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Miscibility and hydrogen bonding in blends of poly(vinyl acetate) with phenolic resin

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Abstract

The miscibility of phenolic resin and poly(vinyl acetate) (PVAc) blends was investigated by differential scanning calorimeter (DSC), Fourier transform infrared spectroscopy (FT-IR) and solid state ^{13}C nuclear magnetic resonance (NMR). This blend displays single glass transition temperature (T_g) over entire compositions indicating that this blend system is miscible in the amorphous phase due to the formation of hydrogen bonding between hydroxyl groups of phenolic resin and carbonyl groups of PVAc. Quantitative measurements on fraction of hydrogen-bonded carbonyl group using both ^{13}C solid-state NMR and FT-IR analyses result in good agreement between these two spectroscopic techniques. According to the proton spin–lattice relaxation time in the rotating frame ($T_{1\rho}^{H}$), the phenolic/PVAc blend is intimately mixed on a scale less than 2–3 nm. Furthermore, the inter-association equilibrium constant and its related enthalpy of phenolic/PVAc blends were determined as a function of temperatures by infrared spectra based on the Painter–Coleman association model. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Phenolic resin; Poly(vinyl acetate); Miscibility

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1. Introduction

Over the past decade, there has been great interest in the study of miscibility and phase behavior of polymer blends, which were important to the improved or modified properties over the individual constituent polymers. However, most polymer blends are immiscible under the absence of specific interaction because the entropy of mixing of two polymers is negligibly small. As a result, several investigations have been carried out with emphasis on hydrogen-bonding interactions as miscibility enhancers [1–4]. In particular, a great amount of literature concerns miscibility of phenolic resin with others [5–7]. The well-known Novolac type phenolic resin, which is a typical phenol–formaldehyde resin, is widely used in industries for the manufacture of paints, insulating and decorative varnishes, adhesive and cast products owing to its low cost, dimension stability, flame retardancy and chemical reactivity. However, the inherent poor impact strength of the phenolic resins limits its application. Many approaches have been explored to improve toughness of phenolic resin by blending with a second modifier such as poly(ethylene oxide) (PEO), phenoxy resin, poly(ε-caprolactone) (PCL) or poly(vinyl alcohol) (PVA) that are widely described in our previous studies [8–11]. Furthermore, the low molecular weight of phenolic resin, usually in the range of 500–2000, is also beneficial for the phenolic to form miscible blends with others high molecular weight polymers.

In order to determine the extent of mixing form of the inter-molecular hydrogen bonding interaction, the Fourier transform infrared (FT-IR) and high-resolution solid-state NMR are widely used to investigate the hydrogen bonding between two polymers, where the frequency, intensity, and width of certain bands are sensitive to the strength and fraction of hydrogen bonding [12–16]. According to the Painter–Coleman association model (PCAM) [17], the fraction of hydrogen-bonded carbonyl group can be predicted by several thermodynamic parameters including molar molecular weight, molar volume, self-association and inter-association equilibrium constants. In general, the self-association equilibrium constant is determined by using low molar mass molecules in an inert solvent such as cyclohexane by following the Whestsel and Lady (L&D) methodology [18]. The inter-association equilibrium constant of a polymer blend is determined by using the PCAM. Although the

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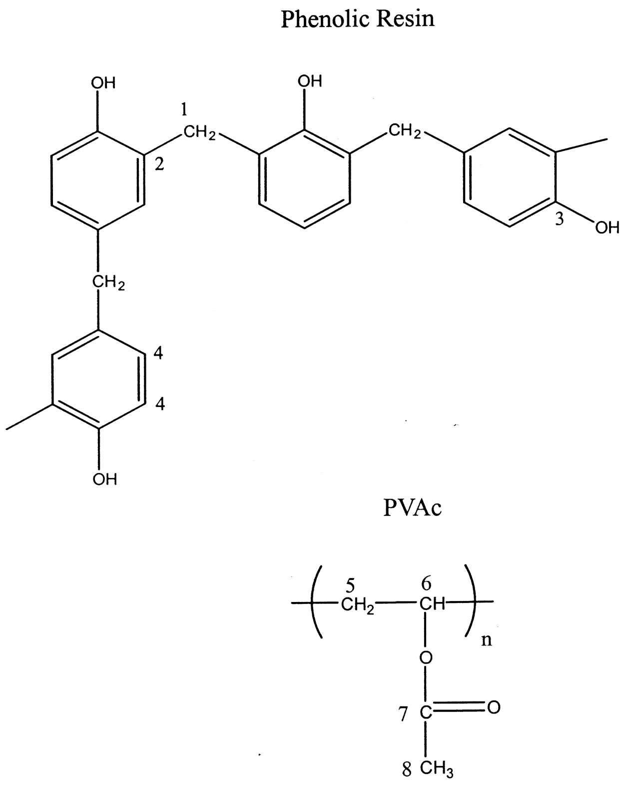

Phenolic Resin

PVAc

Fig. 1. Chemical structures of phenolic and PVAc.

self-association equilibrium constant is obtained from model compound, however, the relative magnitudes of the inter- and self-association equilibrium dictate the contribution of the free energy of mixing rather than their individual absolute values [19]. If the inter-association is more favorable than the self-association, the polymer blend is expected to be miscible such as poly(vinylphenol)/poly(vinylpyrrolidone) blend system [20,21]. Conversely, if the self-association is more favorable than the inter-association, the resulted blend tends to be immiscible or partially miscible.

