Effect of Inert Diluent Segment on the Miscibility Behavior of Poly(vinylphenol) with Poly(acetoxystyrene) Blends

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ABSTRACT: Polymer blends of poly(vinylphenol) (PVPh) and poly(styrene-*co*-vinylphenol) with poly(*p*-acetoxystyrene) (PAS) were prepared by solution casting from tetrahydrofuran solution. The thermal properties and hydrogen bonding of the blends were investigated by differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy. Although hydrogen bonding existed between the PVPh and PAS segments, the experimental results indicated that PVPh is immiscible with PAS as shown by the existence of two glass-transition temperatures over the entire composition range by DSC. This phenomenon is attributed to the strong self-association of PVPh, intramolecular screening, and functional group accessibility effects of the PVPh/PAS blend system. However, the incorporation of an inert diluent moiety such as styrene into the PVPh chain renders the modified polymer to be miscible with PAS. Copolymers containing between 16 and 51 mol % vinylphenol were fully miscible with PAS according to DSC studies. These observed results were caused by the reduction of the strong self-association of PVPh and the increase of the interassociation between PVPh and PAS segments with the incorporation of styrene on the PVPh chain. According to the Painter–Coleman association model, the interassociation equilibrium constant of PVPh/PAS blends was determined by a model compound and polymer blend. Good correlation between these two methods was obtained after considering the intramolecular screening and functional group accessibility effect in the polymer blend. © 2002 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 40: 1661–1672, 2002

Keywords: miscibility; hydrogen bonding; poly(vinylphenol); poly(styrene-*co*-vinylphenol); poly(acetoxystyrene)

INTRODUCTION

Poly(vinylphenol) (PVPh) and a number of polymers with functional groups, such as carbonyl, ether, and pyridine groups, have been reported to be miscible in the amorphous phase as a result of interassociation hydrogen bonding between the hydroxyl group of PVPh and functional groups of the second polymers.[1–5] Hydrogen bonding of the self-association (K_B) and interassociation equilib-

rium constants (K_A) can be obtained by Fourier transform infrared spectra as well as determine the number or fractions of functional groups that are "hydrogen bonded" or "free" according to the Painter–Coleman association model (PCAM).[6] In general, the self-association equilibrium constant is determined from low molar mass molecules (model compound) diluted by an inert solvent (nonpolar group) such as cyclohexane according to the Whetsel and Lady[7] methodology. Moreover, the interassociation equilibrium constant can be determined by two methods, that is, Coggeshall and Saier[8] methodology using model compounds and the polymer blend using PCAM. However, these self- and interassociation equilibrium con-

stants cannot be obtained independently from their mixtures. Fortunately, the relative magnitudes of the inter- and self-association equilibrium constants are more important that dominantly determine the contribution of the free energy of mixing rather than their individual absolute values. If the interassociation is strongly favored over self-association, then the polymer blend is expected to be miscible such as the poly(p-vinylphenol)/poly(N-vinylpyrrolidone) blend system ($K_A/K_B \doteqdot 100$).[9,10] Conversely, if the self-association is stronger than the interassociation, then the blend tends to be immiscible or partially miscible as this PVPh/poly(p-acetoxystyrene) (PAS) blend system.

In our previous study,[11] we discovered that the phenolic/PAS blend is totally miscible on the basis of a single glass-transition temperature (T_g) resulting from the formation of hydrogen bonding between the hydroxyl of the phenolic and the carbonyl of PAS. Furthermore, the interassociation equilibrium constant for the phenolic/PAS blend ($K_A = 64.6$) is greater than the self-association equilibrium constant ($K_B = 52.31$), implying that the tendency toward forming interhydrogen bonding of the phenolic resin and PAS dominates the self-association of the phenolic resin in the mixture. Nonetheless, in this study, we found that the PVPh/PAS blend is immiscible as shown by the existence of two T_g's over the entire composition range by differential scanning calorimetric (DSC) analyses. Initially, this observation seems counterintuitive because of the expected hydrogen bonding between the hydroxyl group of PVPh and the carbonyl group of PAS. However, the polymer-chain architecture is significantly different from the low molar mass molecule because of intramolecular screening and functional group accessibility[12–17] caused by the chain connectivity. The intramolecular screening effect is caused by an increase in the number of contacts by the same polymer chain as a result of the self-bending back of the polymer chain, and the number of interassociation hydrogen bonds per unit volume in the polymer blend will be less relative to the model compound. Moreover, the spacing between the functional group along a polymer chain and bulky side group also significantly reduces the interassociation hydrogen bonds per unit volume because of the so-called functional-group accessibility effect. This effect is attributed to steric crowding and shielding.[15]

Therefore, the interassociation equilibrium constant between the polymer blend and the model compound should be different after considering the intramolecular screening, functional-group accessibility effects, and polymer-chain architecture. In this study, we found that the interassociation equilibrium constant of the PVPh/PAS blend ($K_A = 43.1$) is smaller than the self-association equilibrium constant of pure PVPh ($K_B = 66.8$), indicating that the pure PVPh favored intrachain hydrogen bonding by themselves. As a result, the PVPh/PAS blend system is immiscible, showing two T_g's as a result of relatively weaker interassociation between the hydroxyl group of PVPh and the carbonyl group of PAS. However, the corresponding interassociation equilibrium constant obtained from model compounds ($K_A = 134.8$) is significantly higher than the self-association equilibrium constant of pure PVPh ($K_B = 66.8$), indicating that the hydroxyl group of PVPh and the carbonyl group of PAS are able to obtain a miscible polymer blend inherently. To consider this effect, the incorporation of an inert diluent such as styrene into the PVPh chain should be able to reduce the self-association of pure PVPh and increase the intermolecular association between the hydroxyl group of PVPh and the carbonyl group of PAS. Furthermore, the standard interassociation equilibrium constant (reference molar volume = 100 cm³/mol) will increase with the incorporation of styrene into the PVPh chain. The purpose of this study is to determine the miscibility window of poly(styrene-co-vinylphenol) (PSOH)/PAS blends and to calculate the interassociation equilibrium constant between the hydroxyl group of PVPh and the carbonyl group of PAS.

