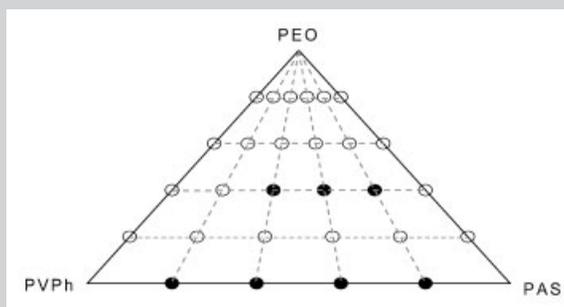


Summary: The miscibility and hydrogen-bonding behaviors of ternary polymer blends of poly(ethylene oxide) (PEO)/poly(vinyl phenol) (PVPh)/poly(acetoxystyrene) (PAS) were investigated by using DSC and Fourier transform infrared spectroscopy (FTIR). The PEO is miscible with both PVPh and PAS based on the observed single T_g over the entire composition range. FTIR was used to study the hydrogen-bonding interactions between PEO with PAS and PVPh, respectively. Quantitative analyses show that the strength of hydrogen-bonding strength is of the order of the hydroxyl-ether inter-association of PVPh/PEO blend > the hydroxyl-hydroxyl self-association of pure PVPh > the hydroxyl-carbonyl inter-association PVPh/PAS blend at room temperature. Furthermore, the addition of PEO is able to enhance the miscibility of immiscible PVPh/PAS binary blends at lower (20 wt.-%) or higher (60 and 80 wt.-%) PEO content. However, there exists a closed immiscibility loop in the phase

diagram at 40 wt.-% PEO content due to the “ $\Delta\chi$ ” and “ ΔK ” effects in this hydrogen-bonded ternary polymer system. Therefore, an interesting and unusual sandwich phase diagram has been observed in this ternary polymer blend.



Ternary phase diagram of the PEO/PAS/PVPh system.

Miscibility Enhancement on the Immiscible Binary Blend of Poly(vinyl phenol) and Poly(acetoxystyrene) with Poly(ethylene oxide)

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Introduction

Multicomponent polymer blends are of significant industrial importance due to a convenient and attractive route for obtaining new polymeric materials. Increasing the number of polymer components in a polymer blend makes the system much more complicated; however, it does provide enhanced design flexibility for the control of multiple properties. In general, three categories of ternary polymer blend phase diagram were observed in this field. First category is based on the works of Scott^[1] and Tompa^[2] on the ternary polymer blends that polymer B, which is miscible with each of polymers A and C, can compatibilize the immiscible binary pair A and C. Polymer B acts as a “compatibilizer” to reduce the size domain of heterogeneous phase separation structure. Classical examples are

the ternary blends of PVDF/PMMA/PEMA,^[3] poly(vinyl phenol) (PVPh)/PMMA/PEMA,^[4] and SAN/PMMA/PEMA.^[5] The second category is that when all three binary pairs are individually miscible, a completely homogeneous has been observed such as PECH/PMMA/poly(ethylene oxide) (PEO),^[6] PVDF/PVAc/PMMA,^[7] phenolic/phenoxy/PCL^[8] and PHB/PEO/PECH,^[9] PAEK/PEEK/PEI,^[10] PEI/PET/PBT,^[11] and PCL/PBzBA/PphMA.^[12] The third category is a closed immiscibility loop phase diagram that is observed when all three binary pairs are also individually miscible. The phase separation is caused by the difference in the interaction energy of the binary system, the so-called “ $\Delta\chi$ ”^[13] and “ ΔK ”^[14] effects in ternary polymer blends such as phenoxy/PMMA/PEO,^[15] PVPh/PVAc/PEO,^[14] SAA/PMMA/PEO,^[16] and phenolic/PEO/PCL^[17] blend systems. Here, an interesting different ternary polymer

blend phase diagram involving hydrogen bonding among their polymer segments was made up besides these three categories of ternary phase diagram.

The interesting result is from our previous study^[18] that the polymer blend of PVPh and poly(acetoxystyrene) (PAS) is immiscible because the intra-molecular association of the PVPh component is more favorable than the inter-molecular interaction between PVPh and PAS segments due to the strong intra-molecular screening effect^[19] in this binary blend system. To enhance the miscibility of this immiscible binary blend of PVPh/PAS, two methods were proposed in our previous studies.^[18,20] One is the incorporation of styrene moiety (diluent segment) into the PVPh main chain, which is able to enhance its miscibility with PAS due to decrease of the strong self-association in the PVPh component in the PVPh/PAS blend.^[18] The other method was prepared by partial hydrolyses of PAS in both acidic and basic solutions to produce a series of PVPh-*co*-PAS copolymers.^[20] These homopolymer segments are linked into the same polymer chain; single glass transition temperatures and the effect of sequence distribution on T_g were found and discussed in our previous study.^[20]

