polymer

The study of hydrogen bonding and miscibility in poly(vinylpyridines) with phenolic resin

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Abstract

The hydrogen bonding and miscibility behaviors of poly(2-vinylpyridine) (P2VP) or poly(4-vinylpyridine) (P4VP) with phenolic resin were investigated by differential scanning calorimetry and Fourier transform infrared spectroscopy (FTIR). These blends have a single glass transition over the entire composition range indicating that these blends are able to form a miscible phase due to the formation of inter-molecular hydrogen bonding between hydroxyl of phenolic and pyridine ring of poly(vinylpyridines). Furthermore, FTIR studies on the hydrogen-bonding interaction between the hydroxyl group of phenolic and pyridine ring of poly(vinylpyridines) at various compositions and temperatures indicate that the greater inter-association for P4VP than P2VP due to the steric hindrance effect on specific interaction between these two polymers. Finally, inter-association equilibrium constants of phenolic/P2VP and phenolic/P4VP blends were determined by model compounds. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Hydrogen bonding; Steric hindrance; Effect polymer blend

1. Introduction

Most polymer blends are immiscible with each other due to the absence of specific interaction. In general, to obtain a miscible blend system, it is usually necessary to ensure that favorable specific interactions exist between two polymers, such as hydrogen bonding [1–5], dipole–dipole, charge transfer and acid–base complexation. It is well known that the great influence of the solvent medium can control the complex formation. For example, the poly(vinyl phenol) (PVPh)/poly(N,N-dimethyl acrylamide) (PDMA) blend yields the complexes in dioxane, but no precipitation occurred in DMF [6]. Since solvent molecules also can participate in hydrogen bonding interaction, therefore, they can compete with PDMA for hydroxyl group site in PVPh. The affinity of hydrogen bond acceptor of the inter-molecular interaction can be estimated by the infrared frequency difference ($\Delta \nu$) between the hydrogen-bonded hydroxyl absorption and free hydroxyl absorption of phenol (a model compound for PVPh). The result indicates that the dioxane is a weaker hydrogen bond acceptor ($\Delta \nu = 235 \text{ cm}^{-1}$) than the DMF ($\Delta \nu = 340 \text{ cm}^{-1}$). As a result, in this study, the phenolic/poly(vinylpyridines) blends

were prepared by solution casting from the *N,N*-dimethylformamide (DMF) solution to avoid the complex formation.

The inter-molecular interaction through hydrogen bonding can be characterized by Fourier transform infrared spectroscopy (FTIR), because the specific interaction will affect the local electron density and the corresponding frequency shift can be observed [7–11]. Furthermore, this type of interaction has been widely described in terms of association model by Painter and Coleman [12]. They suggested that by adding an additional term into a simple Flory–Huggins expression is able to account for the free energy of the hydrogen bonding formation for the free energy of mixing of two polymers as expressed by Eq. (1)

$$\frac{\Delta G_N}{RT} = \frac{\Phi_1}{N_1}\ln \Phi_1 + \frac{\Phi_2}{N_2}\ln \Phi_2 + \Phi_1\Phi_2\chi_{12} + \frac{\Delta G_H}{RT} \quad (1)$$

where Φ and N are the volume fraction and the degree of polymerization, respectively; χ is the 'physical' interaction parameter and subscripts 1 and 2 refer to the blend components. ΔG_H is the free energy change contributed by the hydrogen bonding between two components, which can be estimated by FTIR [13]. This equation ignores the free volume change and other complications [14,15].

The purposes of this study are to investigate the miscibility and specific interaction between phenolic and poly(vinylpyridines) and compare with the inter-association

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strength between phenolic and poly(vinylpyridines) in their 2 and 4 isomer forms. Moreover, the inter-association equilibrium constants and of phenolic/poly(2-vinylpyridine) (P2VP) and phenolic/poly(4-vinylpyridine) (P4VP) blends were determined by model compounds.