EXPERIMENTAL

Samples

PVPh with a weight-average molecular weight (M_w) of 9000–10,000 was purchased from PolyScience. PAS was obtained through radical polymerization of the PAS monomer using azobisisobutyronitrile initiator (1 wt % based on monomer) at 60 °C under a nitrogen atmosphere, and the PSOH copolymers were obtained from poly(styrene-co-acetoxystyrene) copolymers after deprotection of the acetyl group. A detailed synthesis of PAS and PSOH is described in our previous study. Here, we point out that the PSOH copolymer sequence is nearly random in nature because the product of the reactivity ratios is near
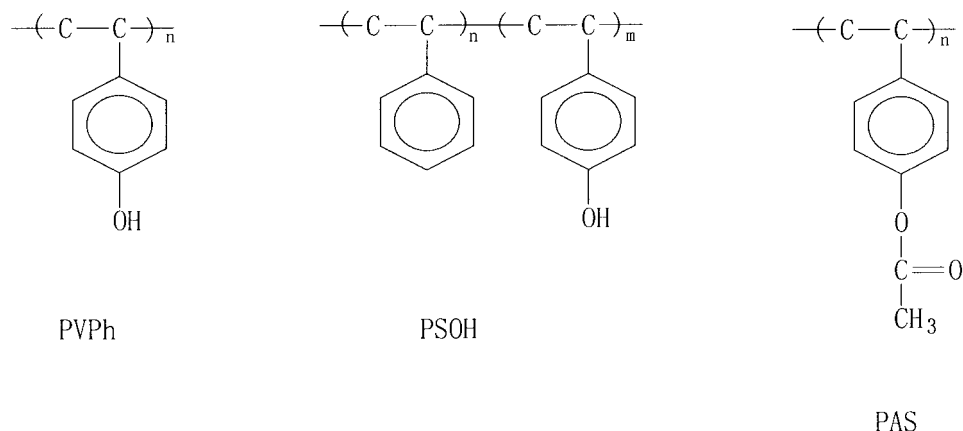
Scheme 1

1.6 (r_1 = 2.34, r_2 = 0.72), and monomers introduced into the polymer chain are essentially random. The chemical structures of PVPh, PSOH, and PAS are illustrated in Scheme 1.

Blend Preparation

Polymer blends of PVPh/PAS and PSOH/PAS with various compositions were prepared by solution-blending. Tetrahydrofuran (THF) solution containing 5 wt % polymer mixture was stirred for 6–8 h, and the solution was allowed to evaporate slowly at room temperature for 1 day. The film of the blend was then dried at 50 °C for 2 days.

Characterizations

DSC

The T_g of the blend was performed using a DSC instrument from DuPont (DSC-9000) with a scan rate of 20 °C/min and a temperature range of 30–180 °C. The measurement was made using 5–10 mg sample on a DSC sample cell after the sample was quickly cooled to 30 °C from the melt of the first scan. The T_g was obtained as the inflection point of the jump heat capacity.

Infrared Spectroscopy

Infrared spectra of the polymer blend films were determined with the conventional NaCl dish method. The THF solution containing the blend was cast onto a NaCl disk and dried under condition similar to that used in the bulk preparation. The film used in this study was thin enough to obey the Beer–Lambert law. Fourier transform infrared (FTIR) measurements were recorded on a Nicolet Avatar 320 FT-IR spectrophotometer, and 32 scans were collected with a spectral resolution of 1 cm^{-1}. For the solution sample, an adequately sealed cell with NaCl windows and 0.05 mm sample thickness was used. All model compound solutions in the absorption range obeyed the Beer–Lambert law. Cyclohexane was selected as the solvent because the specific conformation of cyclohexane is favorable in this study.

RESULTS AND DISCUSSION

PVPh/PAS Blend Analyses

DSC has been extensively used to investigate the miscibility of polymer blends. Figure 1 shows DSC thermograms for pure PVPh, pure PAS, and various PVPh/PAS blends. All PVPh/PAS blends indicate two T_g's, implying that PVPh/PAS is an immisicible blend system, although hydrogen bonding between the hydroxyl group of PVPh and the carbonyl group of PAS is expected. This phenomenon is due to the strong self-association of the PVPh component and the relatively weaker self-association in the interassociation hydrogen bonding, revealing that the intramolecular association of the PVPh component is more favorable than the intermolecular interaction between the PVPh and PAS segments. Figure 2 describes the infrared spectra of the carbonyl stretching measured at 25 °C ranging from 1680 to 1820 cm^{-1} for pure PAS and various PVPh/PAS blends. The carbonyl stretching frequency is split into two bands at 1760 and 1735 cm^{-1} corresponding to the free
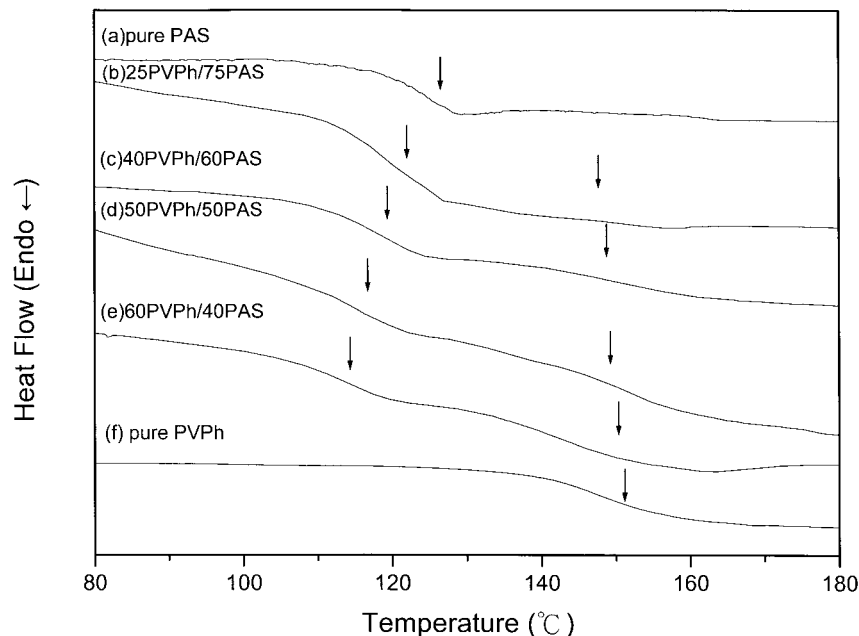
Figure 1. DSC scans of the PVPh/PAS blends with different compositions: (a) 0/100, (b) 25/75, (c) 40/60, (d) 50/50, (e) 60/40, and (f) 0/100.