In this study, the ternary hydrogen-bonding polymer blend of PEO/PAS/PVPh was investigated by using DSC and Fourier transform infrared spectroscopy (FTIR). The addition of PEO is able to enhance the miscibility of the immiscible PVPh/PAS binary blend at lower (20 wt.-%) and higher (60 and 80 wt.-%) PEO contents. Here, the third method is proposed to enhance miscibility of this immiscible binary blend of PVPh/PAS. However, an immiscibility phase diagram was found at 40 wt.-% PEO content due to the so-called $\Delta\chi$ and ΔK effects in this hydrogen-bonded ternary polymer system. Therefore, an interesting and unusual sandwich ternary phase diagram was observed in this ternary polymer blend in addition to the above three categories of ternary phase diagrams.

Experimental Part

Materials

Polymers used in this study were PEO, PVPh, and PAS. The PEO with $\bar{M}_n = 20\,000 \text{ g} \cdot \text{mol}^{-1}$ was obtained from Aldrich Co. of USA. The PVPh with a $\bar{M}_w = 9\,000\text{--}11\,000 \text{ g} \cdot \text{mol}^{-1}$ was purchased from Polyscience Inc. of USA. The synthesis of PAS was carried out by free radical polymerization in benzene at 80 °C under nitrogen environment by using the 2, 2'-azoisobutyronitrile (AIBN) initiator. The product was purified by dissolution in benzene and reprecipitation into cyclohexane. The product was dried in a vacuum oven at 80 °C for 12 h. Molar mass and polydispersity index were determined at room temperature by GPC using THF as the mobile phase with $\bar{M}_n = 21\,500 \text{ g} \cdot \text{mol}^{-1}$ and $\bar{M}_w = 28\,000 \text{ g} \cdot \text{mol}^{-1}$.

Preparation of Blend Samples

The ternary polymer blends of PEO/PAS/PVPh with various compositions were prepared by solution blending. Tetrahy-

drofuran solution containing 5 wt.-% polymer mixture was stirred for 6–8 h and then allowed to evaporate slowly at room temperature for 1 d. The film of the blend was then dried at 50 °C for 2 d to ensure that it is free from any residual solvent.

Differential Scanning Calorimetry (DSC)

The glass transition temperature (T_g) of a polymer blend was determined by using a DSC (Du-Pont, DSC model 2900). The scan rate was 20 °C · min⁻¹ ranging from 0 to 170 °C with 5–10 mg sample on a DSC sample cell, and the specimen was quickly cooled to -80 °C after the first scan. The T_g value was obtained at the midpoint of the transition point of the heat capacity (C_p) change with scan rate of 20 °C · min⁻¹ and temperature range of -80–200 °C.

Infrared Spectra

The IR spectra were recorded by a Nicolet Avatar 320 FTIR spectrometer. In all cases, at least 32 scans with an accuracy of 1 cm⁻¹ were signal-averaged. IR spectra of polymer blend films were determined by using the conventional NaCl disk method. The THF 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.

Results and Discussion

Binary Blend System

The DSC was used to assess the miscibility of polymer blend by measuring the glass transition temperature of the blend composition. Most accepted experimental criterion to establish miscibility of pair of polymer is the presence of a single T_g between those of the pure polymers. Figure 1 shows the DSC thermograms of PEO/PAS and PEO/PVPh blends with various compositions recorded during the second heating scan. All these binary compositions exhibit a single T_g based on DSC analyses and their thermal properties are summarized in Table 1, which strongly suggests that all compositions are miscible with homogeneous phase. Compared with Figure 1(a) and (b), we have found that the binary blends of PEO/PAS = 60/40 and 40/60 have the melting temperatures of the PEO component. Nonetheless, melting temperatures of the PEO are missing for binary blends of PEO/PVPh = 60/40 and 40/60, revealing that the inter-molecular interaction of PEO/PVPh blend is greater than that of the PEO/PAS blend. For convenience, the dependence of the T_g on the composition of these blends is shown in Figure 2 that can be fitted well by the Gordon-Taylor Equation (1)^[21]

$$T_g = \frac{W_1 T_{g1} + k W_2 T_{g2}}{W_1 + k W_2} \quad (1)$$

where W_1 and W_2 are weight fractions of the compositions, T_{g1} and T_{g2} represent the component glass transition