2. Experimental

2.1. Materials

Polymers used in this study, P4VP and P2VP, were obtained from Aldrich Co. and their weight average molecular weight were 60 000 and 200 000 for P4VP and P2VP, respectively. The phenolic was synthesized with sulfuric acid via a condensation reaction and produced average molecular weights $M_n = 500$ and $M_w = 1200$. The chemical structure of Novolac type phenolic resin contains 0.15 wt% free phenol and consists of phenol rings bridge-linked randomly by methylene groups with 19% *ortho–ortho*, 57% *ortho–para*, and 24% *para–para* methylene bridges that were determined from the solution ^{13}C NMR spectrum [16,17]. The phenolic resin does not contain any reactive methylol group which is capable of causing cross-linking on heating. The chemical structures of phenolic, P2VP and P4VP are illustrated as follows:
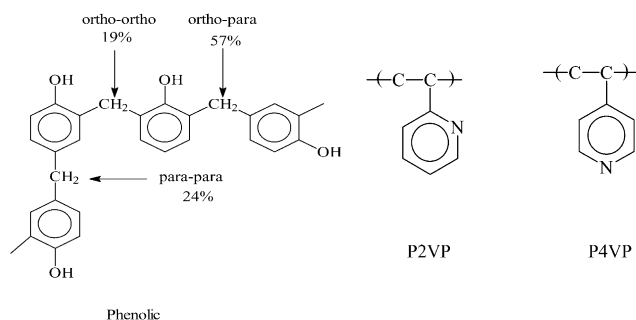
2.2. Blend preparations

Polymer blend between phenolic and poly(vinylpyridines) was prepared through solution casting from DMF solution with 5 wt% polymer mixture to avoid complex formation. The mixture was stirred for 6–8 h and then poured into a Teflon dish. The Teflon dish was placed on a hot plate at 80–100 °C to evaporate the solvent slowly for 2 days. The blend film was then dried at 90 °C in vacuum for at least 1 week.

2.3. Differential scanning calorimetry

The glass transition temperature (T_g) of blend film was measured by a differential scanning calorimetry (DSC) from Du-Pont (DSC-9000). All samples were preheated with a scan rate of 20 °C/min over a temperature range 30–170 °C and maintained at 170 °C for 10 min to ensure complete

removal of residual solvent. The measurement was made using 5–10 mg sample on a DSC sample cell after the sample was quickly cooled to 0 °C from the melt of the first scan. The scan rate was 20 °C/min and T_g was taken as the midpoint of the heat capacity transition between the upper and lower points of deviation from the extrapolated liquid and glass lines.

2.4. Infrared spectroscopy

FTIR measurement was recorded on a Nicolet Avatar 320 FTIR spectrophotometer and 32 scans were collected with a spectral resolution of 1 cm^{-1}. Infrared spectrum of the polymer blend film was obtained by using the conventional NaCl disk method. The DMF 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. IR spectra recorded at elevated temperatures were obtained by using a cell mounted inside the temperature-controlled compartment of the spectrometer. The sample chamber was purged with nitrogen during the process of measurement in order to maintain sample films drying. For the sample in solution form, a sealed cell with NaCl windows and 0.05 mm sample thickness was used. A single optical path was used to study the inter-association equilibrium constant between model compounds of 2-ethylpyridine, 4-ethylpyridine and 2,4-dimethylphenol. All model compound solutions in the absorption range obey the Beer–Lambert law. Cyclohexane was selected as the solvent because the specific conformation of the cyclohexane is favorable in this study.

3. Results and discussion

3.1. Thermal analyses

The miscibility of a polymer blend can be determined by many techniques, including thermal analysis [18], dynamic mechanical analysis [19], microscopy [20] and solid state NMR [21]. In general, the DSC is the most convenient method to determine the miscibility of polymer blends. In this study, the high boiling point solvent DMF (bp = 153 °C) was employed to prepare the solution blends. Under the experimental condition carried out, the residual DMF (probably in ppm or tenths ppm range) may not be able to evaporate totally from the polymer blend. Since the T_g behavior is dependent on the weight (or volume) fractions of components, the presence of residual solvent should not affect appreciably the T_g behavior of the blend. Fig. 1(a) and (b) shows DSC analyses of the phenolic/P2VP and phenolic/P4VP blends at various compositions. The pure phenolic exhibits one T_g at 66.7 °C. Meanwhile, T_gs of pure P2VP and pure P4VP exist at 90.1 and 144.1 °C, respectively. The glass transition temperature and glass transition width are summarized in Table 1 revealing that all phenolic/poly(vinylpyridines) blends show only one single glass transition
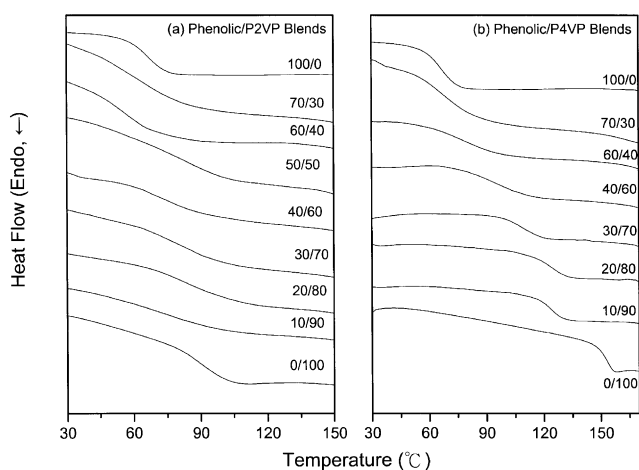
Fig. 1. The DSC scans with different composition for (a) phenolic/P2VP and (b) phenolic/P4VP blends.