The miscibility of the phenolic/PVAc blend system was earlier studied [22]. However, this paper reports an in-depth study using a variety of techniques including differential scanning calorimeter (DSC), FT-IR and solid-state NMR. The aim of this paper is to determine quantitatively the extent of hydrogen bonding and miscibility behavior of phenolic/PVAc blends. The inter-association equilibrium constant and its related enthalpy are calculated at various temperatures by FT-IR and the fraction of hydrogen-bonded carbonyl group at room temperature is determined by FT-IR and solid-state NMR. Both spectroscopic methods are consistent with theoretic results based on PCAM. Meanwhile, the miscibility behavior of polymer blend is investigated by DSC and solid-state NMR from proton spin–lattice relaxation time in the rotating frame ($T_{1\rho}^{H}$).

2. Experimental section

2.1. Materials

PVAc used in this study with M_n of 83,000 was obtained from Aldrich. The phenolic was synthesized with sulfuric acid via a condensation reaction and producing average molecular weights $M_n = 500$ and $M_w = 1200$ that are widely described in the previous study [23]. The chemical structure of Novolac-type phenolic resin, consisting of phenolic rings bridge-linked randomly by methylene groups with 19% ortho–ortho, 57% ortho–para, and 24% para–para methylene bridges, was identified from the solution ^{13}C NMR spectrum. The phenolic resin does not contain any reactive methylene group, which is capable of causing cross-linking on heating. The chemical structures of PVAc and phenolic resin are shown as follows in Fig. 1.

2.2. Blend preparations

Blends of various phenolic/PVAc compositions were prepared by solution casting. THF solution containing a 5 wt% polymer mixture was stirred for 10–12 h and then allowed to evaporate slowly at room temperature for 1 day. The blend was then dried at 50 °C for 2 days.

2.3. Differential scanning calorimeter

T_gs of blends were determined by a DSC with Du-Pont (DSC-9000), with a scan rate of 20 °C min^{-1} over a temperature range of 30–100 °C. The measurement was made using a 5–10 mg sample on a DSC sample cell after the sample was quickly cooled to −50 °C from the melt of first scan. The glass transition temperature is taken as the midpoint of heat capacity transition between the upper and lower points of deviation from the extrapolated liquid and glass lines.

2.4. Infrared spectra

Infrared spectroscopic 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 a film sample, the IR studied was carried out with the conventional NaCl disk method. The THF solution containing the blend was cast onto NaCl disk and dried under conditions similar to those used in the bulk preparation. The film used in this study was sufficiently thin to obey the Beer–Lambert law. IR spectra recorded at elevated temperatures were obtained by using a cell mounted inside the temperature-controlled compartment of the spectrometer.

2.5. Solid state NMR

High-resolution solid-state NMR experiments were carried out on a Bruker DSX-400 spectrometer operating at resonance frequencies of 399.53 and 100.47 MHz for ^{1}H and ^{13}C, respectively. The ^{13}C CP/MAS spectra were

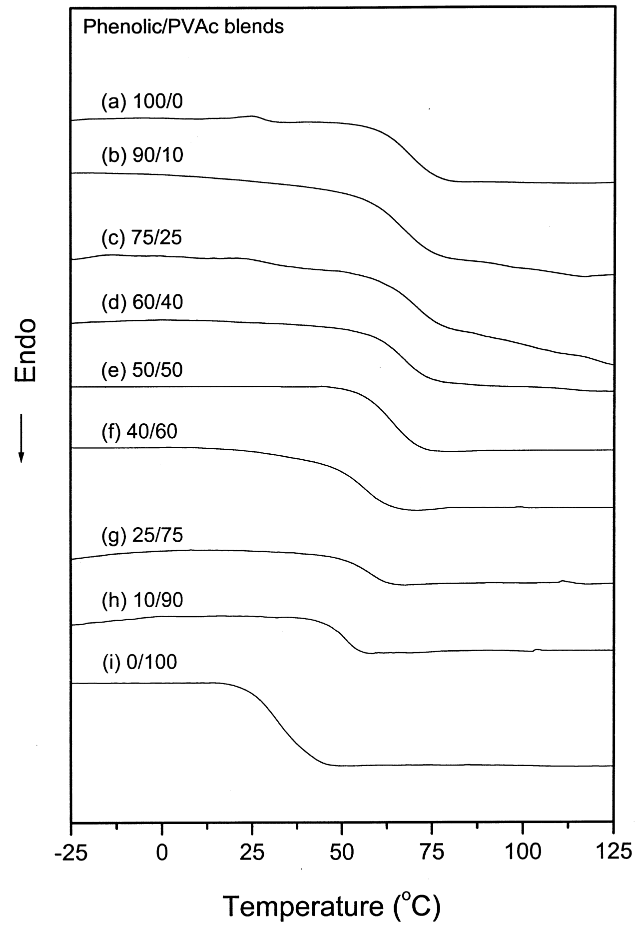

Fig. 2. DSC scans of phenolic/PVAc blends with different compositions: (a) 100/0, (b) 90/10, (c) 75/25, (d) 60/40, (e) 50/50, (f) 40/60, (g) 25/75, (h) 10/90, (i) 0/100.

measured with a 3.9 μs 90° pulse, with 3 s pulse delay time, acquisition time of 30 ms, and 2048 scans were accumulated. All NMR spectra were taken at 300 K using broad band proton decoupling and a normal cross-polarization pulse sequence. A magic angle sample-spinning (MAS) rate of 5.4 Hz was used to eliminate resonance broadening due to the anisotropy of chemical shift tensors. The proton spin–lattice relaxation time in the rotating frame ($T_{1\rho}^{H}$) was measured indirectly via carbon observation using a 90°-τ-spin lock pulse sequence prior to cross-polarization. The data acquisition was performed via ^{1}H decoupling and delay time (τ) ranging from 0.3 to 15 ms with a contact time of 1.0 ms.