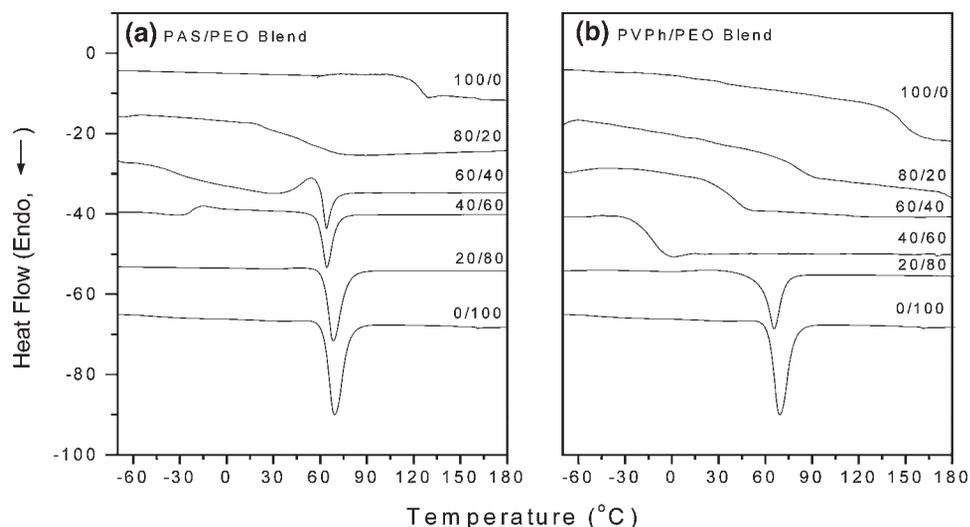


Figure 1. The DSC thermograms of binary blend of (a) PAS/PEO and (b) PVPh/PEO blends with different compositions.

temperatures, and k is fitting constant. In addition, Figure 2 shows $k = 0.14$ for the PEO/PAS blends, and $k = 0.6$ for PEO/PVPh blends. This result is consistent with the finding that the inter-molecular interaction of the binary PEO/PVPh blend is greater than the PEO/PAS binary blend. The high deviation of experimental T_g from the Gordon-Taylor equation at high PEO content shown in Figure 2 is due to the crystallization of PEO in the blends during quenching. This phenomenon indicates that the crystallization of PEO in the blend can change the composition of the amorphous phase, and crystals of PEO are able to act as physical cross-linking points that may hinder the molecular mobility of amorphous phase.

IR spectroscopy has been proven to be a highly effective means of investigating specific interactions between polymers. This tool can be used to study the mechanism

Table 1. Thermal properties of PAS/PEO and PVPh/PEO binary blends.

	T_g	T_m	ΔH_f	T_c	ΔH_c
	°C	°C	J · g ⁻¹	°C	J · g ⁻¹
PAS/PEO					
100/0	122.1				
80/20	13.2				
60/40	-32.3	64.1	5.7	54.2	5.4
40/60	-44.7	64.3	116.2	-15.2	65.3
20/80	-30.1	68.5	152.5		
0/100	-67.0	69.2	175.7		
PVPh/PEO					
100/0	150.0				
80/20	81.4				
60/40	41.1				
40/60	-13.6				
20/80	-11.5	65.6	109.1	26.4	12.6
0/100	-67.0	69.2	175.7		

of inter-polymer miscibility through the formation of hydrogen-bonding or dipole interaction both qualitatively and quantitatively. Figure 3(a) shows scale-expanded IR spectra recorded in the region from 1 680 to 1 800 cm⁻¹ for neat PAS, and various PAS/PEO blends at room temperature. The absorption at 1 760 cm⁻¹ is assigned as the free carbonyl of the PAS. Clearly, the half-width of the free PAS carbonyl peak is increased by blending with PEO. Therefore, a weak hydrogen-bonding interaction existed between the carbonyl group of the PAS and the methylene group of the PEO that has been discussed in our previous study.^[22] In addition, Figure 3(b) illustrates the scale-expanded IR spectra in the range from 2 700 to 4 000 cm⁻¹ of various PVPh/PEO blends measured at room temperature. The pure PVPh shows two distinct bands in the hydroxyl-stretching region. A broadband centered at 3 350 cm⁻¹ and a small shoulder at 3 525 cm⁻¹, corresponding to the multimer hydrogen-bonded hydroxyls and free hydroxyls, respectively. The peak frequency of this broadband shifts to lower wavenumber with increasing PEO content. Meanwhile, the intensity of the free hydroxyl group decreases gradually and disappears eventually with the increase of the PEO content as would be expected. This result reflects a new distribution of hydrogen-bonding formation resulting from the competition between hydroxyl-hydroxyl and hydroxyl-ether interactions. It also reveals that the hydroxyl-ether interaction predominates in PEO-rich blends; therefore, it is reasonable to assign the band at 3 200 cm⁻¹ as the hydroxyl group bonded to the ether group. It is well known that the frequency difference ($\Delta\nu$) between the hydrogen-bonded hydroxyl absorption and free hydroxyl absorption can be used to evaluate the average strength of the inter-molecular interaction.^[23] Therefore, the hydroxyl-ether inter-association ($\Delta\nu = 325$ cm⁻¹) is stronger than the hydroxyl-hydroxyl self-association ($\Delta\nu = 175$ cm⁻¹), and this result