temperature. A single T_g strongly suggests that all these are fully miscible blends with a homogeneous amorphous phase due to the inter-association between the hydroxyl group of phenolic and the pyridine group of poly(vinylpyridines). Furthermore, glass transition width of the phenolic/P4VP blend is narrower than the phenolic/P2VP blend, implying that the phenolic/P4VP is more homogeneous at the molecular scale than the phenolic/P2VP blend system. We need to emphasize that the phenolic resin contains a high density of hydroxyl groups that can interact with numerous other polymers through hydrogen bonding. Hydrogen bonding serves as a physical cross-link in phenolic resin and increases its glass transition temperature (T_g). Meanwhile, the Novolac type phenolic resin possesses a higher T_g than other materials with a similar molecular weight because of its high-density hydrogen bonds. When the phenolic resin is blended with P2VP and P4VP, the resultant T_g are significantly lower than pure phenolic at phenolic rich region due to the interaction between phenolic and poly(vinylpyridines) by removing the strong intramolecular hydrogen bonding of the pure phenolic.

3.2. Fourier transform infrared spectroscopy analyses

FTIR spectrometry has been proven to be a very powerful technique to detect the inter-molecular interaction between two polymers. The IR hydroxyl stretching range of phenolic/poly(vinylpyridines) blends is sensitive to the hydrogen bonding formation. Fig. 2 illustrates scale-expanded infrared spectra of the hydroxyl region of phenolic/P2VP and phenolic/P4VP in the range 2700–4000 cm^{-1} measured at 150 °C. We chose 150 °C for IR measurement because this temperature is above glass transition temperatures of all polymers investigated, indicating that the hydrogen bonding interaction can approach its equilibrium state. The pure phenolic shows two distinct bands in Fig. 2, a shoulder at 3525 cm^{-1} from the absorption of free hydroxyl groups and a broad band centered at 3450 cm^{-1} from the absorption of hydrogen-bonded hydroxyl group. The intensity of the free hydroxyl group at 3525 cm^{-1} decreases gradually with increasing P2VP and P4VP contents. Meanwhile, the band center of hydrogen-bonded hydroxyl group shifts to lower wavenumber with the increase of P2VP and P4VP contents. These results reflect a new distribution of hydrogen bonding interaction due to the competition between hydroxyl–hydroxyl and hydroxyl–pyridines interactions. The average strength of hydrogen bonding can be investigated by the infrared frequency difference ($\Delta\nu$) between the hydrogen-bonded hydroxyl absorption and free hydroxyl absorption [22]. As a result, the average hydrogen bonding strength is in the order of phenolic/P4VP ($\Delta\nu = 275$ cm^{-1}) > phenolic/P2VP ($\Delta\nu = 235$ cm^{-1}) > phenolic/phenoic ($\Delta\nu = 75$ cm^{-1}). In addition, the free hydroxyl absorption intensity in the phenolic/P4VP blend is relatively weaker than the phenolic/P2VP blend, indicating that the P4VP has greater ability to form hydrogen bonding than the P2VP due to the steric hindrance effect on specific interaction between these two polymers.