and hydrogen-bonded carbonyl groups, respectively. These two bands can be readily decomposed into two Gaussian peaks, with areas corresponding to the free carbonyl (1760 cm^{-1}) and hydrogen-bonded carbonyl (1735 cm^{-1}) absorptions. The fraction of the hydrogen-bonded carbonyl group[6] is calculated from eq 1

$$f_b^{C=O} = \frac{A_b/1.5}{A_b/1.5 + A_f} \tag{1}$$

where A_b and A_f are the peak areas corresponding to the hydrogen-bonded carbonyl and free carbonyl groups, respectively. The conversion coefficient of 1.5 is the absorptivity ratio of these two bands, that is, the "free" and "hydrogen bonded" carbonyl groups, in an ester group.[6] Table 1 summarizes the curve-fitting results, indicating that the hydrogen-bonded fraction of the carbonyl group approaches a maximum value for the blend containing 50 wt % PVPh [Fig. 2(d)] and then decreases gradually with an increase in the PVPh content. The observed results offer evidence that the PVPh component indeed has a stronger intramolecular association than intermolecular association because of the strong intramolecular screening effect in this blend system. As a result, the fraction of the hydrogen-bonded carbonyl group decreases with an increasing PVPh content
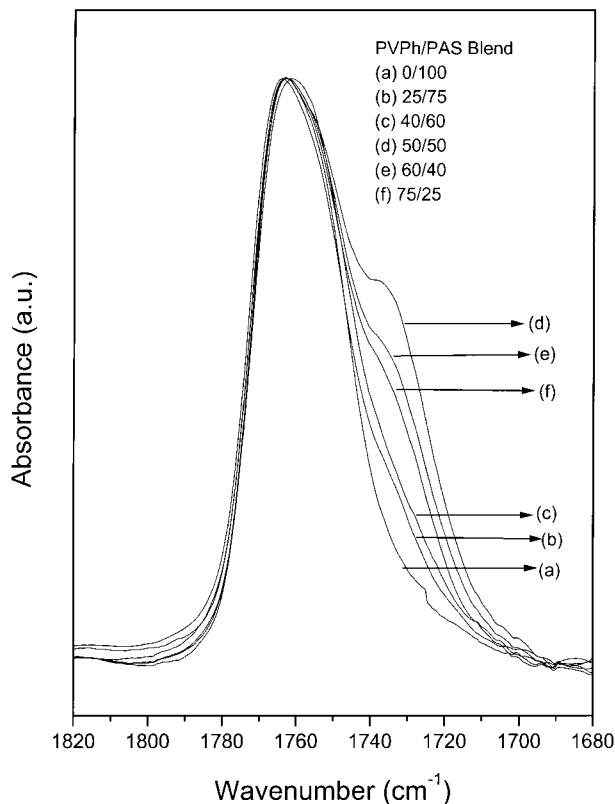

Figure 2. FTIR spectra recorded at room temperature in the 1680–1820 cm^{-1} region for the PVPh/PAS blends: (a) 0/100, (b) 25/75, (c) 40/60, (d) 50/50, (e) 60/40, and (f) 75/25.

Table 1. Curve-Fitting Result of the EPh/TAc Blend at 25 °C

EPh/Tac (wt %)	Free C=O			H Bonded C=O			
	ν (cm^{-1})	$A_f(\%)$	ν (cm^{-1})	$A_b(\%)$	ν (cm^{-1})	$A_b(\%)$	$f_b{}^a$
25/25	1762.2	63.87	1742.4	6.87	1730.0	29.25	36.12
40/60	1761.8	51.05	1742.9	8.27	1728.4	40.68	48.94
50/50	1761.7	46.79	1743.1	11.69	1728.3	41.51	53.20
60/40	1761.3	36.42	1743.4	12.50	1727.7	51.10	63.60
75/25	1760.5	30.88	1743.1	17.06	1727.3	52.04	69.11

[a] f_b: fraction of hydrogen bonding.