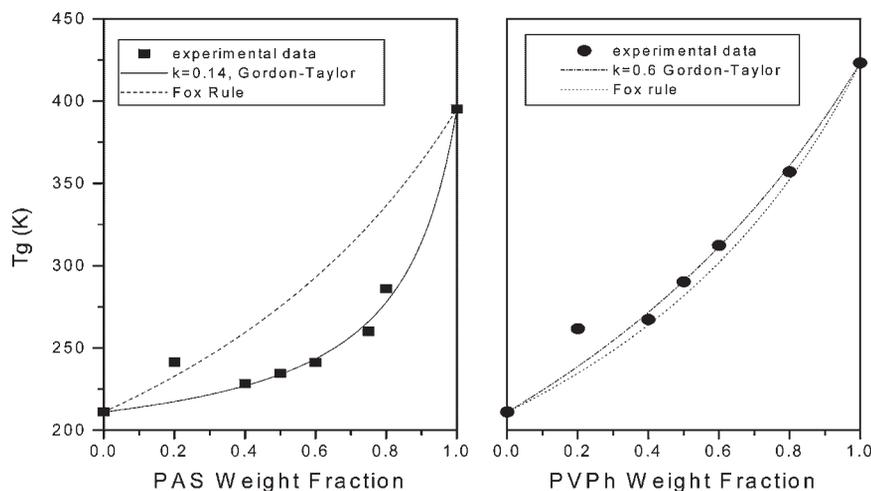


Figure 2. The observed T_g data by DSC versus the T_g values calculated by Gordon-Taylor and Fox equations.

is consistent with the Painter-Coleman association model prediction.^[24]

According to the Painter-Coleman association model, the self-association equilibrium constants, K_B and K_2 , which describe the formation of multimers and dimers, of the PVPh are $K_2 = 21.0$ and $K_B = 66.8$, respectively. K_A describing the inter-association equilibrium constant of PVPh with PEO is 88.3, which has been determined by Coleman et al.²⁴ Therefore, good correlation was found between the Painter-Coleman association model prediction and the IR spectra in the hydroxyl stretching. In addition, compared with the binary polymer blend of PVPh/PAS, the inter-association constant ($K_A < 43.1$) is relatively smaller than the self-association, indicating that the PVPh/PAS

blend may be immiscible or partially miscible due to relatively poorer inter-molecular association. Table 2 lists all the parameters required by the Painter-Coleman association model to estimate thermodynamic properties for the pure PVPh, PVPh/PEO, and PVPh/PAS blends. This result indicates that the hydrogen-bonding strength is the order of the hydroxyl-ether inter-association of PVPh/PEO blend > the hydroxyl-hydroxyl self-association of pure PVPh > the hydroxyl-carbonyl inter-association PVPh/PAS blend at room temperature. This observed result provides the clue that we may obtain a miscible blend between PVPh and PAS through blending with PEO. The addition of PEO into the PVPh/PAS blend is able to reduce the strong self-association and intra-molecular screening effect in the

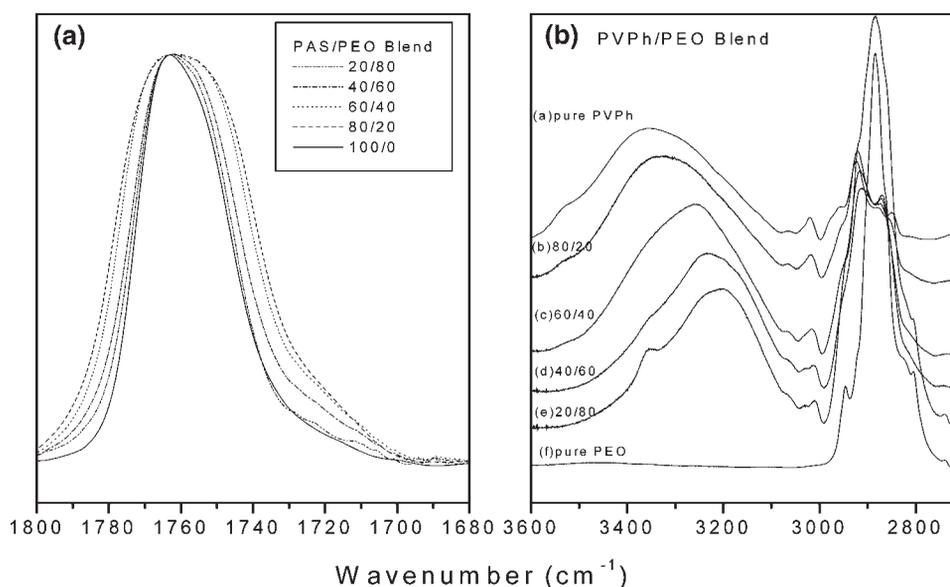


Figure 3. IR spectra of blend of at room temperature in the carbonyl stretching of PAS/PEO blend (a) and hydroxyl stretching of PVPh/PEO blend (b).

Table 2. Summary of the self-association and inter-association parameters of PVPh/PAS and PVPh/PEO blends.