Besides the hydroxyl stretching, the other bands of the pyridine ring are also sensitive to hydrogen bonding
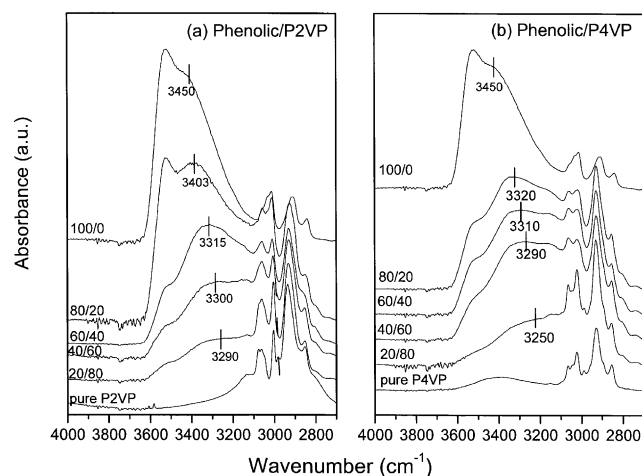
Table 1
Thermal properties of phenolic/P2VP and phenolic/P4VP blends

Phenolic content (wt%)	P2VP		P4VP	
	T_g (°C)	ΔT_g (°C)	T_g (°C)	ΔT_g (°C)
0	90.1	19.3	144.1	9.0
10	87.6	50.5	125.9	13.2
20	85.8	35.9	124.3	18.1
30	79.6	42.1	108.6	20.5
40	68.8	28.1	96.6	18.3
50	64.4	49.2	86.8	21.6
60	58.3	33.2	79.0	26.2
70	55.2	47.1	68.6	28.3
80	30.5	33.0	51.8	29.8
90	23.5	33.0	31.9	31.2
100	66.7	17.0	66.7	17.0

Fig. 2. FTIR spectra recorded at 150 °C at 4000–2700 cm^{-1} region for (a) phenolic/P2VP and (b) phenolic/P4VP blends.
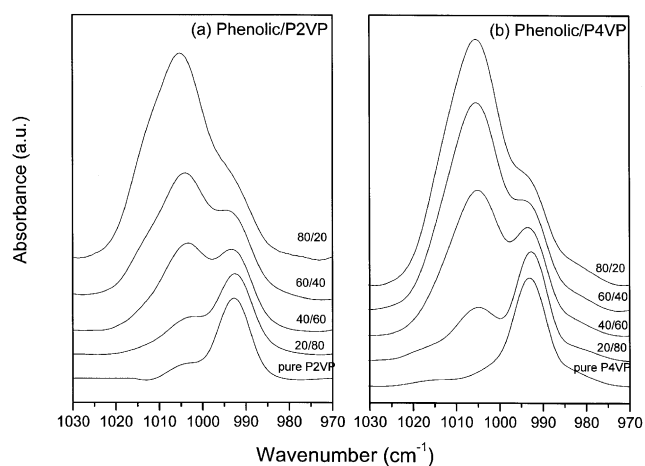
Fig. 3. FTIR spectra recorded at 150 °C at 1030–970 cm^{-1} region for (a) phenolic/P2VP and (b) phenolic/P4VP blends.

interaction including 1590, 993 cm^{-1} for P2VP and 1597, 993 cm^{-1} for P4VP [7]. Unfortunately, the bands at 1590 cm^{-1} for the P2VP and 1597 cm^{-1} for P4VP are difficult to analyze due to overlapping with the 1600 cm^{-1} band from the phenolic. Therefore, only the band at 993 cm^{-1} can be used to analyze the hydrogen bonding interactions between the hydroxyl group of phenolic and the pyridine group of P2VP or P4VP. Fig. 3 shows the scale-expanded infrared spectra in the range 970–1030 cm^{-1} measured at 150 °C for phenolic/P2VP and phenolic/P4VP. Both P2VP and P4VP have a characteristic band at 993 cm^{-1} corresponding to the pure pyridine ring absorption. A new band is assigned to hydrogen-bonded pyridine rings can be observed, corresponding to blends of P2VP at 1003 cm^{-1} and blends of P4VP at 1005 cm^{-1}. All these pyridine frequencies split into two bands, which can be fitted well to the Gaussian function. The fraction of the hydrogen-bonded pyridine ring can be calculated by the following Eq. (2) [12]

$$f_b = \frac{A_b/a}{A_b/a + A_f} \qquad (2)$$

A_f and A_b are the peak areas corresponding to absorptions from the free and the hydrogen-bonded pyridine ring, respectively. The conversion coefficient (a) is the specific absorption ratio of these two bands, free and hydrogen-bonded pyridine ring. The conversion coefficient ($a = 1$) from a similar system has been determined previously [7]. Results from curve fitting are summarized in Table 2, the hydrogen-bonded fraction of the pyridine ring increases with the increase of the phenolic content and the fraction of hydrogen-bonded pyridine groups in P4VP blend is higher than in P2VP blends over the entire composition range. This result is consistent with the previous data in the hydroxyl group analyses.

