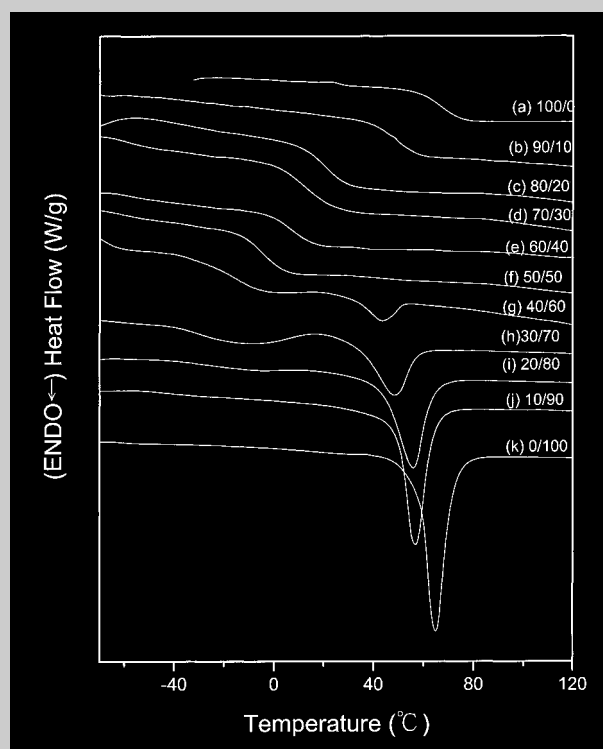


Full Paper: Blends of phenolics with poly(ϵ -caprolactone) (PCL) were prepared by solution casting from the tetrahydrofuran (THF) solution. Differential scanning calorimetry (DSC) and Fourier-Transform infrared spectroscopy (FTIR) were used to examine the miscibility behavior and hydrogen bonding of the blend. This phenolics/PCL blend system is fully miscible based on single glass transition temperature due to the formation of inter hydrogen bonding between hydroxyl of phenolic and carbonyl of PCL. In addition, a negative polymer-polymer interaction energy density “*B*” was obtained based on the melting depression of PCL using the Nishi-Wang equation. Furthermore, FTIR was used to study the hydrogen-bonding interaction between the phenolic hydroxyl group and the PCL carbonyl group at various temperatures and compositions. Moreover, the inter-association equilibrium constant and its related enthalpy of phenolic/PCL blends were determined and used to predict the miscibility window, free energy and fraction of the hydrogen bonding according to the Painter-Coleman association model (PCAM).

The DSC scans of phenolic/PCL 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.



The Study of Miscibility and Hydrogen Bonding in Blends of Phenolics with Poly(ϵ -caprolactone)

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Introduction

Miscible polymer blends provide attractive interest in polymer science due to strong economic incentives arising from their use. However, the entropy of mixing for large molecules is usually small and the miscibility becomes increasingly dependent on the nature of the contribution of the enthalpic term, for example, hydrogen bonding.^[1–3]

Poly(ϵ -caprolactone) is a highly crystalline polymer that is miscible with several amorphous polymers through the hydrogen bonding formation. The miscibility of PCL blends depends on the self-association and inter-association of hydrogen bonding donor polymers. In addition, phenolic resin contains a high density of hydroxyl groups that are able to interact with numerous other polymers

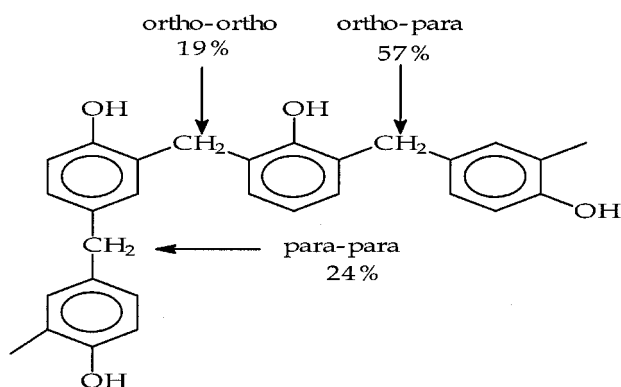
through hydrogen bonding. Therefore, miscible phenolic/PCL blends are expected due to the formation of hydrogen bonding between the phenolic hydroxyl group and the PCL carbonyl group.

Fourier Transform infrared spectroscopy (FTIR) has proved that the stretching of carbonyl and hydroxyl can be an excellent clue to detect molecular interaction.^[4–7] Furthermore, the inter-association equilibrium constant and its related enthalpy can be calculated at various temperatures by FTIR according to the Painter-Coleman Association Model (PCAM).^[8] In this paper, we employ the association parameter of the PCAM to investigate thermodynamic properties of the phenolic/PCL blends and to predict the fraction of hydrogen bonding, free energy and the miscibility window.