Polymer	Molar volume	Molecular weight	Solubility parameter	Self-association equilibrium constant		Inter-association equilibrium constant
	$\text{ml} \cdot \text{mol}^{-1}$	$\text{g} \cdot \text{mol}^{-1}$	$(\text{cal} \cdot \text{ml}^{-1})^{0.5}$	K_2	K_B	K_A
PVPh	100.0	120.0	10.60	21.0	66.8	
PAS	128.6	162.2	10.29			<43.1
PEO	38.10	44.06	9.40			88.3

PVPh component because hydroxyl group of the PVPh is more favorable to interact with the ether group of the PEO.

Ternary Blend System

We have reported that PEO is totally miscible with PAS and PVPh in the amorphous phase due to strong inter-association hydrogen bonding between the hydroxyl group of the PVPh and the ether group of the PEO, and between the carbonyl group of the PAS and the methylene group of the PEO. In general, the DSC analysis is one of the convenient methods to determine the miscibility in polymer blends. The glass transition temperatures of these pure polymers used in this study, PEO, PAS, and PVPh, are -60 , 122 , and 150 °C, respectively. Figure 4 shows the conventional second-run DSC thermograms of the PEO/PAS/PVPh ternary blend containing a constant PEO content (20 wt.-%) with various PAS/PVPh ratios (80:20, 60:40, 40:60, and 20:80). Essentially all these PEO/PAS/PVPh ternary blends possess single T_g , suggesting that these blends are fully miscible with a homogeneous amorphous phase.

Figure 5 shows the IR spectra of the carbonyl stretching measured at room temperature ranging from 1700 to 1800 cm^{-1} for pure PAS, PAS/PVPh = 20/80 blend, and

various PEO/PAS/PVPh ternary blend containing a constant PAS/PVPh ratio (20/80). For the binary PAS/PVPh blend, the carbonyl stretching frequency is split into two bands at 1760 and 1735 cm^{-1} , corresponding to the free and the hydrogen-bonded carbonyl groups, respectively. Interestingly, the fraction of hydrogen-bonded carbonyl groups is increased with constant PEO content at 20 wt.-%. In our previous study on ternary polymer blends of phenolic/PEO/PCL,^[17] the hydrogen-bonded fraction of the carbonyl group of the PCL decreases with the increase in the relative ratio of the PEO to PCL since the inter-association equilibrium constant of hydroxyl-ether is greater than the inter-association equilibrium constant of hydroxyl-carbonyl at room temperature. However, in the same study,^[17] both inter-association constants of phenolic/PEO and phenolic/PCL blends are higher than the self-association constant of the pure phenolic. On the contrary, in this study, the inter-association equilibrium constant of the PVPh/PAS blend ($K_A < 43.1$) is smaller than the self-association equilibrium constant of the pure PVPh ($K_B = 66.8$), indicating that the pure PVPh favors the intra-chain hydrogen bonding. The addition of PEO into the PVPh/PAS blend is able to decrease the strong self-association in the PVPh component since the inter-association equilibrium constant of PVPh with PEO is greater than the

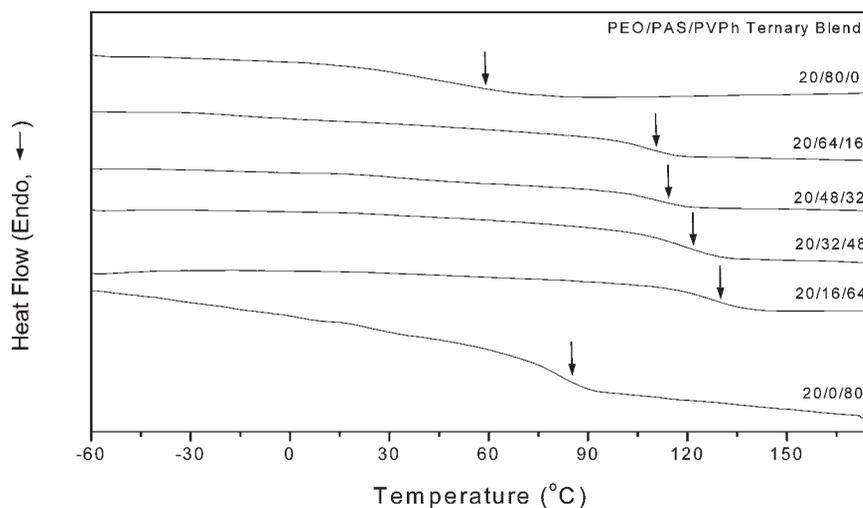


Figure 4. DSC thermograms of ternary blend of PEO/PAS/PVPh containing a constant composition (20 wt.-%) of PEO.