3.3. FTIR analyses at various temperatures

The scale-expanded FTIR spectra of the pyridine ring in phenolic/P2VP and phenolic/P4VP blends at different temperatures are shown in Fig. 4 and the curve fitting results are summarized in Table 3. These results show that the fraction of hydrogen-bonded pyridine ring decrease as the temperatures increased for both P2VP and P4VP blends. In addition, the hydrogen bonding corresponding to pyridines ring for both P2VP and P4VP blends return to their original after these samples are cooled to room temperature, indicating that phase separation does not occur in both phenolic/P2VP and phenolic/P4VP blends, even at a high temperature at 170 °C. These results are also consistent with the DSC analyses since the second run data were obtained by quenching from this temperature (170 °C). Furthermore, the observed recovery of hydrogen bonding fraction (Table 3) is greater than that before heating at room temperature for both phenolic/P2VP and phenolic/P4VP blend systems. It is reasonable to speculate that the chain mobility increases at higher temperature above the T_g of poly(vinylpyridines), chain conformation rearrangement allow for more intimate mixing level and provides better orientation for those inter-association sites between hydroxyl of phenolic and pyridine ring of poly(vinylpyridines).

Table 2
Curve fitting of fraction of hydrogen bonding results of the phenolic/P2VP and phenolic/P4VP blends at 150 °C

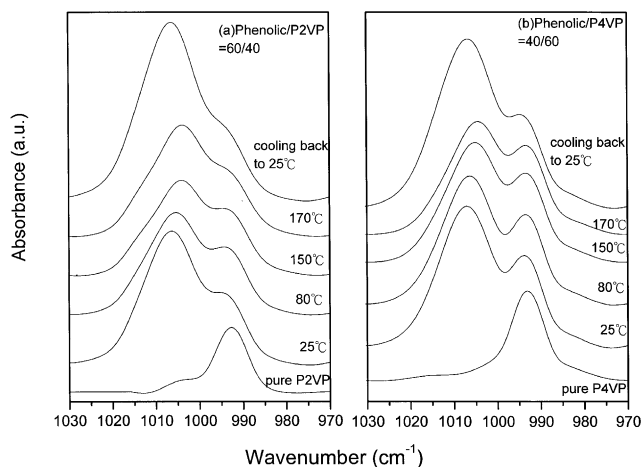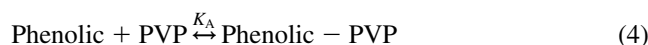| Wt%	Free pyridine ring			H-bonded pyridine ring			fb (%)[a]
	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	A_f (%)	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	A_b (%)	
Phenolic/P2VP							
20/80	993	8.2	66.85	1003	13.0	33.15	33.15
40/60	993	8.2	42.13	1003	13.0	57.87	57.87
60/40	993	9.1	38.72	1003	13.1	61.28	61.28
80/20	993	10.1	24.97	1003	13.2	75.03	75.03
Phenolic/P4VP							
20/80	993	8.0	60.14	1005	13.0	39.86	39.86
40/60	993	9.9	39.98	1005	13.1	60.02	60.02
60/40	993	10.4	35.60	1005	13.2	64.40	64.40
80/20	993	10.4	19.12	1005	13.3	81.88	81.88

[a] Fraction of hydrogen bonding.

Fig. 4. Scale-expanded infrared spectra at 1030–970 cm^{-1} region at various temperatures for (a) phenolic/P2VP = 60:40 blends and (b) phenolic/P4VP = 40:60 blends.

3.4. Estimation of inter-association equilibrium constant (K_A) based on PCAM

According to the Painter–Coleman association model, the typical interaction scheme that was considered in the PCAM based on the competing equilibrium is described as follows

$$\text{Phenolic} + \text{Phenolic} \overset{K_B, K_2}{\leftrightarrow} \text{Phenolic} - \text{Phenolic} \qquad (3)$$

$$\text{Phenolic} + \text{PVP} \overset{K_A}{\leftrightarrow} \text{Phenolic} - \text{PVP} \qquad (4)$$

where K_2 and K_B represent equilibrium constants of hydrogen-bonded dimer and multimer of the self-association of phenolic, respectively. The inter-association equilibrium constant K_A reflects the extent of the hydrogen bonding between phenolic and poly(vinylpyridines). According to the PCAM, K_A can be calculated by two methods. The first method was reported by Coggesthall and Saier [23] for determining K_A and K_B from the dilute solution (model compounds). In general, the first method is used to determine or the hydrogen bonding acceptor polymer that does

