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Prediction of Thermodynamic Properties of Novolak-Type Phenolic Resin and Aliphatic Polyester Blends: Painter−Coleman Association Model Study of Compositional Homogeneity

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ABSTRACT: The interassociation constants of Painter−Coleman association model, obtained from the results of Fourier transform infrared spectroscopy of low molecular weight analogues in dilute solution, were used to predict the thermodynamic properties of phenolic and polyester polymer blends. The miscibility window, phase diagram, and degree of hydrogen bonding were discussed with the transferability of the association constant between the model compound and the polymer blends. All the predicted results coincided with the actual hydrogen bonding, regular photograph, and proton spin−lattice relaxation in the rotating flame ($T_{1\rho}^{H}$). This model provides a reasonable explanation of analogues of phenolic resin blends. The predicted thermodynamic properties are in harmony with the experimental results due to the high hydroxyl group density and low molecular weight of the phenolic resin which improves the compositional homogeneity of the phenolic/polyester blend.

Introduction

Hydrogen bond formation has been proven to be critical in enhancing the miscibility of the various phenolic blends with modifiers containing ether, carbonyl, or hydroxyl functional groups.[1−3] The miscibility of phenolic blends occurs at the molecular level according to NMR measurements.

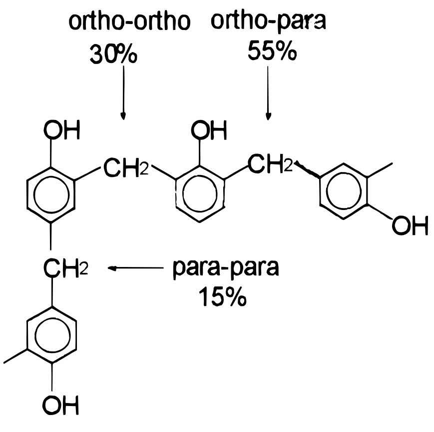
The Painter−Coleman association model (PCAM) was used to predict the thermodynamics of the polymer blend where the specific interactions are present.[4] The main equation used in this model is based on the classical Flory−Huggins relation. In order to use this equation, a series of association constant, such as self-association and interassociation constants,[5] are needed to predict the phase diagrams, miscibility windows, and other thermodynamics properties. However, significant differences were found between the fraction of hydrogen-bonded groups in mixtures of low molecular weight model analogues, e.g., 4-ethylphenol (EPh) and ethyl isobutyrate (EIB), and those in the miscible polymer blend, i.e., poly(4-vinylphenol) (PVPh) and poly(ethyl methacrylate) (PEMA) in a previous study.[6] It is likely that the difference in equilibrium constants for low molecular weight molecules, copolymers, and polymer blends, due to the chain stiffness and the connectivity of the polymer, hinders the transferability of the low molecular weight equilibrium constant to the polymer blend for the calculation of thermodynamic properties.

As known from our previous study,[3] the miscibility of phenolic resin and poly(adipic ester) occurs at the molecular level, and the blend exhibits true compositional homogeneity. The hydroxyl group of the phenolic resin interacts whenever possible with another modifier that contains a hydrogen-bonding functional group, and the effects of chain connectivity and stiffness are minimized in the phenolic blend system. The purpose of this research is to demonstrate that the equilibrium constant of low molecular weight analogues can be transferred to predict the thermodynamic properties of the phenolic/polyester blend using Painter-Coleman Association Model within experimental error.

The phenolic blend system caused some difficulties in carrying out the calculation of the PCAM parameters. In this study, the ester-containing polymer with a carbonyl group provides the proton acceptor group, which can interact with proton donor polymer (e.g., phenolic resin). In addition to the number of hydrogen-bonding configurations of the polymer chain, the miscibility also depends on the strength of interassociation. Detailed analysis of infrared spectra provides the interassociation equilibrium constants and enthalpies.[4] The prediction of thermodynamic properties is achieved based upon the PCAM. The degree of hydrogen bonding and the phase diagram of the blends of phenolic resin and aliphatic polyester were investigated by FT-IR, regular photography, and proton spin−lattice relaxation ($T_{1\rho}^{H}$) of solid-state NMR. The effects of a carbonyl group in the polymer chain on the miscibility will also be discussed.

Experimental Section

The novolak-type phenolic resin was synthesized in this laboratory as previously[7] described. The chemical structure of Novolak-type phenolic resin, consisting of phenol 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 methylol group which is capable of causing cross-linking on heating. The structure of the novolak-type phenolic resin is described as follows:



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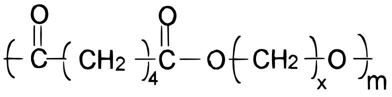
The synthesis of the poly(adipic ester) family [including poly(ethylene adipate) (PEA), poly(butylene adipate) (PBA), poly(hexamethylene adipate) (PHA), poly(octamethylene adipate) (POA), and poly(decamethylene adipate) (PDA)] is detailed as follows:[3,8] The adipic acid, ethylene glycol, 1,4-butanediol, 1,6-hexanediol, 1,8-octanediol, 1,10-decanediol, and *p*-toluenesulfonic acid are extrapure reagent grade. Polyesterifications of adipic acid with ethylene glycol, 1,4-butanediol, 1,6-hexanediol, 1,8-octanediol, and 1,10-decanediol in the presence of the foreign acid (*p*-toluenesulfonic acid) as catalyst are carried out under a reaction temperature of 140 °C for 3 h, with the diol-to-diacid ratio being 1. The products are characterized by IR, GPC, and ^{1}H and ^{13}C NMR. The repeating unit of the poly(adipic ester) family is described as follows:



$$\left(\overset{O}{\overset{\|}{C}}\left(CH_2\right)_4\overset{O}{\overset{\|}{C}}-O\left(CH_2\right)_x O\right)_m$$

where $x = 2$ for PEA, $x = 4$ for PBA, $x = 6$ for PHA, $x = 8$ for POA, and $x = 10$ PDA. The number of repeated units of the modifier is close to 80.