at a higher PVPh composition. Figure 3 determines infrared spectra ranging from 2700 to 4000 cm^{-1} of pure PVPh and various PVPh/PAS blends. The pure PVPh polymer exhibits two bands in the hydroxyl-stretching region of the infrared spectrum. A very broad band centered at 3350 cm^{-1} is attributed to the wide distribution of the hydrogen-bonded hydroxyl group, whereas
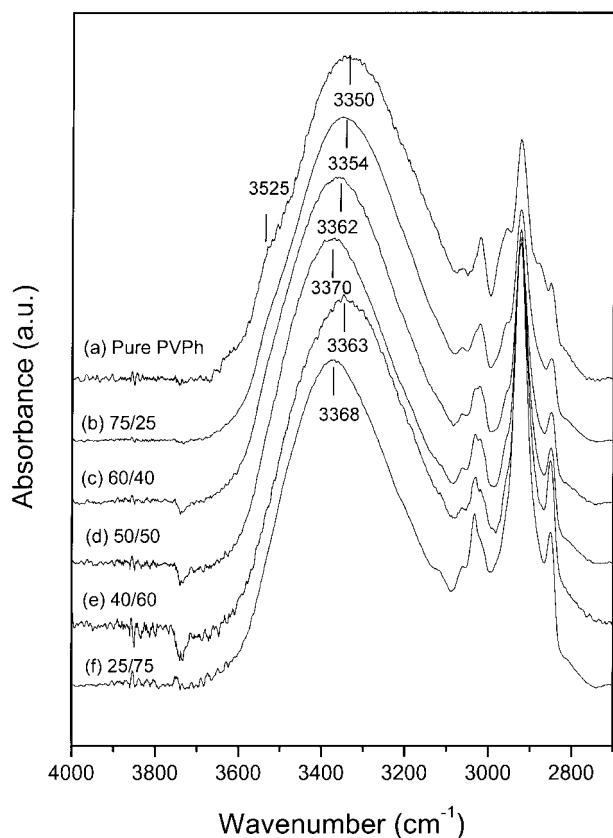

Figure 3. FTIR spectra recorded at room temperature in the 2700–4000 cm^{-1} region for the PVPh/PAS blends: (a) pure PVPh, (b) 75/25, (c) 60/40, (d) 50/50, (e) 40/60, and (f) 25/75.

the narrower band at 3525 cm^{-1} is from the free hydroxyl group of pure PVPh. The broad hydrogen-bonded hydroxyl band of PVPh shifts gradually into higher frequency with an increasing PAS content up to 50 wt % of the PAS at 3370 cm^{-1} [Fig. 3(d)]. This change is from the switch from the intramolecular hydroxyl–hydroxyl bond to the intermolecular hydroxyl–carbonyl bond, indicating that a hydrogen-bonding interaction exists between the PAS carbonyl group and the hydroxyl group of PVPh. Moskala et al.[18] have used the frequency difference ($\Delta\nu$) between the hydrogen-bonded hydroxyl absorption and free hydroxyl absorption to investigate the average strength of the intermolecular interaction. In this study, we found that the interassociation between hydroxyl group of PVPh and the carbonyl group of PAS is weaker than the self-association of the PVPh component. In addition, the PVPh component indeed possesses greater intramolecular association than intermolecular association. Furthermore, these two immiscible T_g's shift lower relative to their homopolymers because of this phenomenon.

However, Figure 4 displays various infrared spectra of ethylphenol (EPh)/tolyl acetate (TAc) mixtures recorded at room temperature in the region from 1680 to 1820 cm^{-1}. This free TAc carbonyl peak at 1760 cm^{-1} is well separated from the carbonyl group that is hydrogen bonded to the isolated EPh at 1740 cm^{-1} and multimer EPh at 1730 cm^{-1}. The detailed physical picture is described in Figure 5. The corresponding area is able to decompose into three Gaussian peaks, and the curve-fitting results are summarized in Table 1, revealing that the fraction of the hydrogen-bonded carbonyl group increases with increasing EPh content. Certainly, the fraction of the hydrogen-bonding model compound is significantly higher than that from the polymer blend
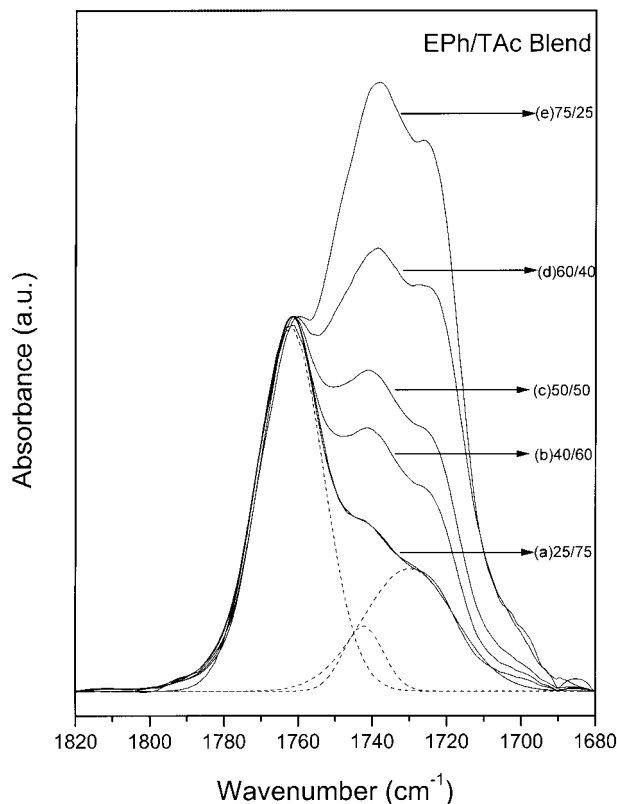
Figure 4. FTIR spectra recorded at room temperature in the 1680–1820 cm^{-1} region for ethylphenol/tolyl acetate mixtures: (a) 25/50, (b) 40/60, (c) 50/50, (d) 60/40, and (e) 75/25.

because both intramolecular screening and functional-group accessibility effects are not present in the low molar mass mixture. Nonetheless, the observed result provides the clue that we can obtain a miscible blend between PVPh and PAS

through modification of these two polymers. The incorporation of styrene moiety into the PVPh polymer chain can dilute and decrease the strong self-association in the PVPh component in the PVPh/PAS blend. Thus, the fraction of the intermolecular hydrogen-bonding density will increase with an increasing polystyrene (PS) content in the PSOH copolymer.