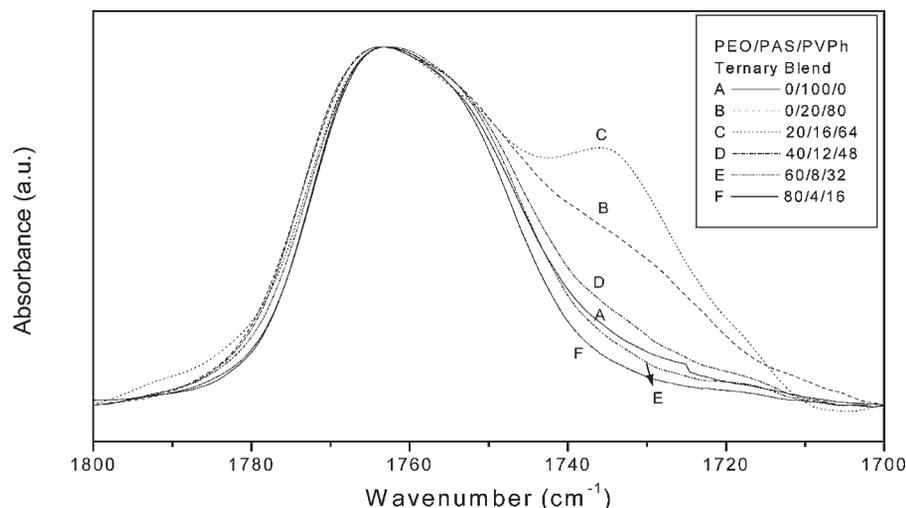


Figure 5. IR spectra recorded at room temperature at 1700–1800 cm^{-1} region for ternary PEO/PAS/PVPh blends.

self-association equilibrium constant of the pure PVPh. As a result, the fraction of hydrogen-bonded carbonyl group of the PAS is increased with the PEO content at 20 wt.-% since the probability of the hydroxyl-carbonyl hydrogen bonding is increased.

Now, we turn our attention to those ternary blends containing a higher PEO content at 40 wt.-%. Figure 6 shows the second-run DSC thermograms of various PEO/PAS/PVPh ternary blends containing a fixed 40 wt.-% PEO. The binary PEO/PAS, PEO/PVPh, and ternary PEO/PAS/PVPh = 40/48/12 blends show a single T_g . However, ternary polymer blends of PEO/PAS/PVPh = 40/36/24, 40/24/36, and 40/12/48 have two T_g s, implying that they are immiscible in the amorphous phase. In general, the phase separation in a ternary blend can be caused by the so-called $\Delta\chi$ and ΔK effects, which is the difference in physical and

hydrogen-bonding interactions between PVPh/PEO and PVPh/PAS. The PVPh is more favorable to interact with PEO than the PAS which is defined as ΔK effect since the difference in inter-association equilibrium constant tends to induce phase separation. At a higher PEO content (40 wt.-%), the hydroxyl group of the PVPh tends to interact totally with the ether group of the PEO so that the fraction of hydrogen-bonded carbonyl group of the PAS decreases with the increase in the PEO content and the PAS phase tends to induce phase separation as shown in Figure 5. Compared with the PEO/PAS/PVPh = 20/16/64, the fraction of hydrogen-bonded carbonyl group of the PAS in PEO/PAS/PVPh = 40/12/48 is substantially less.

Figure 7 shows the second run DSC thermograms of various PEO/PAS/PVPh ternary blends containing a constant PEO content of 60 and 80 wt.-%. Essentially all these

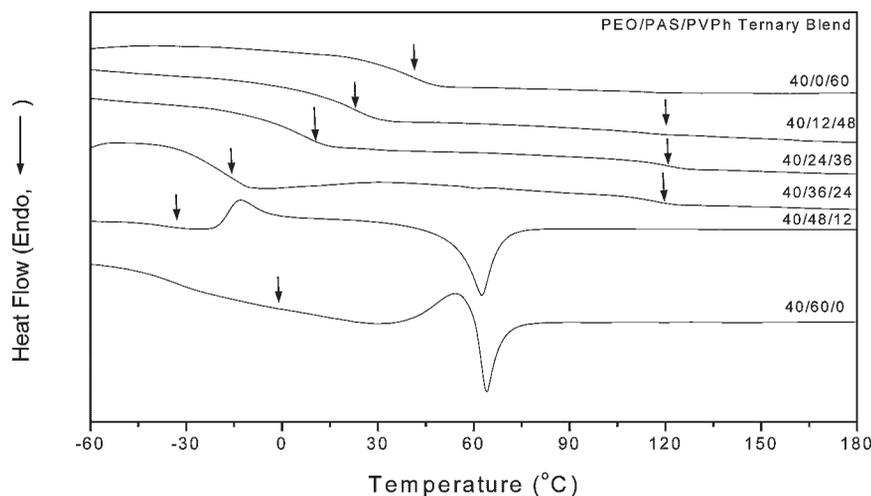


Figure 6. DSC thermograms of ternary blend of PEO/PAS/PVPh containing a constant composition (40 wt.-%) of PEO.