The novolak analogue, 2,4-dimethylphenol (2,4-xylenol), was obtained from the Lancaster Synthesis Co. (Windham, NH) with a purity of 97% and was used as received. The cyclohexane−ethyl acetate, purchased from the Tokyo Kasei Kogyo Co. Ltd., was used as a model compound of poly(adipic ester).

Infrared spectra were obtained on a FT-IR spectrometer (Bio-Rad FTS-155, Hercules, CA). In all cases, at least 16 scans with an accuracy of 2 cm^{-1} were signal-averaged. For liquid samples, an adequate permanently-sealed cell with NaCl windows and 0.05 mm thickness (Wilmad, NJ) was used. A single optical path was used to study the interassociation between 2,4-xylenol and ethyl acetate. The Beer−Lambert law was obeyed for all model compound solutions in the absorption range. Cyclohexane was used as solvent in this study due to favored conformations.[9,10] For the film sample, the phenolic resin/PEA blend was prepared by the solution-casting method. These two materials were mixed in THF (1% (w/v)) at room temperature in the desired compositions. The mixed solution was stirred for 6−8 h, and the solution was allowed to evaporate slowly at room temperature for about 24 h. The blended films were then dried at 50 °C for 2 days and annealed at 140 °C for 2 h under vacuum. IR studies were carried out with the conventional NaCl disk method. The samples were scanned at a resolution of 2 cm^{-1} at various temperatures. The IR spectra recorded at elevated temperature were obtained by using a heating cell mounted inside the sample compartment of the spectrometer. A maximum temperature of 180 °C was used in this case, since it was determined independently that a significant chemical change may occur at 190 °C or higher.

High-resolution solid-state ^{13}C NMR experiments were carried out on a Bruker DSX-300 spectrometer operating at resonance frequencies of 300.13 and 75 MHz for ^{1}H and ^{13}C, respectively. The proton spin−lattice relaxation times (in the rotating frame) were measured via carbon signal intensities using a $90_x-\tau-$spin lock pulse sequence prior to cross-polarization. Acquisition was performed with ^{1}H decoupling, and the delay times (τ) ranged from 0.2 to 16 ms. The ^{13}C CP/MAS spectra were measured with a pulse angle of 90°; pulse width, 3.9 μs; pulse delay time, 3 s; acquisition time, 3 s; spectral width, 3500 Hz; number of data points per spectrum, 4 K; number of scans, 1K. The measurements was performed at 300 K with broad-band decoupling, normal cross-polarization pulse sequence, and magic angle sample spinning (MAS) of 5.4 kHz. The chemical shifts of ^{13}C spectra are reported in ppm relative to glycine as an external reference standard. The signal noise for the methylene of glycine measured with the four scans and a pulse angle of 90° was larger than 45.

Miscibility Guide Phase Calculator software (MG&PC)[4] was used to calculate the thermodynamic properties of the polymer blends.

Results and Discussion

Estimation of Interassociation Parameters (K_A).

As indicated by the Painter−Coleman equation,[4] the quantity $\Delta G_H/RT$ was defined as the free energy contribution due to the change in hydrogen bonding upon mixing. It is necessary to determine a set of equilibrium constants describing self-association and interassociation to predict phase diagrams, miscibility windows, and maps of polymer blend systems involving specific interactions. We will try to use the PCAM to predict thermodynamic properties of the phenolic blend that contains high hydroxyl group density. Although the equilibrium constants of low molecular weight molecules are significantly different from those determined for a comparable miscible polymer, the degree of hydrogen-bonded carbonyl is considerably less than those for two similar low molecular weight analogues in other polymer blend systems due to the chain stiffness and connectivity, as mentioned in the Introduction. We anticipate that the high hydrogen groups and low molecular weight of the phenolic resin will minimize the difference caused by chain stiffness and connectivity. As the results suggest, the PCAM model is still relevant in the current system.

Table 1. Self-Association Parameters for Phenolic Blends[11]

association	equilibrium constant, K (25 °C)	enthalpy, Δh (kcal/mol)
dimer formation	23.29 (K_2)	−4.246 (h_2)
multimer formation	52.31 (K_B)	−6.110 (h_B)

The equilibrium constant of the phenolic blend is determined from infrared methodology as described in a previous study.[11] Enthalpies of self-association (Δh) of phenolic resins were estimated from the observed shifts of the associated hydroxyl band referred to the free hydroxyl bands ($\Delta\nu_{OH}$) for the hydroxyl band of 2,4-xylenol derived previously[11] as follows:

$$-\Delta h\ (\text{kcal mol}^{-1}) = 2.564 + 0.0122\Delta\nu_{OH}\ (\text{cm}^{-1}) \quad (1)$$