Experimental Part

Materials

PCL used in this study is TONE polymer P-787 purchased from Union Carbide Corporation with $\bar{M}_n = 80000$. The phenolic was synthesized with sulfuric acid via a condensation reaction and gave average weights of $\bar{M}_n = 500$ and $\bar{M}_w = 1200$. 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 was determined from the solution ^{13}C NMR spectrum.^[15, 16] The phenolic resin does not contain any reactive methylol group which is capable of causing cross-linking on heating. The chemical structure of phenolic resin is described as follows:



Blend Preparations

Phenolic/PCL blends with various compositions were prepared by solution casting. The tetrahydrofuran 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 d. The resulting film of the blend was then dried at 50°C for additional 2 d to remove the residual solvent.

Differential Scanning Calorimetry (DSC)

Thermal analysis was carried out on a DSC instrument from Du-Pont (DSC-9000) with scan rate of $20^\circ\text{C}/\text{min}$ and temperature range of 30 – 100°C . Approximately 5–10 mg of each blend was weighted and sealed in an aluminium pan. This sample was quickly cooled to -100°C from the melt for the first scan and then scanned between -100 to 150°C at $20^\circ\text{C}/\text{min}$. The glass transition temperature is at the midpoint of the specific heat increment. The DSC was also used to study the isothermal crystallization from the melt at 80°C for 10 min, cooled rapidly to crystallization temperature (T_c) and then maintained at T_c for 12 h. After isothermal crystallization was completed, the sample was cooled at 0°C and heated to 100°C at a rate of $10^\circ\text{C}/\text{min}$ to measure the melting temperature (T_m).

Infrared Spectroscopy

For FTIR analyses, polymer blend films of various compositions were determined by using the conventional NaCl disk method. Samples were prepared by casting the THF solution directly onto a NaCl disk and dried under conditions similar to those used in the bulk preparation. All the films employed in this study are thin enough to obey the Beer-Lambert law. Infrared spectra were recorded on a Nicolet Avatar 320 FT-IR spectrophotometer and 32 scans at a resolution of 1 cm^{-1} were collected. Since the sample contains hydroxyl groups which are water sensitive, a pure nitrogen flow was used to purge the IR optical box in order to maintain sample film dry. A high temperature-controlled cell mounted in the spectrometer was used to obtain spectra at elevated temperature to an accuracy of $\pm 2^\circ\text{C}$.

Results and Discussion

Thermal Analysis

Figure 1 shows the DSC thermograms for pure phenolic, pure PCL and various phenolic/PCL blends. The pure phenolic displays one T_g at 64.62°C and the melting temperature for the pure PCL is at 60.94°C . The T_g of the phenolic shifts to lower temperature as the PCL content in the blend is increased. Meanwhile, the melting temperature of the PCL component in the blend decreases with the increase of the phenolic content. A melting

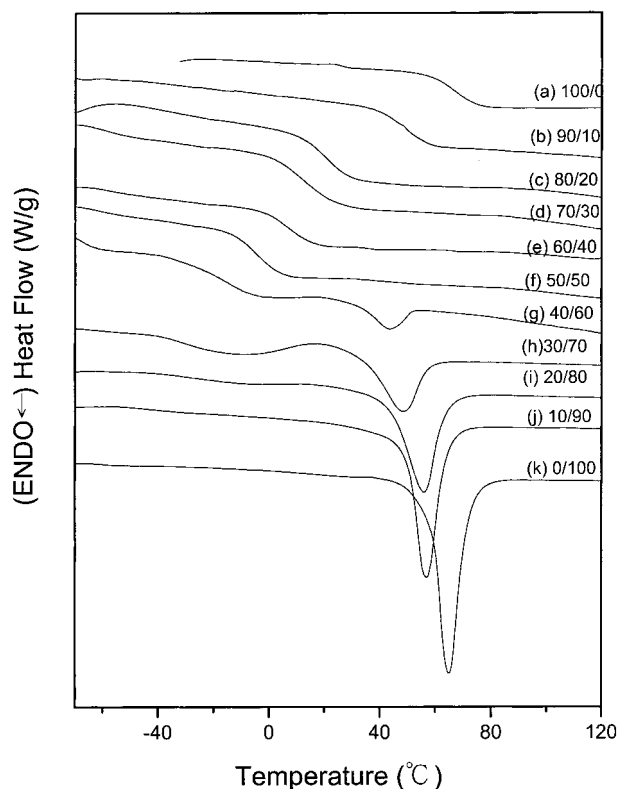
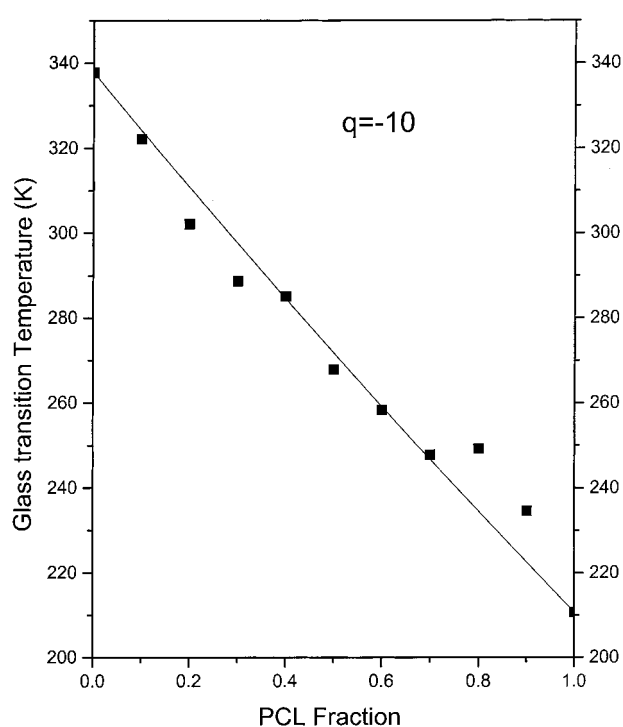