3. Results and discussion

3.1. Thermal analyses

Thermal characterization of polymer blends is a well-known method for determining the miscibility of polymer blends. The miscibility between any two polymers in the amorphous state is detected by the presence of a single glass transition temperature (T_g). Fig. 2 shows the DSC analyses of phenolic/PVAc blends with various compositions that exhibit a single glass transition temperature over the entire compositions, indicating that this polymer pair is fully miscible forming a homogeneous amorphous phase.

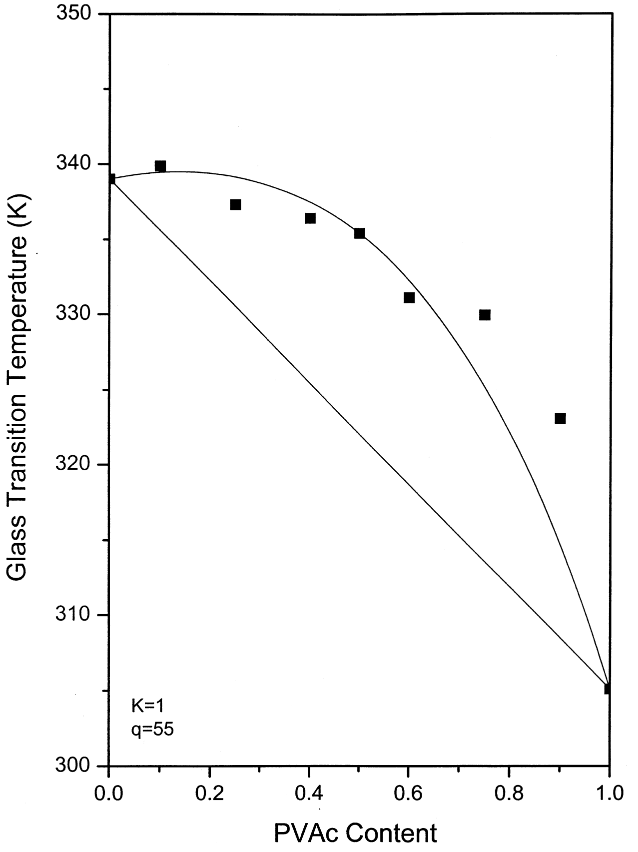

Fig. 3. T_g vs. composition curves based on (■) experimental data and (—) the Kwei equation.

The dependence of T_g on the composition of the miscible phenolic/PVAc blend is shown in Fig. 3. Over the years, a number of equations have been offered to predict the glass transition temperature behavior of a miscible blend. In general, the Kwei equation is applicable to the polymer blends with specific interactions as follows [24]:

$$T_g = \frac{W_1 T_{g1} + kW_2 T_{g2}}{W_1 + kW_2} + qW_1 W_2 \tag{1}$$

where W_1 and W_2 are the weight fractions, T_{g1} and T_{g2} represent the glass transition temperatures, and k and q are the fitting constants. The nonlinear least-squares 'best fit' values obtained for this relationship were $k = 1$ and $q = 55$. The parameter q is corresponding to the strength of hydrogen bonding in the blend and relatively large value for q reflecting a strong intermolecular interaction between phenolic and PVAc.

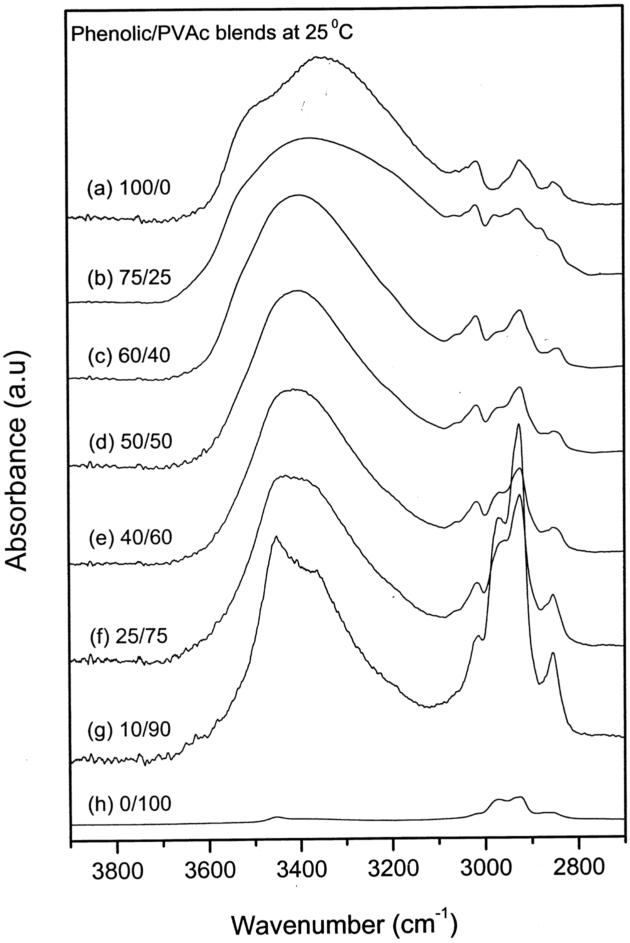

Fig. 4. FT-IR spectra recorded at 25 °C in the 2700–3900 cm^{-1} regions for phenolic/PVAc blends: (a) 100/0, (b) 75/25, (c) 60/40, (d) 50/50, (e) 40/60, (f) 25/75, (g) 10/90, (h) 0/100.