Table 3
Curve fitting of fraction of hydrogen bonding results of the phenolic/P2VP and phenolic/P4VP blends at various temperatures

	25 °C	80 °C	150 °C	170 °C	Cooling back to 25 °C
Phenolic/P2VP					
20/80	56.40	38.22	33.15	30.22	57.04
40/60	62.89	61.67	57.87	55.32	64.86
60/40	75.41	65.80	61.28	60.49	82.85
80/20	85.88	82.51	75.03	74.02	88.97
Phenolic/P4VP					
20/80	60.03	50.83	39.86	34.11	61.12
40/60	69.99	65.94	60.02	56.51	70.87
60/40	76.93	72.14	64.40	61.60	83.86
80/20	86.92	84.32	81.88	76.83	89.63

not contain the carbonyl group such as pyridine ring or ether group. As a result, the K_A for pyridine ring or ether group with hydroxyl group is usually determined by model compounds. The second method is using the numerical method to determine K_A according to PCAM based on the fraction of hydrogen bonding of carbonyl group [12]. However, this method is only suitable for systems containing carbonyl groups. As a result, the inter-association equilibrium constants were determined by model compounds in this study. However, we need to emphasize here that the inter-association equilibrium constant from model compounds is not equal to the corresponding polymer blend due to two more important chain connectivity effect, intramolecular screening and functional group accessibility [24–29]. In this study, we intend to compare the inter-association constant between phenolic/P2VP and phenolic/P4VP blends. Both 2-ethyl pyridine and 4-ethyl pyridine contain pyridine rings that were selected as model compounds for P2VP and P4VP, respectively. The 'free' hydroxyl bond absorption of 0.02 M 2,4-dimethylphenol solution containing various concentrations of 2-ethyl pyridine and 4-ethyl pyridine in cyclohexane are used herein for quantitative measurements. Notably, the FTIR from various concentrations of 2-ethyl pyridine and 4-ethyl pyridine solutions as a background must be prescanned before addition of the 2,4-dimethylphenol. Fig. 5 shows infrared spectra in the hydroxyl-stretching region of the 2,4-dimethylphenol in cyclohexane containing different concentrations of 2-ethyl pyridine (a) and 4-ethyl pyridine (b). The intensity of the free hydroxyl absorption at 3620 cm^{-1} decreases with increasing 2-ethyl pyridine and 4-ethyl pyridine concentrations. Furthermore, the absolute intensity of the free hydroxyl group at 3620 cm^{-1} is assumed to be a measure of the amount of free hydroxyl in the mixture. The absorption at 3150 cm^{-1} is attributed to the hydrogen bonding between the hydroxyl and ethyl pyridines. The method proposed by Coggesthall and Saier [23] involving the calculation
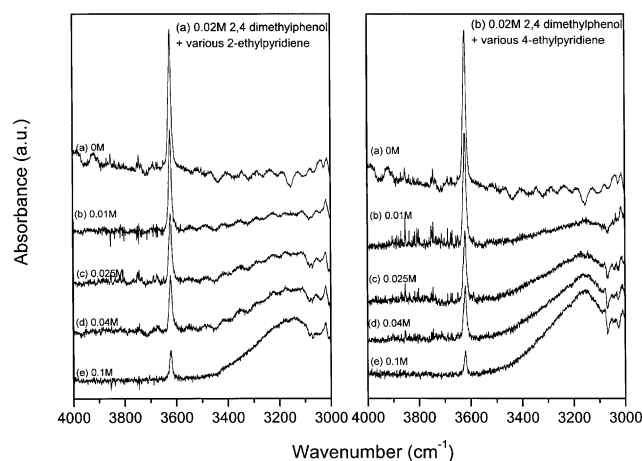

Fig. 5. FTIR spectra of the hydroxyl stretching region of 0.02 M 2,4-dimethylphenol containing various ethyl pyridine concentrations for (a) 2-ethyl pyridine and (b) 4-ethyl pyridine.