Table 1 summarizes the values of the constants and enthalpies of self-association of the phenolic resin. The interassociation between 2,4-xylenol and ethyl acetate was investigated by taking the IR spectra of the 2,4-xylenol and ethyl acetate in cyclohexane solutions. The interassociation constant (K_A) reflects the tendency of the hydrogen-bonding association between phenolic and polyester units. In this study, the “free” OH band absorption at a fixed 2,4-xylenol concentration (0.02 M) and varying ethyl acetate concentrations in cyclohexane was used for quantitative measurement. It was necessary to prescan the FT-IR before the 2,4-xylenol was added into the various concentrations of ethyl acetate solution to determine the background. The method proposed by Coggeshall and Saier[12] involved the calculation of an association constant, K_a (in L mol^{-1}), from the following equation:

$$K_a = \frac{1 - f_m{}^{OH}}{f_m{}^{OH}(c_A - (1 - f_m{}^{OH})c_B)} \quad (2)$$

where c_A and c_B are the concentrations of ethyl acetate and 2,4-xylenol in mol L^{-1}, respectively. $f_m{}^{OH}$ is the fraction of free hydroxyl of 2,4-xylenol. Table 2 summarizes the data of $f_m{}^{OH}$ of 2,4-xylenol for various concentrations of cyclohexane−ethyl acetate solution. The intrinsic interassociation constant K_a (7.43) can be obtained from extrapolation to zero concentration of ethyl acetate. K_a has to be modified to become K_A by dividing the molar volume of the phenolic repeated unit

Table 2. f_m^{OH} and K_a of 2,4-Xylenol for Various Cyclohexane−Ethyl Acetate Cyclohexane Concentrations

concn of ethyl acetate (mol/L)	f_m^{OH}	K_a
0.08	0.653	7.26
0.1	0.601	7.22
0.2	0.442	6.67
0.25	0.394	6.48
0.4	0.298	6.09
0.5	0.257	5.96

Table 3. Associated Equilibrium Constant and Enthalpy of Phenolic Resin/PEA Blend

association	equilibrium constant, K (25 °C)	enthalpy, Δh (kcal/mol)
interassociation between phenolic resin and PEA	89.52 (K_A)	−4.11 (h_A)

(0.083 L mol^{-1} at 25 °C). The interassociation equilibrium constant, K_A, obtained from this procedure was 89.52.

The absorption shift of the hydrogen-bonding hydroxyl group occurring at 3493 cm^{-1} in the mixture of 2,4-xylenol with ethyl acetate is concentration independent. Substituting the absorption shift into eq 1, the enthalpy of the association between 2,4-xylenol and ethyl acetate was calculated to be −4.11 kcal mol^{-1}. The equilibrium constant and enthalpy of the phenolic blend are summarized in Table 3. The fact that K_A is found to be much higher than K_2 and K_B implies that the tendency toward hydrogen bonding of the phenolic resin and polyester dominates over the self-association of the phenolic resin in the mixture.

Degree of Hydrogen Bonding. One of the best-known methods to investigate the miscibility of polymer is to determine the degree of hydrogen bonding as a function of blend composition.[4,9,13,14] The main objective of the research described in this work is to reveal the fraction of hydrogen-bonded carbonyl group for comparable compositions between those of the simulation and the experiment. The IR band of the carbonyl group of polyester stretching is far from other absorptions; thus, it is advantageous to measure variations when mixed with the hydroxyl group of the phenolic resin. As one can see from Figure 1, the fraction of hydrogen-bonded carbonyl groups can be measured as a function of the composition of the phenolic resin/PEA ($x = 2$) at 120 °C (higher than the T_g of the polymer blend). It is straightforward to distinguish and quantify those carbonyl groups that are hydrogen bonded with the hydroxyl groups of the phenolic resin and those that are not. The relative intensity increases with increasing phenolic content. When PEA was mixed with the phenolic resin, the overlapping peaks broadened gradually. Therefore, the stretch vibration of the hydrogen-bonded carbonyl groups is readily attributed to the hydroxyl group of the phenolic. The band may be readily decomposed into two Gaussian peaks, with areas corresponding to the hydrogen-bonded (1713 cm^{-1}) and free carbonyl absorptions (1743 cm^{-1}). The fraction of the hydrogen-bonded carbonyl group can be calculated from the following equation:[4]

$$f_b = \frac{A_b/1.5}{A_b/1.5 + A_f} \qquad (3)$$

where A_b is the area of the hydrogen-bonded carbonyl absorption, A_f is the area of the free carbonyl absorption, and the conversion coefficient 1.5 is the ratio of absorptive coefficients of two bands of the "free" and the "associated" carbonyl group in an ester group.[4] Peak decomposition reveals that only two bands matched the spectrum of the blend quite satisfactorily in the carbonyl region. As reported previously,[4,9,13,14] the 1713 cm^{-1} band was broader than that of 1743 cm^{-1}, reflecting a reasonably wider hydrogen bond distance distribution and steric structure in the polymer blend. From the relative absorption coefficients for the two carbonyl stretching vibrations, the fraction of interacting species could be calculated from the fractional area of the 1713 cm^{-1} band, which was summarized in Table 4. It is clear that PEA associated with the phenolic resin directly and no phase separation occurred up to 120 °C, and the hydrogen-bonded fraction increases with increasing phenolic content.