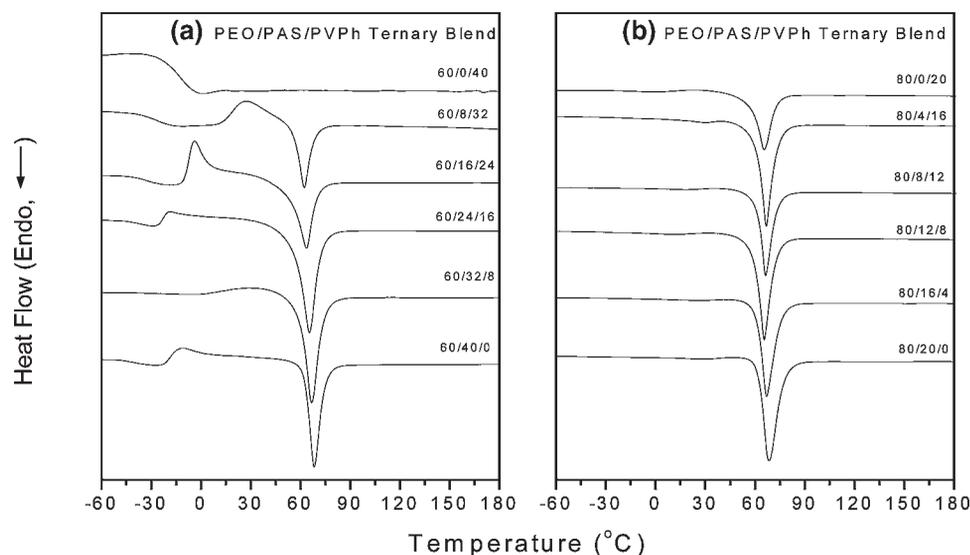


Figure 7. DSC thermograms of ternary blend of PEO/PAS/PVPh containing a constant composition (60 wt.-%) of PEO (a) and 80 wt.-% PEO (b).

ternary blends show one single glass transition temperature, indicating that these ternary blends are all miscible in the amorphous phase. In addition, the melting temperature of the PEO decreases with the increase of the PVPh content, also indicating that the PEO/PVPh blend inter-molecular interaction is greater than the PEO/PAS blend. All thermal properties in those ternary polymer blends are summarized in Table 2. At a higher PEO content, the PEO component is analogous to the introduction of a solid-state good solvent to the mixture of two immiscible polymer blends of PAS/PVPh. Although the fraction of the hydrogen-bonded carbonyl group of the PAS decreases significantly at higher PEO content, eventually all hydroxyls of the PVPh completely interacted with ether groups of the PEO as shown in Figure 5. Taking into account the PEO compositions, the

excess PEO content still has the weak hydrogen-bonding interaction with the carbonyl group of the PAS. As a result, this ternary polymer blend of PEO/PAS/PVPh is totally miscible at higher PEO contents.

Figure 8 shows the IR spectra of the hydroxyl stretching measured at room temperature ranging from 2700 to 4000 cm^{-1} for PAS/PVPh = 20/80 blend and various PEO/PAS/PVPh ternary blends containing a constant PAS/PVPh ratio (20/80). Compared with the binary blend of PAS/PVPh = 20/80 and ternary blend of PEO/PAS/PVPh = 20/16/64, the fraction of the PVPh free hydroxyl in PEO/PAS/PVPh ternary blend is greater than the binary PAS/PVPh blend due to decrease of the strong self-association in the PVPh component as mentioned previously. In the meantime, the hydroxyl-stretching band becomes broader,

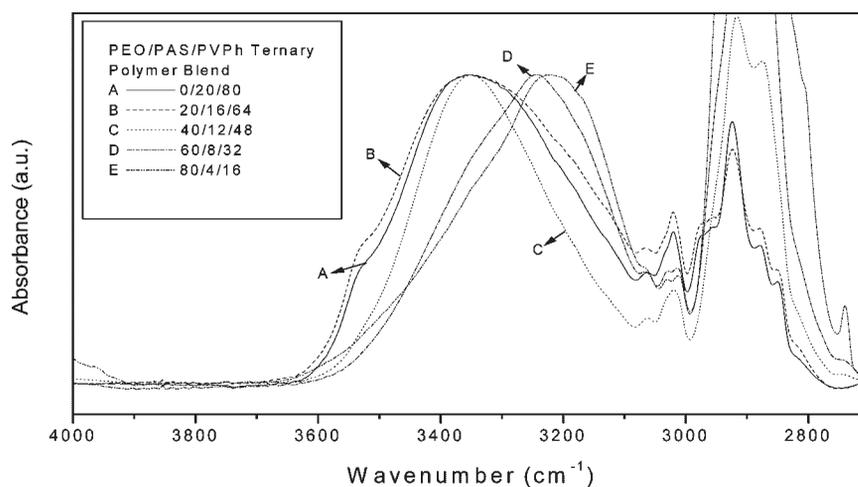


Figure 8. IR spectra recorded at room temperature at 2700–4000 cm^{-1} region for ternary PEO/PAS/PVPh blends.