Figure 1. The DSC scans of phenolic/PCL blends with different compositions: (a) 100/0 (b) 90/10 (c) 75/25 (d) 60/40 (e) 50/50 (f) 40/60 (g) 25/75 (h) 10/90 (i) 0/100.

Table 1. Thermal properties of phenolic/PCL blends.

Phenolic/ PCL blend	T_g °C	T_m °C	ΔH_f J/g	T_c °C	ΔH_c J/g
100/0	64.62				
90/10	49.01				
80/20	29.01				
70/30	15.55				
60/40	11.96				
50/50	-5.31				
40/60	-14.74	43.52	3.57	15.59	-6.55
30/70	-25.30	48.87	24.43		
20/80	-23.91	55.95	53.38		
10/90	-38.56	56.99	62.08		
0/100	-62.38	60.94	70.24		

Figure 2. T_g versus composition curves based on: (■) experimental data and (—) Kwei equation.

depression is characteristic of a miscible polymer blend in melting state where thermodynamic equilibrium is achieved under the process. Thermal properties of phenolic, PCL and their blends are summarized in Table 1. All phenolic/PCL blends show only one single glass transition temperature (T_g). A single T_g strongly suggests that these two components are fully miscible in the amorphous phase. The dependence of the T_g on the composition of the miscible phenolic/PCL blends is shown in Figure 2. Different equations have been proposed to correlate T_g with polymer blend miscibility or random copolymer as a function of composition. The most popular equation is the Kwei equation^[9] as follows (Equation (1)):

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

where w_1 and w_2 are weight fractions of the compositions, T_{g1} and T_{g2} represent the corresponding glass transition temperatures, and k and q are fitting constants. The Kwei equation can apply to polymer blends with specific interaction, such as hydrogen bonding in polymer blend system. $k = 1$ and $q = -10$ are obtained from the non-linear least squares "best fit" values. Where q is a parameter corresponding to the strength of hydrogen bonding in the blend, reflecting a balance between the breaking of the self-association and the forming of the inter-association hydrogen bonding. In this study, a negative q of "-10" was calculated, indicating a weaker intermolecular interaction between PCL and phenolic than the self-association of phenolic. As a result, a special interaction must exist between these two polymers to reduce the phenolic intra-hydrogen bonding. The deviation of experimental T_g from the Kwei equation at high PCL content is due to the crystallization of PCL in these blends during quenching. The presence of PCL crystals in this miscible blend is able to act as physical cross-linking points to hinder the molecular mobility of the amorphous phase.

Analyses of Melting Temperature Depression

The depression of the melting point of a crystalline polymer blended with an amorphous polymer can reveal important information on miscibility and polymer-polymer interaction parameter. The morphological effect and thermodynamic reasons cause the melting temperature depression. To eliminate the morphological effect on melting temperature depression, the method of Hoffman and Weeks^[10] has been used to determine the equilibrium melting temperatures for phenolic/PCL blends. Figure 3 displays the Hoffman-Weeks plots to obtain the equilibrium melting temperatures for the pure PCL (T_m^0) and various phenolic/PCL blends (T_{m2}^0). The equilibrium melting temperature of PCL decreases with increasing weight fraction of phenolic due to the decrease in chemical potential by the addition of second component. The data obtained in this study was analyzed by the Nishi-Wang equation^[11] based on the Flory-Huggins theory.^[12] The melting temperature depression is given by Equation (2):

$$T_m^0 - T_{m2}^0 = -T_m^0 \frac{B V_{2u}}{\Delta H_{2u}} \phi_1^2 \quad (2)$$

where $\Delta H_{2u}/V_{2u}$ is the latent heat of fusion of 100% crystalline component per unit volume and B denotes the interaction energy density between blend components, T_m^0 and T_{m2}^0 are the equilibrium melting temperatures of the pure crystallizable component and in the blend, respectively. R is the universal gas constant. Figure 4 shows the melting temperature depression for phenolic/PCL blends increases linearly with the increase of volume fraction of the phenolic components. The weight fraction is con-