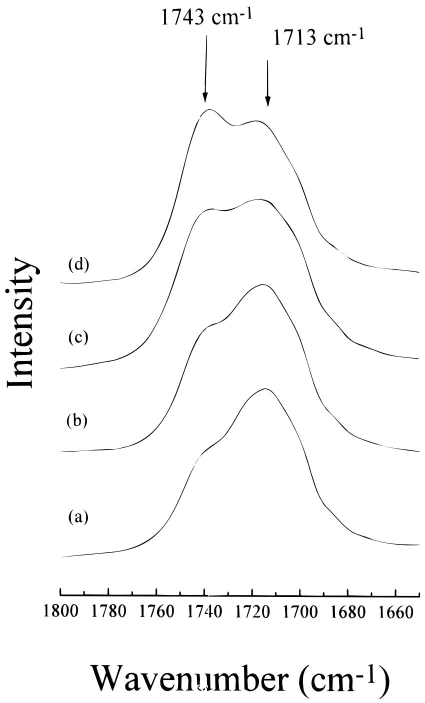


Figure 1. IR spectra of the carbonyl stretching region of the varying phenolic resin/PEA blends composition at 120 °C. (a) 90/10, (b) 80/20, (c) 70/30, and (d) 60/40 (wt %).

Table 4. Curve-Fitting Data of Infrared Spectra of Phenolic Resin/PEA Blends with Various Compositions at 120 °C

phenolic resin/PEA (w/w)	"free" C=O			H-bonded C=O			
	ν,[b] cm^{-1}	$W_{1/2}$,[c] cm^{-1}	A_f, %	ν, cm^{-1}	$W_{1/2}$, cm^{-1}	A_{HB}, %	f_b[a]
90/10	1743	23.85	19.58	1714.2	37.02	80.42	0.732
80/20	1743	22.92	20.99	1714.9	38.46	79.01	0.715
70/30	1743	25.85	33.00	1713.7	39.27	67.00	0.575
60/40	1743	28.17	37.57	1714.6	39.37	62.43	0.526
40/60	1747	35.29	54.95	1713.1	39.71	45.05	0.353

[a] Calculated from eq 3. [b] ν, chemical shift. [c] $W_{1/2}$, full width at half-maximum (fwhm).

Figure 2 shows representative examples of infrared spectra in the carbonyl stretching region for the 90/10 (wt %) phenolic resin/PEA blend films recorded at various temperatures. The results of curve-fitting from IR spectra are summarized in Table 5. Results show that approximately 80% of the carbonyl group of PEA was found to be hydrogen-bonded in the 90/10 (wt %) phenolic resin/PEA blend at 40 °C. The fraction of hydrogen-bonded carbonyl group decreases as the temperature increases; when it is cooled to 40 °C, consequently, the original fraction of hydrogen bonding can be determined.

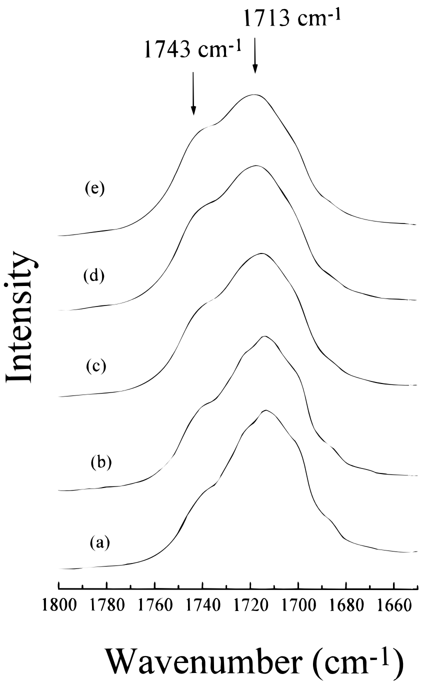


Figure 2. IR spectra of the carbonyl stretching region of the 1800−1650 cm $^{-1}$, for the 90/10 phenolic resin/PEA blend as a function of temperature. (a) 40, (b) 80, (c) 120, (d) 160, and (e) 180.

Table 5. Curve-Fitting Data of Infrared Spectra of Phenolic Resin/PEA 90/10 Blends at Various Temperatures

	"free" C=O			H-bonded C=O			
temp, °C	ν,[b] cm^{-1}	$W_{1/2}$,[c] cm^{-1}	A_f, %	ν, cm^{-1}	$W_{1/2}$, cm^{-1}	A_{HB}, %	f_b[a]
40	1742.1	21.6	14.60	1712.5	35.63	85.40	0.795
80	1742.0	22.66	18.62	1712.8	35.50	81.38	0.744
120	1743.2	23.85	19.58	1714.2	37.01	80.42	0.732
160	1743.4	23.55	21.14	1715.9	38.04	78.86	0.713
180	1743.8	25.64	23.65	1715.9	38.40	76.35	0.683
160	1743.8	24.96	21.96	1715.6	38.13	78.04	0.703
120	1742.7	22.99	20.57	1713.4	38.10	79.43	0.720
80	1743.0	23.26	16.73	1713.2	36.80	83.27	0.768
40	1742.6	23.42	15.53	1712.5	38.47	84.47	0.784

[a] Calculated from eq 3. [b] ν, chemical shift. [c] $W_{1/2}$, full width at half-maximum (fwhm).