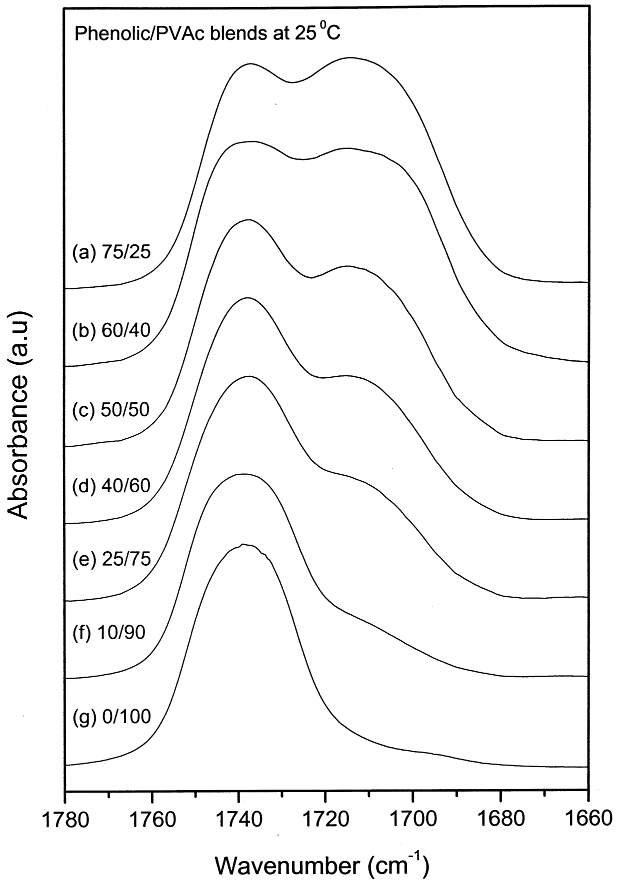

Fig. 5. FT-IR spectra recorded at 25 °C in the 1650–1800 cm^{-1} regions for phenolic/PVAc blends: (a) 75/25, (b) 60/40, (c) 50/50, (d) 40/60, (e) 25/75, (f) 10/90, (g) 0/100.

3.2. Fourier transform infrared spectroscopy analyses

FT-IR is a particularly suitable method to determinate the presence of specific interactions between various groups in polymer blends due to the force constants is sensitive to both inter- and intra-molecular interactions. Fig. 4 shows scale-expanded infrared spectra in the hydroxyl-stretching region with various compositions of phenolic/PVAc blends at room temperature. The spectrum of the pure phenolic shows a broad band at 3350 cm^{-1} and a shoulder at 3525 cm^{-1}, corresponding to the multimer hydrogen-bonded (self-associated) hydroxyl groups and the free hydroxyl groups, respectively. The intensity of the free hydroxyl band decreases with the increase of the PVAc content in the blend. It is expected that large portion of these 'free' OH groups is consumed by forming the inter-association hydrogen bonds between the PVAc and the phenolic. Meanwhile, the band (at about 3420 cm^{-1}), appears with the increase of the PVAc content as the result of the decrease in the free hydroxyl band. In addition, portion of the self-association hydrogen bonds (at 3350 cm^{-1}) are broken off to form the inter-association hydrogen bonds [17]. This phenomenon reveals that a new distribution of hydrogen bonding formation resulting from the competition between hydroxyl–hydroxyl and hydroxyl–carbonyl interactions. Therefore, the hydroxyl group of phenolic resin and the carbonyl of group of PVAc indeed have the strong hydrogen bonding.

The infrared spectra of various phenolic/PVAc blends in the carbonyl stretching regions at room temperature are shown in Fig. 5. The carbonyl stretching frequency splits into two bands at 1737 and 1713 cm^{-1}, corresponding to the free and the hydrogen-bonded carbonyl groups, which can be fitted well to the Gaussian function. The fraction of the hydrogen-bonded carbonyl group can be calculated by using an appropriate absorptive ratio ($a_R = a_{HB}/a_F = 1.5$) that has been discussed in the previous study [17]. The curve fitting results for phenolic/PVAc blends as a function of component and temperature are summarized in Table 1. The fraction of hydrogen-bonded carbonyl increases with the increase of the phenolic content at room temperature. This result is consistent with the previous result in the hydroxyl group analyses. In addition, Fig. 6(a) displays the infrared spectra within the carbonyl stretching region of the phenolic/PVAc = 60/40 blend at different temperatures, where the fraction of hydrogen-bonded carbonyl group

Table 1
Curve fitting results of fraction of hydrogen-bonded carbonyl of phenolic/PVAc with various compositions at room temperature

Phenolic (wt%)	Free C=O			H-bonded C=O			fb (%)
	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	A_f (%)	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	A_b (%)	
0.25	1739.5	18.49	56.77	1711.1	28.98	43.23	33.67
0.40	1739.6	18.52	49.31	1711.5	27.99	50.69	40.66
0.50	1740.0	18.75	42.02	1712.0	27.57	57.98	47.91
0.60	1739.6	19.74	33.61	1711.7	26.44	66.39	56.83
0.75	1739.6	21.46	23.58	1711.8	25.97	76.42	68.36

decreases with the increase in temperatures. Table 2 summarizes fractions of hydrogen-bonded carbonyl group of the PVAc at various temperatures and compositions of phenolic/PVAc blends. Meanwhile, Fig. 6(b) shows the hydroxyl stretching region of the phenolic/PVAc = 60/40 blend at different temperatures. The free hydroxyl band increases and the multimer hydrogen bonding shifts to higher frequency with the increase of temperature, suggesting that the inter-association hydrogen bonding between phenolic and PVAc becomes weaker with the increases of temperature.

