
50/10/40		47.9	
50/20/30		53.2	
50/30/20	28.1		75.7
50/40/10	38.4		81.8
65/7/28		64.3	
65/14/21		33.6	
65/21/14		41.2	
65/28/7		35.1	
80/4/16		53.6	
80/8/12		37.2	
80/12/8		41.2	
80/16/4		39.9	

hydroxyl–carbonyl inter-association at room temperature, revealing that the phase separation behavior is based on the $\Delta\chi$ and the ΔK effect in the hydrogen bonded ternary polymer system. In this study, the inter-association equilibrium constant between BPA/PVP is greater than that of the BPA/PVAc and the solubility parameter difference between BPA/PVP is smaller than the BPA/PVAc, thus the miscibility improvement by increasing PVP content at a fixed BPA content (50 wt%) is come from the $\Delta\chi$ and the ΔK effect.

Fig. 6 shows the infrared spectra recorded at room temperature in the hydroxyl (a), carbonyl of PVAc (b), and carbonyl of PVP (c) vibration regions for a series of ternary blends containing a constant 50 wt% of BPA. In the BPA/PVAc = 50/50 binary blend, the hydrogen bonded hydroxyl group of the PVAc specific interaction is located at 3400 cm^{-1} as shown in Fig. 6(a). The band at 3400 cm^{-1} is gradually shifted to 3200 cm^{-1} with increasing PVP/PVAc ratios. This change is come from the switch from the relatively weaker inter-molecular hydroxyl–carbonyl interaction of the PVAc to the relatively stronger inter-molecular hydroxyl–carbonyl interaction of PVP. Therefore, we know that the hydrogen bonding strength and its miscibility is increased with increasing of the PVP/PVAc ratio based on the observed hydroxyl vibration shifting to lower wavenumber. Fig. 6(b) shows the infrared spectra of the carbonyl stretching of the PVAc measured at room temperature ranging from 1700 to 1780 cm^{-1} for these ternary blends. The same trend is also observed as that shown in Fig. 2(b), the carbonyl stretching frequency also splits into only two bands at 1740 and 1710 cm^{-1}, corresponding to the free and the hydrogen-bonded carbonyl groups. The carbonyl absorptions of the PVP are also shown in Fig. 6(c), the wavenumbers at 1654 and 1680 cm^{-1} are also assigned as the hydrogen bonded and free carbonyls of the PVP. The fraction of hydrogen-bonded carbonyl group of the PVP can be calculated using an appropriate curve fitting method and the fitting results are summarized in Table 5. Fractions of hydrogen-bonded carbonyl groups from PVAc and PVP are both decreased with increasing PVP/PVAc ratio at a fixed BPA content. However, we need to point here that the total number of hydrogen-bonded carbonyl of the PVP is increased with increasing PVP/PVAc ratio, implying that the miscibility is enhanced through increasing PVP/PVAc ratio. In our previous study [34], we found that the T_g of the poly(vinyl phenol-*co*-acetoxystyrene-*co*-vinyl pyrrolidone) copolymer depends on the frequency difference between the free and hydrogen bonded hydroxyl groups, rather than with the fraction of hydrogen bonding. In this study, we also found that the miscibility behavior is also dependent on the hydrogen bonding strength as shown in Fig. 6(a), not consistent with the fraction of the hydrogen-bonded carbonyl group.

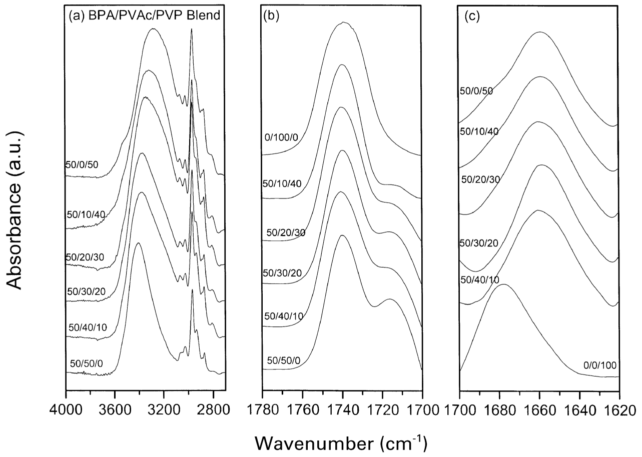

Fig. 6. Infrared spectra of ternary blend of BPA/PVAc/PVP containing a constant composition (50 wt%) of BPA at room temperature in the hydroxyl region (a), carbonyl region of PVAc (b), and carbonyl region of PVP (c).