Table 6. Properties of Pure Polymers Used in This Study

polymer	molar volume (mL/mol)	molecular mass (g/mol)	solubility (cal/mL)$^{0.5}$	polymer DP
Novolak-type phenolic resin	84[a]	105[a]	12.05	6[a]
$((CH_2)_3CO_2)_n$	69.1	86.1	10.04	80[a]
$((CH_2)_4CO_2)_n$	85.6	100.13	9.65	80[a]
$((CH_2)_5CO_2)_n$	102.1	114.16	9.38	80[a]
$((CH_2)_6CO_2)_n$	118.6	128.19	9.19	80[a]
$((CH_2)_7CO_2)_n$	135.1	142.22	9.05	80[a]
CH_2	16.5	14.03	8.00	

[a] Measured directly. The other data were estimated using a group contribution method proposed by Coleman et al.[4]

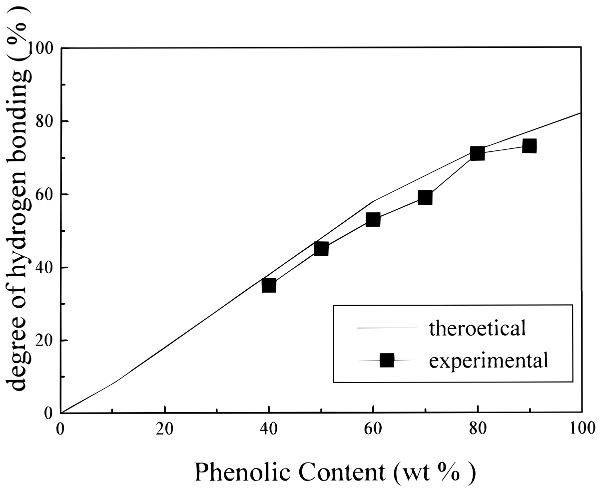


Figure 3. Comparison of theoretical (solid line) and experimental (■) degree of hydrogen bonding of the carbonyl group in the phenolic resin/PEA blends as a function of composition at 120 °C.

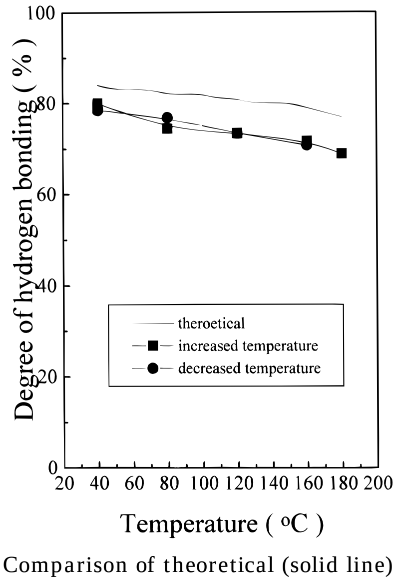


Figure 4. Comparison of theoretical (solid line) and experimental (■, increased temperature; ●, decreased temperature) degree of hydrogen bonding of the carbonyl group in the 90/10 phenolic resin/PEA blend as a function of temperature.

To calculate the thermodynamic properties of the blends using MG&PC software,[4] a series of characteristic data, i.e., molar volume, molecular weight of repeated unit, degree of polymerization, and solubility parameters, of the neat polymer at 25 °C are also required, in addition to the interassociation (K_A) and self-association (K_2, K_b) constants and enthalpies (h_A, h_2, h_b). Except for the degree of polymerization and molar volume of the phenolic resin, which were measured directly, all polymer properties can be estimated with the MG&PC software. Table 6 summarizes the polymer properties employed in this study. In the MG&PC method, there is no distinction between the specific repeated unit of polymer containing n methylene groups and the average specific repeated unit of copolymer containing the same number of methylenes per ester group. Using PEA, $((CH_2)_2COO(CH_2)_4COO)_n$, as an example, this is converted into $((CH_2)_3COO)_n$ in PCAM.

The ability of PCAM to predict the degree of hydrogen bonding on the carbonyl group is demonstrated in Figure 3, where the experimental results and theoretical prediction are plotted together with results as a function of composition at 120 °C. As can be seen from Figure 3, the experimental value agrees well with the prediction for hydrogen bonded carbonyl groups at 120 °C. The model provides a precise prediction of the degree of hydrogen bonding at various compositions at 120 °C.

There is also a correlation between the degree of hydrogen bonding and the temperature; a representation of theoretical and experimental values of hydrogen-bonding fraction as a function of temperature is superimposed in Figure 4 for comparison, and quantitative

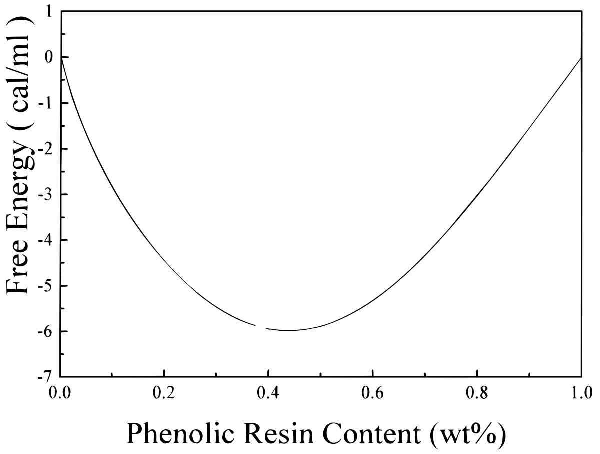


Figure 5. Total free energy of mixing (ΔG_m) in phenolic resin/PEA blends as a function of composition at 120 °C.

values are summarized in Table 5. The fraction of hydrogen-bonded carbonyl groups of PEA decreases with increasing temperature and follows the prediction within error. The reversible hydrogen-bonding fraction, which is continuously broken and formed with increasing and decreasing temperature, is consistent with an equilibrium process. The excellent agreement suggests the applicability of PCAM in the current blend system.