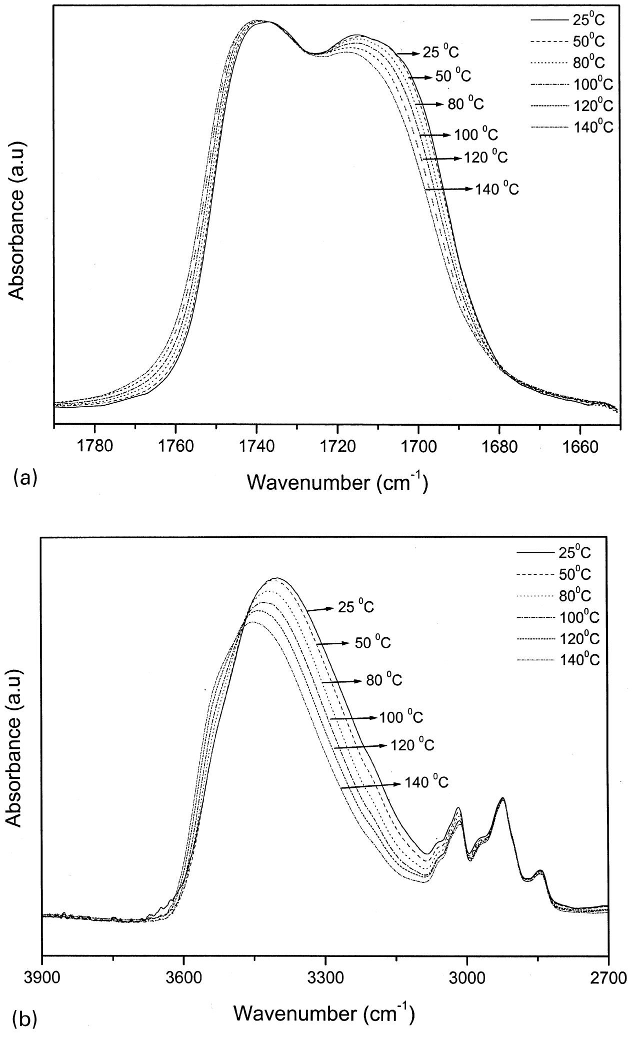

Fig. 6. FT-IR spectra of the 60:40 wt% phenolic/PVAc blend in the carbonyl vibration region (a) and the hydroxyl vibration region (b) recorded at different temperatures.

3.3. Solid-state NMR analyses

Solid-state NMR spectroscopy provides quantitative information concerning phase behavior and specific interaction of polymer blends. The ^{13}C CP/MAS spectra of phenolic/PVAc blends with various compositions at room temperature are shown in Fig. 7, where Fig. 7(a) gives the peak assignments of four major peaks of the phenolic. The peak at 152.1 ppm corresponds to the hydroxyl-substituted carbon in the phenolic ring (C–OH). Peaks at 115.8 and 129.4 ppm correspond to the ortho unsubstituted carbon and the other carbons in the phenol ring, respectively. Meanwhile, the other resonance at 35 ppm corresponds to the methylene carbons. Fig. 7(h) displays the spectrum of the PVAc with four resonance peaks, while Fig. 1 presents the corresponding carbons. All peak assignments of structures (Fig. 1) are shown in Fig. 8.

The chemical shift of the carbonyl carbon of the PVAc increases with the increase in phenolic content. A downfield shift of 3 ppm is observed in the phenolic/PVAc = 75/25 blend relative to the pure PVAc. It is well known that the existence of specific interaction in polymer blends will affect the chemical environment of the neighboring molecules and cause changes of magnetic shielding, therefore, the chemical shift moves to downfield. Similar chemical shift is also observed for the hydroxyl-substituted carbon of phenolic resin, which shifts downfield with the increase of PVAc content. A downfield shift of 2.3 ppm is observed in the phenolic/PVAc = 25/75 blend relative to the pure phenolic, indicating intermolecular hydrogen bonding between the hydroxyl group of phenolic resin and the carbonyl group of PVAc. These results are consistent with the previous FT-IR results (Figs. 3 and 4).

In general, the fraction of hydrogen-bonded carbonyl group can be calculated from FT-IR measurement. In this study, the carbonyl carbon (C-7) NMR resonance (Fig. 7) is partially resolved into two peaks with the increase of phenolic content. This change in line shape is assigned to the hydrogen-bonded carbonyl groups [13]. The contribution of a second signal related to the hydrogen-bonded carbonyl group is similar to that observed in the FT-IR spectra

Table 2
The fraction of hydrogen-bonded carbonyl group with various compositions and temperatures

Phenolic (wt%)	fb (%)				
	25 °C	80 °C	100 °C	120 °C	140 °C
0.25	33.67	30.05	25.33	23.00	23.35
0.40	40.66	36.33	36.09	35.54	34.74
0.50	47.91	44.99	43.70	43.41	42.79
0.60	56.83	53.58	53.02	51.01	49.88
0.75	68.36	66.04	65.20	63.16	61.96

(Fig. 4). The spectra of the carbonyl carbon resonance of various phenolic/PVAc blends at room temperature are shown in Fig. 8, revealing that the relative intensity of the hydrogen-bonded and free carbonyl increases with phenolic content. By integrating the respective areas of the contributions corresponding to the hydrogen-bonded and free carbonyl groups, the fractions of hydrogen-bonded carbonyl groups can be obtained. Fig. 9 compares the fractions of hydrogen-bonded carbonyl groups that are obtained by FT-IR, NMR and theoretical prediction based on PCAM. This result reveals that solid-state NMR and FT-IR results have a good correlation between experimental data and the predicted fraction of hydrogen-bonded carbonyl group. We need to emphasize that the theoretical fraction of hydrogen-bonded carbonyl group is obtained from the MG&PC software program and the related thermodynamic parameters will be calculated in the following section.