PSOH/PAS Blend Analyses

Glass-transition behaviors of PSOH/PAS blends containing various vinylphenol contents in the PSOH copolymer were examined by DSC, and the results are illustrated in Figure 6. Table 3 summarizes the T_g behaviors for all PSOH/PAS blends revealing that these copolymers containing 16–50 mol % of vinylphenol are fully miscible with PAS on the basis of one T_g. Figure 7 depicts the miscibility window for PSOH/PAS blends where the x axis is the weight fraction of the PAS content in the blend where the y axis is the molar percentage of vinylphenol in the PSOH copolymer. PAS is completely miscible with the PSOH copolymer containing 16–50 mol % of vinylphenol.

According to the Painter–Coleman association model, two major factors are responsible for the increase in the miscibility window. First, when the difference in the solubility parameters of the two blend components is lower, the corresponding χ will also be lower. The incorporation of PS (δ = 9.48 cal/cm^3) into PVPh (δ = 10.6 cal/cm^3) is expected to decrease its solubility parameter difference at a certain PVPh content with PAS (δ = 10.29 cal/cm^3). Second, the relative strength of
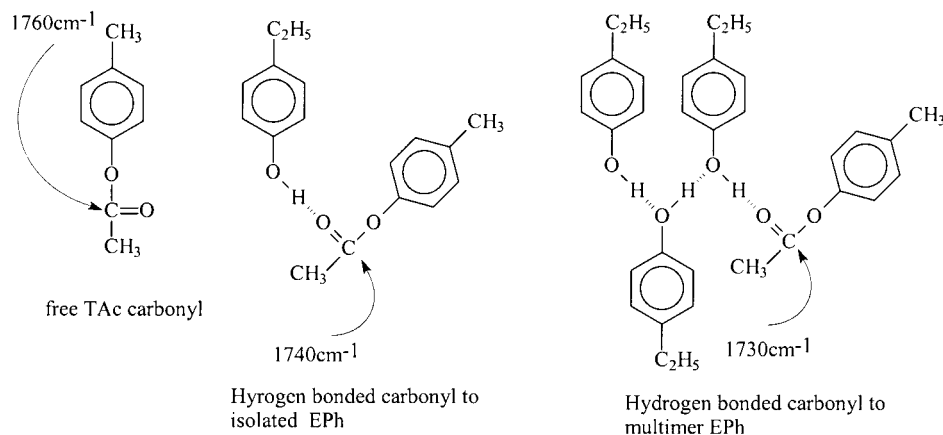

Figure 5. Physical pictures of interaction between ethylphenol and tolyl acetate.
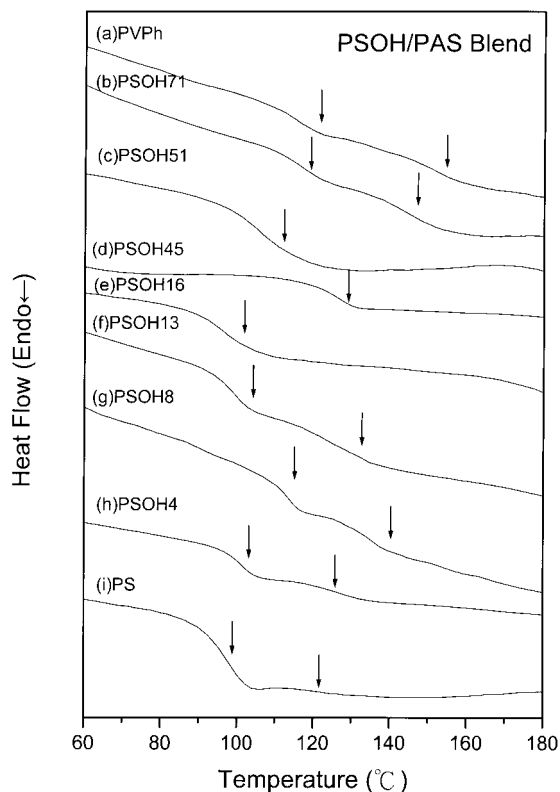
Figure 6. DSC curves of PSOH/PAS = 50/50 blends containing different vinylphenol contents in PSOH copolymers: (a) pure PVPh, (b) PSOH71, (c) PSOH50, (d) PSOH45, (e) PSOH16, (f) PSOH13, (g) PSOH8, (h) PSOH4, and (i) pure PS.

Table 3. T_g Behavior of PSOH/PAS Blend by Varying Vinylphenol Content in the PSOH Copolymer

Polymer	PAS (wt %)	T_g(°C)		
PVPh	25	123.7		154.9
	50	115.8		152.4
	75	117.2		153.9
PSOH71	25	108.1		123.1
	50	116.1		144.6
	75	120.6		145.8
PSOH50	25		116.6	
	50		105.8	
	75		105.8	
PSOH45	25		126.4	
	50		116.9	
	75		122.7	
PSOH16	25		124.6	
	50		96.7	
	75		125.6	
PSOH13	25	106.3		122.6
	50	104.5		133.6
	75	104.13		122.6
PSOH8	25	105.5		121.2
	50	100.0		133.5
	75	95.8		116.9
PSOH4	25	106.5		122.9
	50	101.3		127.4
	75	105.2		124.7
PS	25	97.7		123.5
	50	97.7		123.0
	75	98.6		124.2

the interassociation against the self-association (K_A/K_B) will increase with an increase of the PS content in the PSOH copolymer and results in a more-favorable trend for miscibility. However, we need to emphasize here that the PSOH copolymer containing a lower vinylphenol content is immiscible as a result of a larger difference in the solubility parameter and a lesser total number of hydrogen bonds of the blend. Therefore, the PSOH/PAS blend system reveals a miscibility window between 16 and 50 mol % in the PSOH copolymer. Interestingly, Figure 8 displays the infrared spectra measured at 25 °C ranging from 1680 to 1820 cm^{-1} for various PSOH/PAS = 75/25 blends containing different vinylphenol contents