Prediction of Free Energy. The free energy of the phenolic resin/PEA blend at 120 °C is simulated for the mixture in the liquid state. Figure 5 shows that the free energy (ΔG_m) was predicted to be negative for all the compositions at 120 °C. A minimum value of ΔG_m, -5.98 cal/cm^3, occurred when the phenolic content was about 45 wt %. This polymer blend system was completely miscible at 120 °C. Figure 6 shows the total free energies of mixing (ΔG_m) of phenolic resin/PEA 60/40 blends at different temperatures from 57 to 197 °C. The free energy of mixing is negative throughout this temperature range, and a minimum value appeared at 107 °C. A two-phase region would occur in the blend. One, UCST, occurred at a lower temperature in the blend, and the other was the LCST region. However, the LCST is far higher than the degradation temperature of polymer blend. From the free energy of mixing (ΔG_m) of the system at different temperatures, it was possible to calculate the enthalpy of the mixing (ΔH_m) by using the Gibbs−Helmholtz relationship:

$$\partial(\Delta G_m/T)/\partial(1/T) = \Delta H_m \tag{4}$$

$$\Delta G_m = \Delta H_m - T\Delta S_m \tag{5}$$

The enthalpy of the mixing (ΔH_m) was predicted to be positive below 65 °C and negative above it, while the entropy of mixing ($-T\Delta S_m$) was negative below 110 °C and positive above it. The enthalpy term at lower temperature and the entropy term at high temperature indicated that the polymer blend tends to be miscible. From the prediction, it may be concluded that the phenolic resin/PEA blend system is miscible. The difference in solubility parameters between phenolic and PEA was 2.01 and is large enough to cause the phase separation at moderate temperatures in the general case. However, in this study, the phase separation occurred at low temperature only. This indicates that hydrogen bonding between the phenolic resin and PEA affects the phase diagram significantly. The equilibrium constant of interassociation, K_A, was higher than the equilibrium constants of self-association, K_2 and K_B, at 25 °C, implying that the hydrogen bonding between the phenolic resin and PEA was higher than the self-association of the phenolic resin. The phase separation would not occur at moderate temperature.

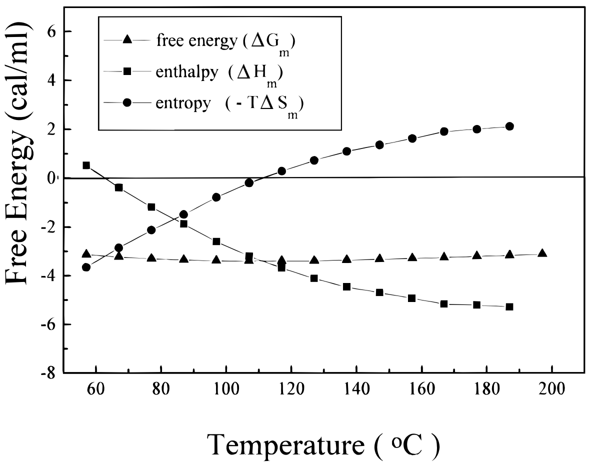


Figure 6. Total free energy (ΔG_m, enthalpy (ΔH_m, ■), and entropy ($-T\Delta S_m$, ●) of mixing for 60/40 phenolic resin/PEA blends as function of temperature.

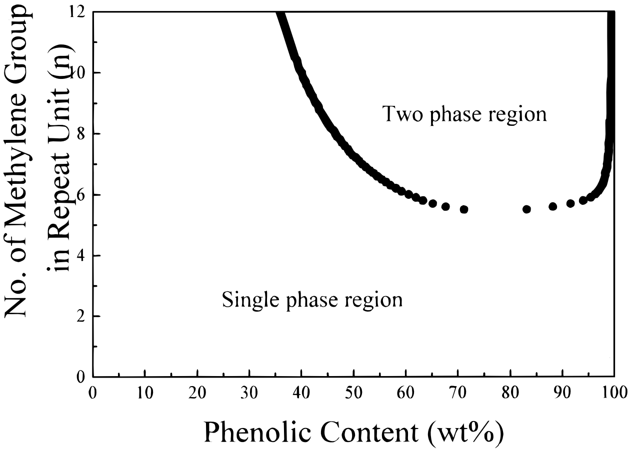


Figure 7. Theoretical predictions of the miscibility window for phenolic resin/aliphatic polyester at 120 °C.

Calculation of Phase Diagrams of Miscibility Windows. The prediction of the miscibility window was done at 120 °C for phenolic resin/aliphatic polyester blend, and the result is presented in Figure 7. The *x*-axis shows the weight fraction of phenolic resin in the blends, and the *y*-axis shows the number of methylene groups in every carbonyl group. The repeating units were 80 and 6 for aliphatic polyester and phenolic resin, respectively. The phenolic resin was predicted to be completely miscible in the amorphous state with aliphatic polyester containing 0−6 methylene groups for every specific repeating unit. Consequently, aliphatic polyester corresponds to zero methylene group in the specific repeating unit. As shown in Figure 7, the family of aliphatic polyester is predicted to be immiscible when seven methylene groups are added to the aliphatic polyester specific repeating unit at 120 °C.