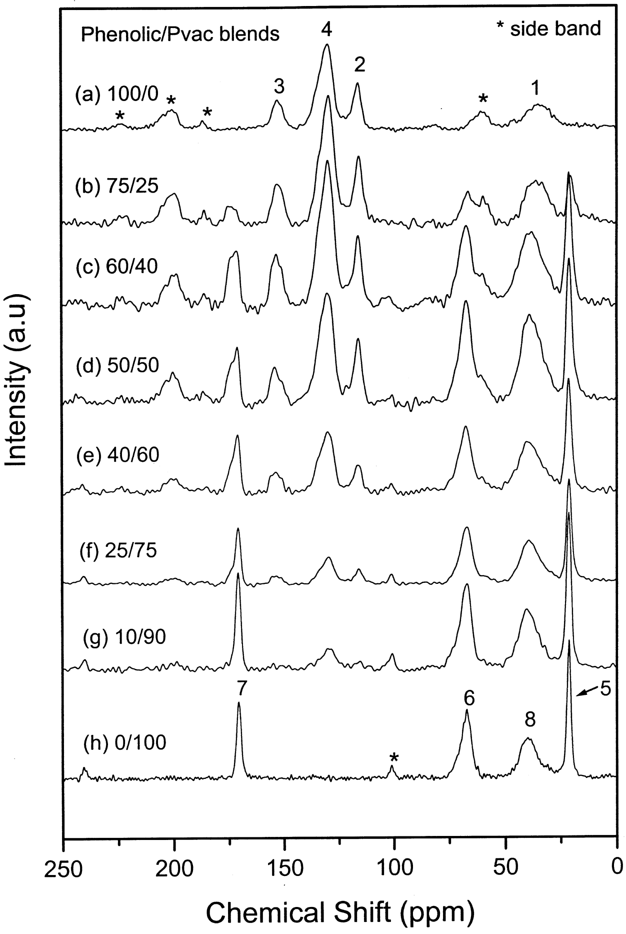

Fig. 7. ^{13}C CP/MAS spectra at room temperature for phenolic/PVAc blends: (a) 100/0, (b) 75/25, (c) 60/40, (d) 50/50, (e) 40/60, (f) 25/75, (g) 10/90, (h) 0/100.

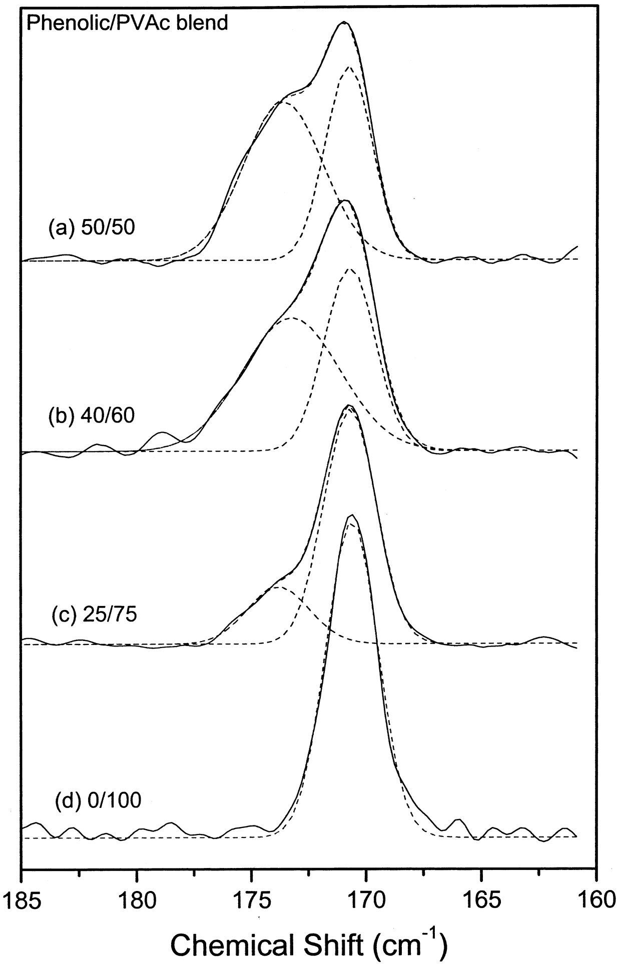

Fig. 8. Curve fitting the ^{13}C CP/MAS spectrum for phenolic/PVAc blends (a) 50/50, (b) 40/60, (c) 25/75, (d) 0/100.