Fig. 7 shows the phase diagram of the ternary blends of BPA/PVAc/PVP based on DSC analyses. The presence BPA is able to enhance the immiscible of binary blends of PVAc and PVP, and the miscibility window shifts to the rich PVP region due to the significant $\Delta\chi$ and ΔK effect. This result is also consistent with previous Coleman et al. study on prediction of different inter-association equilibrium constant (ΔK) and solubility parameter ($\Delta\chi$) of a ternary hydrogen bonded polymer blend [20]. Compared with previous Pomposo et al. studies on the PVPh/PEMA/PMMA ternary hydrogen bonded polymer blend, the PVPh is miscible with other components with more than 65 wt% of the PVPh [18]. This BPA/PVAc/PVAc ternary blend system is totally miscible only with BPA content of 50 wt% due to larger entropy change. In general, a low molar mass of component usually can act as a plasticizer to improve the processability and flexibility of a polymer by

Table 5
Curve fitting results of BPA/PVAc/PVP blends at room temperature

BPA/PVAc/PVP	Free C=O			H-bonded C=O			fb (%)[a]
	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	A_f (%)	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	A_b (%)	
PVAc							
50/10/40	1712.3	6.6	10.47	1740.5	19.2	89.53	7.24
50/20/30	1714.1	14.5	17.27	1739.5	18.2	82.73	12.21
50/30/20	1714.2	14.8	23.44	1739.5	18.2	76.57	16.97
50/40/10	1715.0	16.5	25.27	1740.4	19.6	74.73	18.40
50/50/0	1714.5	15.4	31.74	1739.7	17.8	68.26	23.67
PVP							
50/0/50	1687.9	17.3	23.51	1658.5	26.7	76.49	71.45
50/10/40	1680.0	11.9	14.57	1658.0	23.2	85.42	81.85
50/20/30	1680.5	10.7	9.059	1658.4	23.2	90.94	88.54
50/30/20	1681.2	8.6	3.753	1657.9	24.5	96.25	95.18
50/40/10	1680.5	4.3	0.271	1657.4	22.4	99.73	99.64

[a] fb: fraction of hydrogen bonding.

reducing its T_g. It is interesting to notice that the thermal property of this miscible ternary blend does not decrease with the increase of the BPA content due to strong hydrogen bonding existing in this ternary polymer system. Consequently, we consider that the dihydric phenol is a good compatibilizer for this immiscible binary polymer blend retaining thermal properties of the original blend.

4. Conclusions

The phase behavior and hydrogen bonding of the ternary blend of BPA/PVAc/PVP have been investigated by using DSC and FTIR analyses. The addition of BPA is able to enhance the miscibility of the PVAc/PVP immiscible binary blend and eventually transforms into a miscible blend with one single T_g, when a sufficiently large amount of the BPA is present. The inter-association equilibrium constant ($K_C = 6000$) between the hydroxyl group of the BPA and the carbonyl group of the PVP is found substantially higher than the $K_A = 172$ from the hydroxyl–carbonyl group of the PVAc and the $K_B = 66.8$ from the hydroxyl multimer formation. This result implies that the tendency of forming the hydrogen bonding between BPA and PVP is more favorable than the inter-association of the BPA with PVAc and the self-association of the BPA by forming the intra-molecular hydrogen bonding. In addition, the solubility parameter difference between BPA and PVP is smaller than that of the BPA and PVAc, revealing that the physical interaction is more favorable in the BPA/PVP blend system. Therefore, the miscibility window is shift to the PVP-rich region due to the significant $\Delta\chi$ and the ΔK effect.

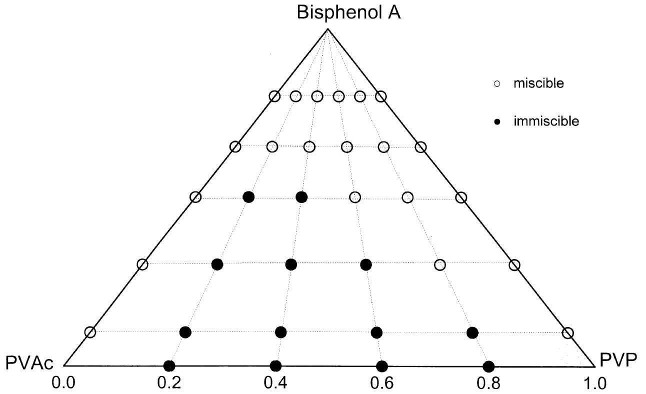

Fig. 7. Ternary phase diagram of the BPA/PVAc/PVP system. The open circles represent miscible ternary blend and the full circles represent immiscible ternary blend.

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