Table 2. Curve-Fitting Result of the PVPh/PAS Blend at 25 °C

PVPh/PAS (wt %)	Free C=O			H Bonded C=O			f_b[a]
	ν (cm^{-1})	$W_{1/2}$(cm^{-1})	A_f(%)	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	A_b(%)	
25/25	1763.7	18.37	79.51	1746.7	30.25	20.49	14.66
40/60	1762.2	18.82	69.07	1744.4	31.46	30.93	22.99
50/50	1763.6	17.10	51.94	1740.7	30.95	48.06	38.15
60/40	1763.5	16.92	57.05	1743.0	32.21	42.95	33.41
75/25	1763.8	17.49	68.90	1743.9	30.74	31.10	23.13

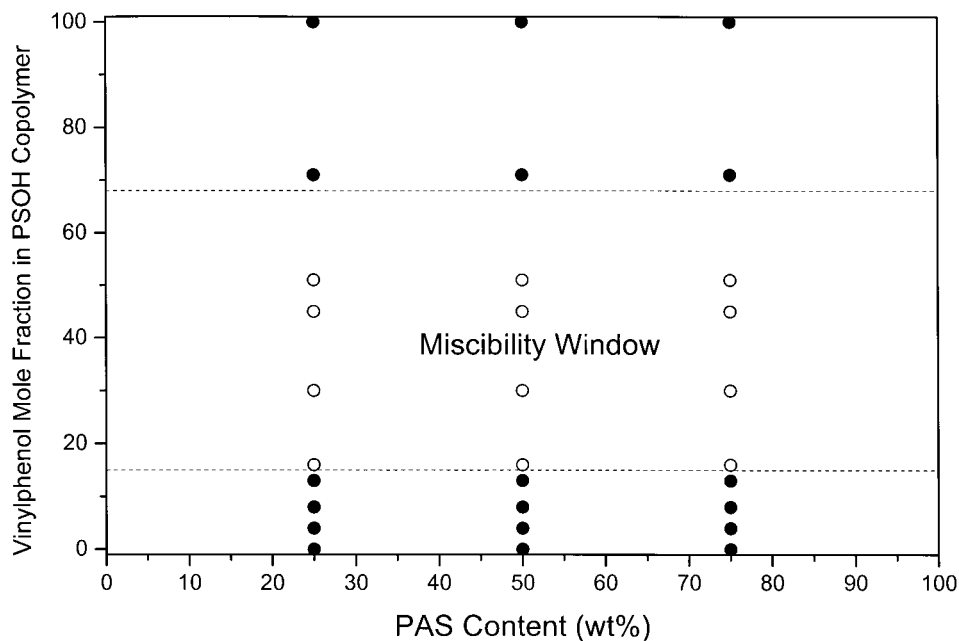[a] f_b: fraction of hydrogen bonding.

Figure 7. Miscibility window of PSOH/PAS blends.

in the PSOH copolymers. The fraction of the hydrogen-bonded carbonyl group is in the order of PSOH50 > pure PVPh > PSOH71 > PSOH8, revealing that PSOH50/PAS = 75/25 has the greatest intermolecular interaction between the hydroxyl group of PVPh and the PAS carbonyl group, and this result is consistent with previous miscibility windows.

Estimation of Interassociation Equilibrium Constant (K_A)

According to PCAM, the interassociation equilibrium constant K_A can be calculated by two methods. The first method was reported by Coggesthall and Saier[8] involving the calculation of the hydrogen-bonding association constant, Ka (in Lmol^{-1}), that can be expressed by the following equation:

$$Ka = \frac{1 - f_m^{OH}}{f_m^{OH}[C_A - (1 - f_m^{OH})C_B]} \quad (2)$$

where C_A and C_B denote the concentrations of TAc and EPh in moles per liter, whereas f_m^{OH} represents the fraction of the free hydroxyl group of EPh that is defined as follows
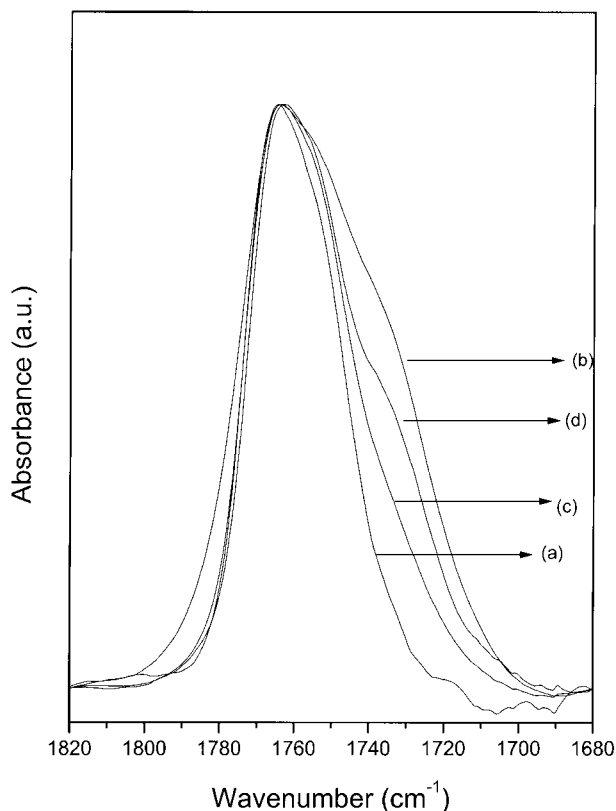
$$f_m^{OH} = \frac{I}{I_0} \quad (3)$$