More detailed information concerning the phenolic/PVAc blend is obtained from the proton relaxation behavior. The spin–lattice relaxation time in the rotating frame $T_{1\rho}^{\mathrm{H}}$ was measured to examine homogeneity of polymer blends on the molecular scale. The magnetization of resonance is expected to decay according to the following exponential function model [25]:

$$M_\tau = M_0 \exp(-\tau/T_{1\rho}(H)) \quad (2)$$

where τ is the delay time used in the experiment and M_τ is the corresponding peak intensity. $T_{1\rho}^{\mathrm{H}}$ can be obtained from the slope of $ln(M_\tau/M_0)$ vs τ. The $T_{1\rho}^{\mathrm{H}}$ relaxation behaviors of these blends are shown in Fig. 10 (PVAc, 24 ppm) and Fig. 11 (phenolic, 115 ppm), respectively. The $T_{1\rho}^{\mathrm{H}}$ values derived from the binary exponential analysis are

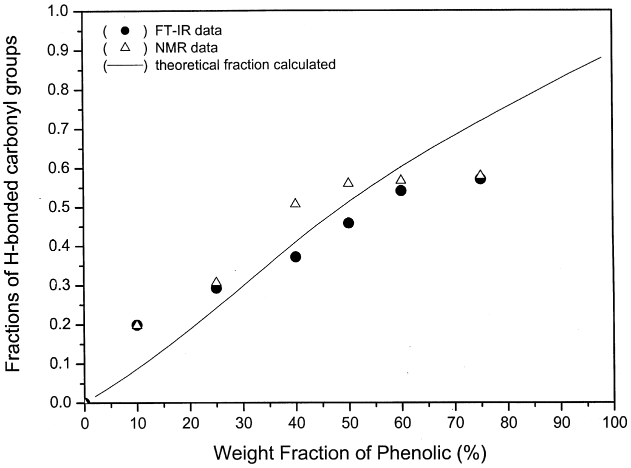

Fig. 9. Fractions of hydrogen-bonded carbonyl groups vs. composition: (●) FT-IR data, (Δ) NMR data, (—) theoretical fraction calculated.

summarized in Table 3. A single $T_{1\rho}^{H}$ value was obtained for all blends, indicating good miscibility and dynamic homogeneity in these blends. The maximum diffusive path length L can be estimated using the approximated Eq. (3) [26]

$$\langle L^2 \rangle = (6DT_i) \tag{3}$$

For $T_{1\rho}^{H}$ of 10 ms and an effective spin diffusion coefficient (D) of 10^{-16} m^2 s^{-1}, the dimensions of these phenolic/PVAc blends are below 2–3 nm in the amorphous phase.

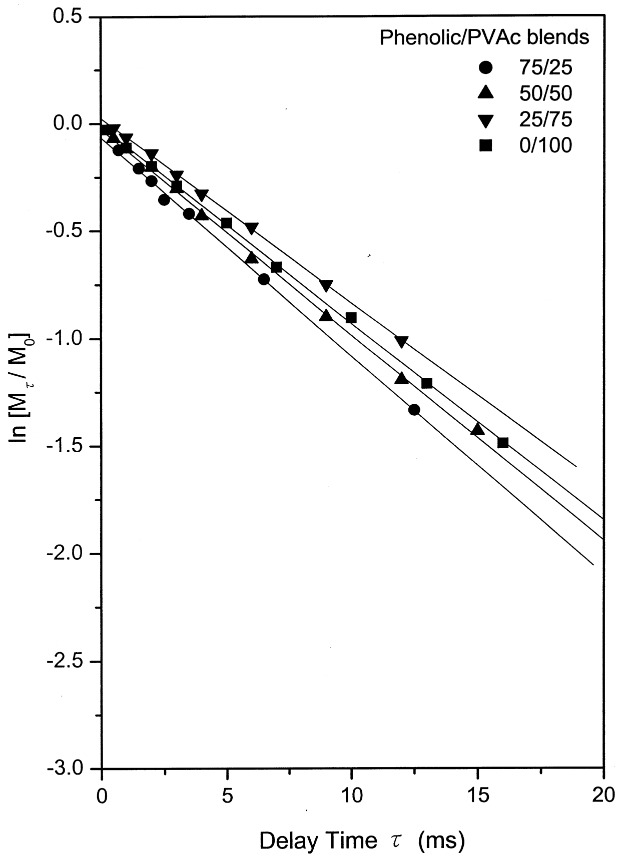

Fig. 10. Logarithmic plot of resonance intensity of PVAc C-5 vs. delay time.

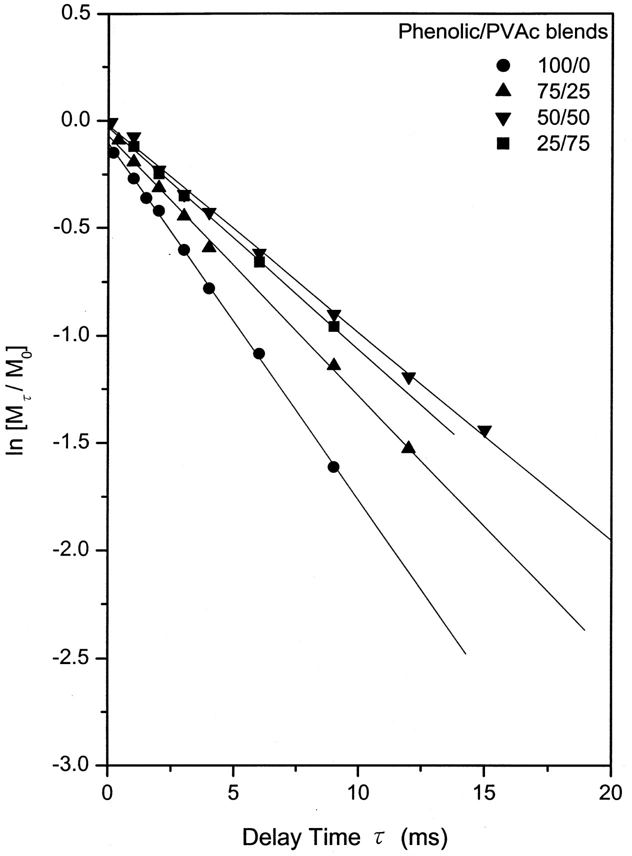

Fig. 11. Logarithmic plot of resonance intensity of phenolic C-2 vs. delay time.