In Figure 8, the binodal phase diagrams for the phenolic resin/aliphatic polyester were simulated over the temperature range from −100 to 300 °C. There were four phenolic blends with aliphatic polyester containing 3−6 methylene groups in the specific repeating unit. The first blend, with $x = 4$ (PBA), was predicted to be completely miscible over −40 °C. When more methylene groups were added into the specific repeating unit, e.g., $x = 6$ (PHA) and $x = 8$ (POA), a two-phase region appeared in the phenolic-rich blends

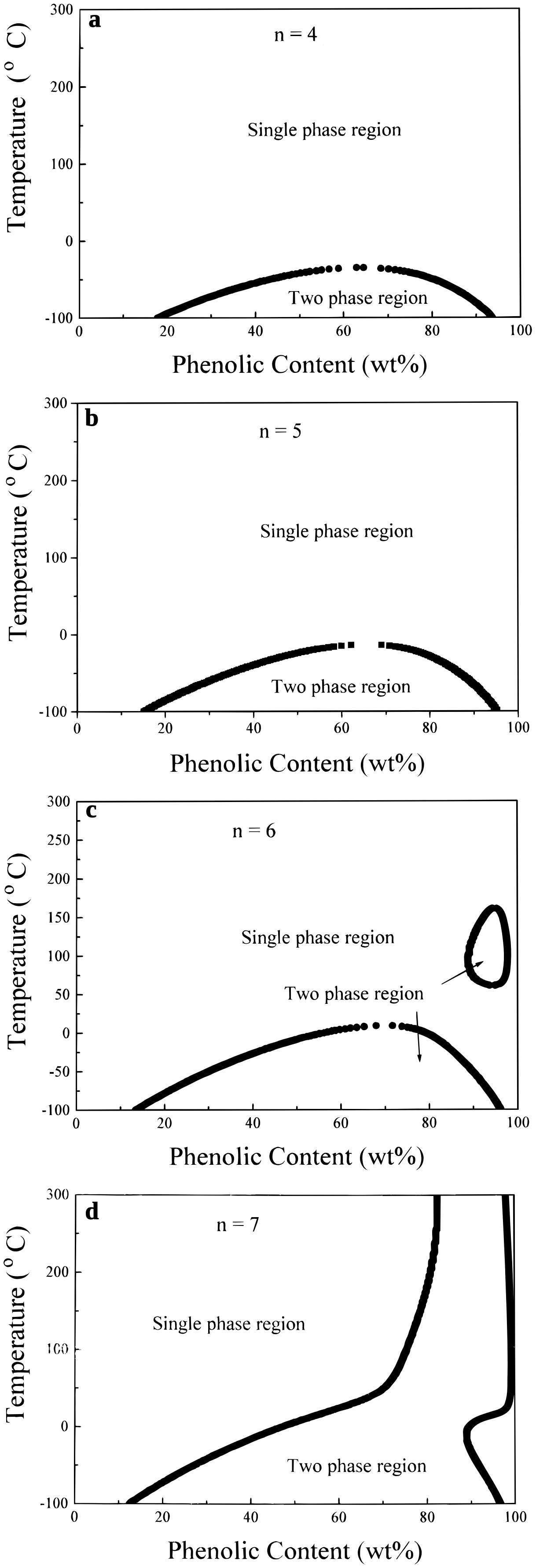


Figure 8. Calculated binodal phase diagrams of phenolic resin/aliphatic polyester blends with varying numbers of methylene groups in the specific repeating units in aliphatic polyester. (a) $n = 4$, PBA; (b) $n = 5$, PHA; (c) $n = 6$, POA; and (d) $n = 7$, PDA (n is the number of methylene in the specific repeating unit).

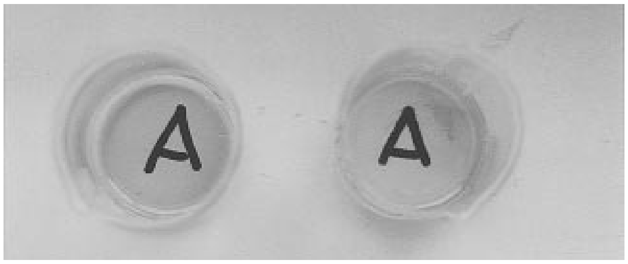


Figure 9. Regular photograph of phenolic resin/aliphatic polyester blends with varying numbers of methylene groups in the specific repeating units in aliphatic polyester. (a) 60/40 phenolic resin/POA ($n = 6$) and (b) 60/40 phenolic resin/PDA ($n = 7$) (n is the number of methylene groups in the specific repeating unit).

at temperatures below −10 and 20 °C, respectively. Upon further addition of methylene groups, $x = 10$ (PDA), the immiscible region in the phase diagram was extended throughout the entire temperature range. A significant effect on the phase diagrams can be seen when just one methylene group is added into the aliphatic polyester specific repeating unit.

Regular photographs of phenolic resin/aliphatic polyester blends are shown in Figure 9. The 60/40 (wt %) phenolic resin/POA ($x = 8$) blend at 20 °C is miscible; however, phase separation occurred when two methylene groups were added to the POA, as shown in Figure 9. Although there were some assumptions in the association model and inherent errors in the determination of equilibrium constants, enthalpy, solubility parameter, and molar volume of polymer, the predicted phase diagram still agreed quite well with the regular photographs of phenolic resin/aliphatic polyester blends.