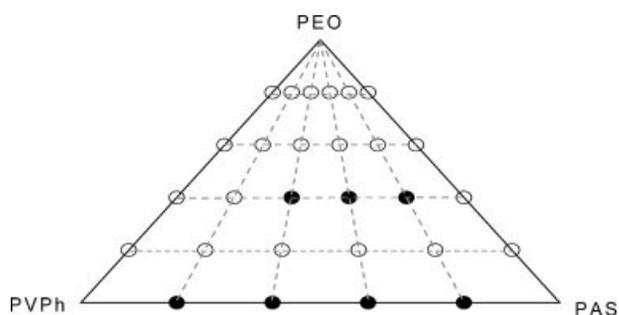


Figure 9. Ternary phase diagram of the PEO/PAS/PVPh system. The open circles represent miscible ternary blend and the full circles represent immiscible ternary blend.

suggesting that there are more different types of hydroxyl groups in PEO/PAS/PVPh than PVPh/PAS binary blends. Therefore, the addition of PEO component is able to disturb the strong self-association of the PVPh and induces more PVPh hydroxyls to form hydrogen bonds with PAS carbonyls. On the contrary, in the case of the immiscible ternary polymer blend of PEO/PAS/PVPh = 40/12/48, the hydroxyl-stretching band becomes narrower, indicating that the hydroxyl group of the PVPh completely interacts with the PEO ether group; therefore, the PAS phase tends to phase separation in this composition. At higher PEO contents (60 and 80 wt.-%), the peak frequency of the broadband shifts to lower wavenumber with increasing PEO content. This result reflects a new distribution of hydrogen-bonding formation resulting from the competition among hydroxyl-hydroxyl, hydroxyl-carbonyl, and hydroxyl-ether interactions. Clearly, in this ternary polymer blend, the hydrogen-bonding strength is also of the order of the hydroxyl-ether inter-association of PVPh/PEO blend > the hydroxyl-hydroxyl self-association of pure PVPh > the hydroxyl-carbonyl inter-association PVPh/PAS blend at room temperature, which is consistent with the one

previously mentioned. Again, although the hydroxyl-ether interaction is predominate at higher PEO content, the excess PEO is able to interact with the PAS through the weak hydrogen-bonding interaction between the methylene group of PEO and the carbonyl group of PAS. In summary, the ternary phase diagram of PEO/PAS/PVPh blends is illustrated in Figure 9 based on the T_g property summarized in Table 3. The immiscible polymer blend of PAS/PVPh is able to transform to miscible blend by addition of the PEO component at higher and lower contents by decreasing the strong self-association of the PVPh and the compatibilizer effect. However, there exists a closed immiscibility loop in the phase diagram at 40 wt.-% PEO content due to the $\Delta\chi$ and ΔK effects in this hydrogen-bonded ternary polymer system. Here, an interesting and unusual ternary phase diagram was proposed.

Conclusion

The phase behavior and hydrogen bonding of ternary blends of PEO/PAS/PVPh have been investigated by using DSC and FTIR analyses. Although the hydrogen bonding existing between PVPh and PAS segments is expected, experimental results indicated that PVPh is actually immiscible with PAS due to the strong self-association of the PVPh and the intra-molecular screening effect of the PVPh/PAS blend system. However, the incorporation of PEO into the PVPh/PAS blend is able to form fully miscible blends at either high or lower PEO content by decreasing the strong self-association of the PVPh and compatibilizer effect. However, there exists a closed immiscibility loop in the phase diagram at 40 wt.-% PEO content due to $\Delta\chi$ and ΔK effects in this hydrogen-bonded ternary polymer system. Good correlation was found between the DSC and FTIR analyses.

Table 3. Thermal properties of PEO/PAS/PVPh blends.

PEO/PAS/ PVPh	T_g °C	T_m °C	ΔH_f J · g ⁻¹	T_c °C	ΔH_c J · g ⁻¹
20/64/16	127.7				
20/48/32	121.1				
20/32/48	112.8				
20/16/64	110.3				
40/12/48	23.0	113.9			
40/24/36	5.6	119.8			
40/36/24	-19.2	117.4			
40/48/12	-37.5	62.6	54.8	-13.0	48.5
60/8/32	-26.6	62.4	31.4	27.3	26.8
60/16/24	-32.7	63.6	66.3	-3.9	52.6
60/24/16	-37.0	65.4	77.7	-18.5	28.4
60/32/8	-28.4	66.8	98.9	31.8	20.8
80/4/16	-33.7	66.5	116.2		
80/8/12	-38.1	66.7	125.6		
80/12/8	-26.5	66.8	132.1		
80/16/4	14.2	66.9	133.8		

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