3.4. Painter–Coleman association model analyses

By applying the PCAM, it is necessary to determinate the values of the equilibrium constants describing the self-association, inter-association and other properties of thermodynamics. The self-association equilibrium constants, K_2 and K_B corresponding to the hydroxyl–hydroxyl interaction of phenolic, represent the formation of hydrogen-bonded 'dimer' and 'multimer'. In general, the self-association equilibrium constant is determined from low molar mass molecules in an inert solvent such as cyclohexane by using the Whestsel and Lady (L&D) methodology. The inter-association equilibrium constant (K_A) reflects the

Table 3
$T_{1\rho}$ values (ms) for pure phenolic, PVAc and their blends

Phenolic/PVAc	Phenolic C-2	PVAc C-5
100/0	6.01	–
75/25	8.24	9.82
50/50	10.35	10.44
25/75	9.65	11.62
0/100	–	10.88

Table 4
Equilibrium constants at various temperatures of hydrogen bonding formation of phenolic/PVAc blend

Temperature (°C)	Phenolic self-association equilibrium constant		Inter-association equilibrium constant
	K_2	K_B	K_A
80	7.90	10.48	29.62
100	5.77	6.57	22.53
120	4.35	4.32	18.25
140	3.37	2.95	11.04

tendency of the hydrogen bonding between the hydroxyl group of phenolic and the carbonyl group of PVAc. Taking into account the chain connectivity, intramolecular screening and functional group accessibility difference between model compounds and the corresponding polymer blend [27–29]. As a result, in this study, the values of K_A were calculated at different temperatures with various phenolic/PVAc polymer blend compositions from a least squares fit of the stoichiometric equations as follows [17]:

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

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

where Φ_A and Φ_B are the volume fractions of non-self associated species A and self associating species B, Φ_{0A} and Φ_{B1} are the corresponding volume fractions of the isolated PVAc and the phenolic segment, and r is the ratio of molar volume, V_A/V_B. The values of K_2 and K_B estimated from previous measurements are 23.29 and 52.31 [30] at room temperature using the model compound based on Whestsel and Lady (L&D) methodology. In order to calculate the inter-association constants (K_A), the methodology of a 'least square' method has been widely detailed in previous studies [31]. We choose measured temperatures above 80 °C to obtain the fraction of hydrogen-bonded carbonyl group because this temperature is above both individual glass transition temperatures. Fractions of hydrogen-bonded carbonyl at various temperatures of various phenolic/PVAc blends are summarized in Table 2. The self-association and inter-association equilibrium constants at various temperatures are listed in Table 4. Meanwhile, the inter-association enthalpy in this temperature range based on the Van't-Hoff expression can be calculated and extended to room temperature [16]. Table 5 summarizes these equilibrium constants and their related enthalpies, molar volumes, molecular weights, and solubility parameters of phenolic/PVAc blends. The observed $K_A = 83.40$ is higher than $K_2 = 23.29$ and $K_B = 52.31$, implying that hydrogen bonding between phenolic and PVAc is more favorable than intra-molecular hydrogen bonding of the pure phenolic. This result agrees well with T_g compositional relationship based on Kwei equation and also with both FT-IR and solid-state NMR observations.

4. Conclusions

It was found that the phenolic/PVAc blends are miscible in the amorphous phase over the entire compositions. Results obtained by DSC, FT-IR and high-resolution solid-state ^{13}C NMR reveal strong inter-association hydrogen bonds between the hydroxyl group of phenolic and the carbonyl group of PVAc. Quantitative analyses of the fraction of hydrogen-bonded carbonyl groups using ^{13}C solid-state NMR and FT-IR analyses result in good agreement between these two spectroscopic techniques. The proton spin–lattice relaxation measurement in the rotating frame has demonstrated that the blends are homogeneous on a scale less than 2–3 nm. The inter-association equilibrium constant (K_A) for the phenolic/PVAc blend is higher than the self-association equilibrium constant (K_2 and K_B), implying that the tendency towards hydrogen bonding of

Table 5
Summary of self-association, inter-association parameters and other thermodynamic parameters of phenolic/PVAc blend

	Equilibrium constant K (25 °C)	Enthalpy Δh (kcal/mol)		
Self-association[a]				
Dimer formation K_2	23.29	−4.24		
Multimer formation K_B	52.31	−6.11		
Inter-association between phenolic and PVAc	83.40	−4.19		
Polymer	Molar volume (ml/mol)	Molecular weight (g/mol)	Solubility parameter (cal/ml)$^{0.5}$	Degree of polymerization (DP)
Phenolic[a]	84	105	12.05	6
PVAc[b]	69.8	86.1	9.61	714

[a] Ref. [6].

[b] Estimated by using a group contribution method proposed by Coleman et al. [17].

the phenolic resin and PVAc dominates the self-association of the phenolic resin in the mixture.

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