Proton Spin−Lattice Relaxation ($T^{H}_{1\rho}$). Proton spin−lattice relaxation time ($T^{H}_{1\rho}$) is indicative of the phase behavior of this blend. In general, the resolution of various polymer carbon signals of the solid-state ^{13}C NMR spectra was quite good. Interference from spinning side bands was not a problem under the spectral accumulation conditions. Measurements of rotation frame spin−lattice relaxation times were made by using a $90_x-\tau-$SL pulse sequence. The carbon signal intensity decay curves were fitted to a standard first-order kinetic expression. This procedure allowed for the determination of the proton spin−lattice relaxation times for the blends and the polymer components by monitoring the change in carbon signal intensities as a function of delay time (τ).

Figure 10 shows a semi-log plot of carbon signal intensity as a function of delay time (τ) for the benzene ring of 60/40 (wt %) phenolic resin/POA ($x = 8$) and phenolic resin/PDA ($x = 10$) blends at 300 K. For the benzene ring of the 60/40 (wt %) phenolic resin/POA blend, a single-component decay process occurred, with a relaxation time of 2.0 ms. For the benzene ring of the phenolic resin/PDA ($x = 10$) blend, a two-component decay process occurred, with relaxation times of 2.12 and 0.058 ms, as indicated by the change in the slope of the signal intensity plot. The 60/40 (wt %) phenolic resin/POA blend is completely miscible, and the domain size should be less than 2−3 nm. The 60/40 (wt %) phenolic resin/POA blend is immiscible, and the domain size is larger than 2−3 nm. Although the molecular structures are similar for 60/40 (wt %) phenolic resin/POA and phenolic resin/PDA blends, when more methylene was added into the polyester repeating unit, the relaxation times increased and the relaxation behavior changed significantly.

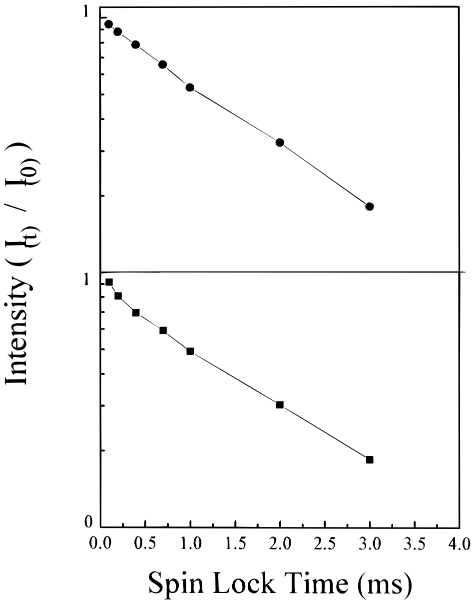


Figure 10. Semi-log plot of carbon signal intensity as a function of delay time (τ) for the carbonyl group of 60/40 (wt %) phenolic resin/POA ($n = 6$ or $x = 8$) and phenolic resin/PDA ($n = 7$ or $x = 10$) blends at 300 K. The slope yields the proton spin−lattice relaxation time in the rotating frame. (a) Benzene ring of 60/40 (wt %) phenolic resin/POA blend and (b) benzene ring of 60/40 (wt %) phenolic resin/PDA blend.

Conclusions

The results presented here suggest that the nature of hydrogen bonding in phenolic resin is satisfactorily predicted by PCAM, and one would expect the characters of phenolic resin, such as the high hydroxyl group density and low molecular weight, to compensate the effect of compositional heterogeneity in the phenolic blend, and thus minimize the chain connectivity and rotational freedom. The functional group of the phenolic blend can hydrogen bond to any of its neighbors that happen to have an appropriate functional group. In low molecular weight materials, hydrogen bonding leads to loss of the rotational freedom of the whole molecular, while the degree of rotational freedom is increased with blending in the phenolic blend. Those effects appeared to be minimized by the differences between the equilibrium constant of the low molecular weight analoge and that of the phenolic resin blend. The factor of K_A/K_B influences the compositional miscibility significantly, leading to compositional heterogeneity or compositional homogeneity in polymer blends. When the ratio of K_A/K_B is more than unity, this implies the ability of intermolecular hydrogen bonding to dominate over intramolecular hydrogen bonding, causing homogeneity. In this phenolic resin/polyester blend, the factor of K_A/K_B is higher than unity, which results in the intermolecular interaction of the phenolic resin and the aliphatic polyester blend system. Although the different of solubility parameters of the two polymers is large enough to cause phase separation, the hydrogen bonding would play a key role in determining the thermodynamic properties of the phenolic resin/aliphatic ester blend system.

The miscibility of the polymer blend depends on the strength of interassociation as well as the number of hydrogen bonding configurations of the polymer chain. When seven methylene groups were added into the specific repeating unit, the phase diagram of the immiscible blend extended thoughout the entire temperature range. The predicted degree of hydrogen bonding and the phase diagram agree with the experimental results of FT-IR, regular photography, and proton spin−lattice relaxation time in the rotating frame, $T_{1\rho}{}^{H}$. It was confirmed that transferability of the parameter between model compounds and polymer blends was acceptable for the phenolic blend system.

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