Figure 8. IR spectra at 1680–1780 cm^{-1} of PSOH/PAS = 75/25 blends containing different vinylphenol contents: (a) PSOH8, (b) PSOH50, (c) PSOH71, and (d) pure PVPh.
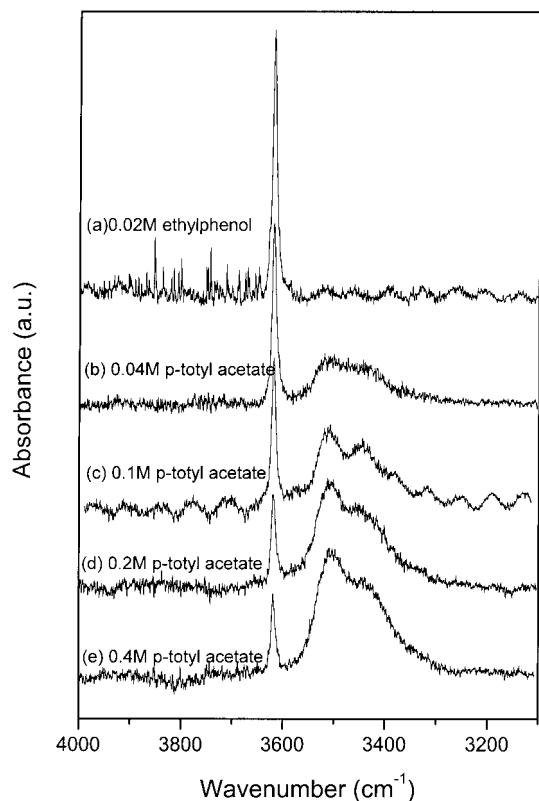
Figure 9. FTIR spectra of the hydroxyl stretching region of 0.02 M ethylphenol containing various *p*-tolyl acetate concentrations: (a) 0 M, (b) 0.04 M, (c) 0.1 M, (d) 0.2 M, and (e) 0.4 M.

where $I_0 = a_F^{OH} \cdot b \cdot c$, I is the intensity of the free hydroxyl band, a_F^{OH} is related to the absorptivity coefficient of 34.2 for EPh obtained previously by Hu et al.,[19] b is the path length (0.05 mm), and c is the concentration. Figure 9 demonstrates the hydroxyl absorption of EPh in cyclohexane containing different concentrations of TAc. The intensity of the free hydroxyl absorption at 3620 cm^{-1} decreases with increasing TAc concentration. The absolute intensity of the free hydroxyl group at 3620 cm^{-1} is considered as a measurement of the amount of free hydroxyl in the mixture on the basis of eq 3. Therefore, the data on the level of f_m^{OH} for EPh containing various concentrations of TAc can be calculated with the *Ka* values. The intrinsic interassociation constant *Ka* of (13.41 Lmol^{-1}) is obtained by extrapolating TAc concentration to zero. *Ka* must be modified into K_A by dividing the molar volume of the phenolic repeated unit (0.1 Lmol^{-1} at 25 °C).[6] The interassociation equilibrium constant, K_A, yielded through this procedure is 134.1.

The second method uses the numerical method to determine K_A according to PCAM on the basis of the fraction of hydrogen bonding of the carbonyl group. The approximate equations[20] are

$$\Phi_B = \Phi_{B1}\left\{\left(1 - \frac{K_2}{K_B}\right) + \frac{K_2}{K_B}\left[\frac{1}{(1 - K_B\Phi_{B1})^2}\right]\right\}$$
$$\times\left(1 + \frac{K_A\Phi_{0A}}{r}\right) \quad (4)$$

$$\Phi_A = \Phi_{0A} + K_A\Phi_{0A}\Phi_{B1}$$
$$\times\left\{\left(1 - \frac{K_2}{K_B}\right) + \frac{K_2}{K_B}\left[\frac{1}{(1 - K_B\Phi_{B1})}\right]\right\} \quad (5)$$

where Φ_A and Φ_B denote volume fractions of non-self-associated species A and self associating species B, respectively; Φ_{0A} and Φ_{B1} are the corresponding volume fractions of the isolated PAS and PVPh segments, respectively; r is the ratio of molar volume, V_A/V_B; self-association equilibrium constants, K_B and K_2, describe the formation of multimers and dimers, respectively; and K_A is the equilibrium constant describing the association of A with B. In addition, K_B and K_2 are 66.8 and 21.0 at 25 °C of pure PVPh.[6] To calculate the interassociation constants (K_A), the methodology of a least-squares method has been widely described in a previous study.[20,21] The interassociation constant of 43.1 was obtained from the PVPh/PAS = 50/50 blend as a result of the highest fraction of hydrogen bonding at this composition.

Table 5 lists all the thermodynamic parameters in this polymer-blend system, indicating that the interassociation equilibrium constant from model compound is greater than the self-association equilibrium constant of pure PVPh. However, the interassociation constant from the polymer blend is relatively smaller than that of the self-association, indicating that the PVPh/PAS blend should be immiscible or partially miscible because of relatively poorer intermolecular association. In general, the interassociation constant of a polymer blend on the basis of model compounds has been described by Pehlert et al.[14] as follows

$$K_A^{Std} = K_A^\infty - \left(\frac{C_A}{R_A^0 + R_A} + \frac{C_B}{R_B^0 + R_B}\right) \quad (6)$$

where R_A^0 and R_B^0 denote the molar volumes of the respective homopolymers; R_A and R_B represent the average molar volume between the A and B

Table 4. f_m^{OH} and Ka of 4-Ethylphenol in Cyclohexane Solution with Various p-Tolyl Acetate Concentrations