Table 4
The f_m^{OH} and K_a of 2,4-dimethylphenol in cyclohexane solution with various 2-ethyl pyridine and 4-ethyl pyridine concentrations

Conc. of ethyl pyridines	Intensity of IR absorption		f_m^{OH}		Inter-association equilibrium constant (K_a^{model})	
	2-EP	4-EP	2-EP	4-EP	2-EP	4-EP
0	0.0321	0.0321	1	1	–	–
0.01	0.0207	0.0201	0.7071	0.6791	99.94	131.88
0.02	0.0161	0.0154	0.5015	0.4579	99.07	113.01
0.025	0.0140	0.0130	0.4361	0.4049	94.21	112.15
0.04	0.0109	0.0096	0.3395	0.2990	72.59	90.20
0.05	0.0099	0.0082	0.3384	0.2557	61.99	82.86
0.1	0.0057	0.0041	0.1775	0.1286	54.53	82.01

of the hydrogen bonding association constant K_a (in l mol^{-1}) is expressed by the following Eq. (5)

$$K_a = \frac{1 - f_m^{OH}}{f_m^{OH}(C_A - (1 - f_m^{OH})C_B)} \tag{5}$$

where C_A and C_B denote the concentrations of 2-ethyl pyridine or 4-ethyl pyridine and 2,4-dimethylphenol in mol l^{-1}, respectively, while f_m^{OH} represents the fraction of free hydroxyl of the 2,4-dimethylphenol. Table 4 lists the data for on the level of f_m^{OH} for the 2,4-dimethylphenol containing various concentrations of 2-ethyl pyridine, 4-ethyl pyridine and the resulting K_a. The intrinsic inter-association constants (K_a) of 101.2 and 113.9 l mol^{-1} were obtained by extrapolating concentration of 2-ethyl pyridine and 4-ethyl pyridine to zero, respectively. This K_a must be converted into K_A by dividing the molar volume of the phenolic repeated unit (0.083 l mol^{-1} at 25 °C) [16]. The inter-association equilibrium constants, K_A, obtained through this procedure are 1219 and 1373 for P2VP and P4VP, respectively.

The equilibrium constant, molar volume, molecular weight, and solubility parameter of the phenolic/P2VP and phenolic/P4VP blends are summarized in Table 5. The observed $K_A = 1219$ and 1373 for P2VP and P4VP are

found to be much higher than $K_2 = 23.29$ from the hydroxyl dimer formation and $K_B = 52.31$ from the hydroxyl multimer formation. These results imply that the tendency toward forming the hydrogen bonding of the phenolic with P2VP and P4VP dominates over the self-association forming the intramolecular hydrogen bonding of pure phenolic. Furthermore, this result is also in good agreement with FTIR observation on hydroxyl stretching region. In addition, the K_A value for P4VP is greater than P2VP due to the steric hindrance effect on specific interaction between these two polymers and is consistent with previous data in infrared spectra data.

4. Conclusions

The phenolic is completely miscible with P2VP and P4VP in the amorphous phase over entire compositions due to the hydrogen bonding between the hydroxyl group of phenolic and the pyridine ring of P2VP and P4VP. A second characteristic to be emphasized is the influence of the nitrogen atom position in the pyridine ring. The infrared spectra data show that the P4VP has a greater ability to form hydrogen bonding than P2VP with phenolic due to the steric

Table 5
Summary of the self-association and inter-association parameters of phenolic/poly(vinylpyridines) blend

	Equilibrium constant, K (25 °C)			
Self-association[a]				
Dimer formation (K_2)	23.29			
Multimer formation (K_B)	52.31			
Inter-association between				
Phenolic and P2VP	1219			
Phenolic and P4VP	1373			

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
P2VP[b]	84.9	105.1	10.85	1904
P4VP[b]	84.9	105.1	10.85	571

[a] Ref. [16].
[b] Estimated by using a group contribution method proposed by Coleman et al. [12].

hindrance effect on the nitrogen atoms in P2VP. The steric hindrance effect indeed plays an important role in forming the inter-molecular hydrogen bonding. In addition, the inter-association constant can be obtained by model compounds according to Painter–Coleman association model. The inter-association equilibrium constants for phenolic/P2VP and phenolic/P4VP blend are higher than the self-association constant of the phenolic, indicating that the tendency toward forming hydrogen bonding between phenolic and poly(vinylpyridines) dominates the intramolecular hydrogen bonding of the phenolic resin in the mixture. In addition, the inter-association equilibrium constant for the phenolic/P4VP is greater than that of the phenolic/P2VP, also revealing that the P4VP has a greater ability to form hydrogen bond than the P2VP.

Acknowledgements

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