Concentration of p-Tolyl Acetate (mol/L)	Intensity of IR Absorption	f_m^{Oh}	K_A (mol/L)	KA^{Std} (Dimensionless)
0.08	0.0235	0.687	13.41	
0.05	0.0225	0.657	12.04	
0.1	0.0177	0.517	10.31	
0.2	0.0118	0.345	10.15	134.1
0.25	0.0104	0.304	9.69	
0.4	0.0091	0.266	7.47	
0.5	0.0074	0.216	7.15	

groups, respectively; C_A and C_B are fitting constants; and K_A^∞ is considered as the intramolecular screening effect using an appropriate r value for a polymer blend of 0.30.[12] Therefore, the interassociation constant is given by

$$K_A^\infty = K_A^{model}(1 - \gamma) \quad (7)$$

where K_A^∞ has a value of $134.1 \times 0.7 = 93.87$ (dimensionless units). Using $C_A = 1630$ and $C_B = 4100$ previously reported by Pehlert et al.[14] for blends of PVPh and poly(vinyl acetate) results in a similar structure between PAS and poly(vinyl acetate). Consequently, eq 6 can be expressed as a function of R_A and R_B for the PSOH/PAS blend as follows

$$K_A^{std} = 93.87 - \left(\frac{1630}{128.6 + R_A} + \frac{4100}{100 + R_B}\right) \quad (8)$$

Considering $R_A = 0$ and $R_B = 0$ indicate that $K_A = 40.19$ for the PVPh/PAS blend system. This value is very close to the data from the numerical

method in the polymer blend, indicating that the thermodynamics properties in a polymer blend can be predicted from analogous model compounds after considering the intramolecular screening and functional-group accessibility effects.

Therefore, the incorporation of an inert diluent moiety such as styrene or dimethylbutadiene[14] into PVPh is able to increase the standard interassociation equilibrium constant as a result of the increase of the R_B value. However, the total numbers of hydrogen bonding significantly decrease, and the solubility parameter difference increases with increasing styrene content in the PSOH copolymers especially for those with a higher styrene content (87–100 mol %). Therefore, an optimum vinylphenol content in the PSOH copolymer is expected to have the most-favorable trend to form a miscible blend because of the competition between these two opposing effects.

In general, the miscibility of an immsicible blend can be enhanced by introducing a suitable functional group to one component capable of

Table 5. Summary of the Self-Association and Interassociation Parameters of PVPh/PAS Blend

	Equilibrium Constant K (25 °C)	Polymer	Molar Volume (mL/mol)	Molecular Weight (g/mol)	Solubility Parameter (cal/mL)$^{0.5}$	Degree of Polymerization (DP)
Self-association[a]		PVPh[b]	100.0	120.1	10.6	86
Dimer formation K_2	21.0	PAS[b]	128.6	162.2	10.29	132
Multimer formation K_B	66.8	PS[b]	93.9	104.1	9.48	132
Interassociation from model compound	134.1					
Interassociation from polymer blend	43.1					

[a] Reference [6].
[b] Estimated with a group contribution method proposed by Coleman et al.[6]

forming intermolecular association with other components.[22] In our previous studies,[23,24] we found that the phenolic group is miscible with PS-*co*-PAS copolymers when its acetoxystyrene content is higher than 45 mol % in the phenolic/PS-*co*-PAS blend system, whereas the vinylphenol content of 13% or higher in the PSOH is also required to make the PSOH/poly(ε-caprolactone) (PCL) blend miscible. However, in this study, the immisicible PVPh/PAS blend needs to incorporate the inert diluent moiety such as styrene into the PVPh component to obtain a miscible blend system because of a reduced stronger self-association of the PVPh component in the blend. In fact, this phenomenon can also be explained with the copolymer repulsion effect.[25,26] The enthalpy of mixing is usually responsible for the miscibility because the contribution from the entropy changes for a polymer blend is usually insignificant. For a binary mixture of homopolymer A with a $C_y D_{1-y}$ copolymer, the expression for the enthalpy of mixing is given by eq 9

$$\frac{\Delta H_{\mathrm{M}}}{V} = B\Phi_1\Phi_2 \qquad (9)$$

where V is the total volume of mixture, Φ_1 and Φ_2 are their respective volume fractions, and y is the molar fraction of component C in copolymer. The B value in eq 9 can be expressed as

$$B = yB_{\mathrm{AC}} + (1-y)B_{\mathrm{AD}} - y(1-y)B_{\mathrm{CD}} \qquad (10)$$

Interaction parameter B has to be negative for a polymer blend to be miscible. Therefore, the miscibility of a blend containing a copolymer depends on the segmental B_{CD} values and the copolymer composition as shown in eq 10. PVPh and PS are immiscible with each other. Therefore, the B value in eq 10 tends to be negative, whereas B_{CD} is positive because of the immiscibility of PVPh and PS. The incorporation of styrene moiety into PVPh makes PVPh more favorable to interact with PAS than PS, and this phenomenon also enhances the miscibility between PVPh and PAS. This concept of the copolymer repulsion effect is consistent with the Painter–Coleman association model in this blend system.

CONCLUSIONS

Miscibility behaviors of blends of PAS with pure PVPh and a series of PSOH copolymers containing various styrene contents have been investigated. Experimental results indicated that the PVPh/PAS blend is an immiscible system based on two T_g's. This immiscibility is caused by the stronger self-association of the PVPh component than the interassociation of the PVPh/PAS blend. However, the incorporation of styrene moiety into the PVPh main chain is able to enhance its miscibility with PAS because of the increase of the standard interassociation equilibrium constant between the hydroxyl group in PSOH copolymers and the carbonyl group in PAS. However, the incorporation of an excessively high PS content (87–100 mol %) into the PVPh tends to increase the solubility parameter difference and decrease the total number or density of hydrogen bonding with PAS, and thus decreases its miscibility. Compromising these two opposing effects, the miscibility window between 16 and 50 mol % vinylphenol content in the PSOH copolymer results in miscible blends with PAS. Furthermore, the interassociation equilibrium constant of PVPh/PAS blends determined by model compounds and a polymer blend exhibits good correlation between these two methods after considering the intramolecular screening and functional-group accessibility effects.

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