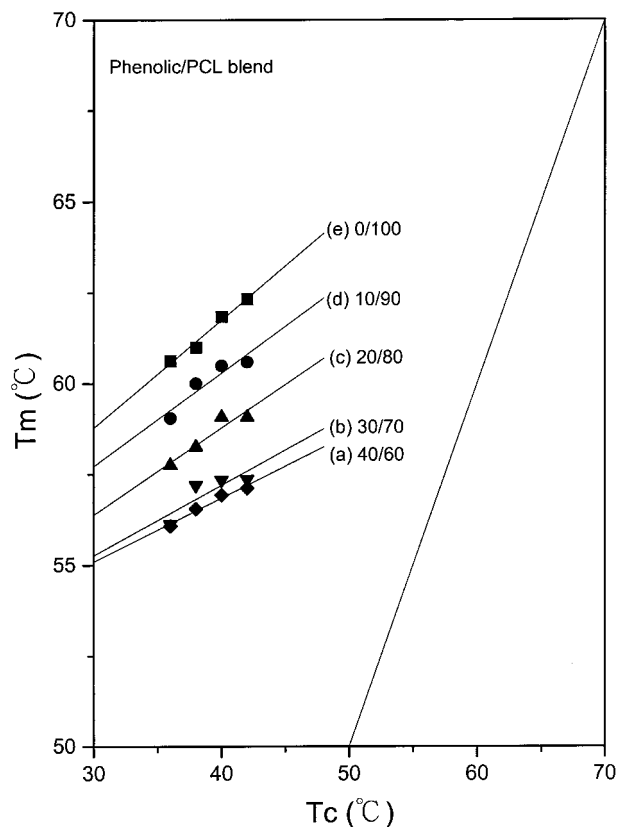


Figure 3. Hoffman-Weeks plots for phenolic/PCL blends: (a) 40/60 (b) 30/70 (c) 20/80 (d) 10/90 (e) 0/100.

verted into the volume fraction using the molar volume of the monomeric unit determined by group contribution method.^[8] Based on Equation (2), values of $V_{2u} = 106.9 \text{ cm}^3/\text{mol}$ ^[8] and $\Delta H_{2u} = 3690 \text{ cal/mol}$ ^[13] were obtained and B value of -12.51 is calculated from the slope in Figure 4. The negative B value is consistent with a miscible blend system.

FTIR Analyses

Infrared spectroscopy has been proven as a powerful tool for investigating specific interaction between polymers and the mechanism of interpolymer miscibility through the formation of hydrogen bonding both qualitatively and quantitatively. The infrared spectra of phenolic/PCL blends recorded at room temperature are rather complicated because the PCL is a semicrystalline polymer. Figure 5 shows infrared spectra of the carbonyl stretching measured at 25°C ranging from 1660 cm^{-1} to 1800 cm^{-1} for phenolic/PCL blends. The carbonyl stretching for the pure PCL is split into two bands, absorption by amorphous and crystalline conformation at 1734 cm^{-1} and 1724 cm^{-1} , respectively. Another contribution at approximately 1708 cm^{-1} is assigned to the PCL carbonyl group that is hydrogen bonded to the phenolic hydroxyl group. The quantitative fraction of hydrogen bonding is difficult

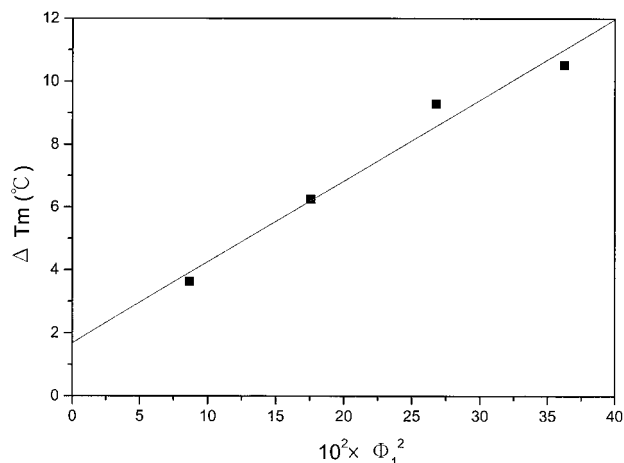


Figure 4. Plots of the equilibrium melting temperature depression versus the square of the volume fraction of phenolic.

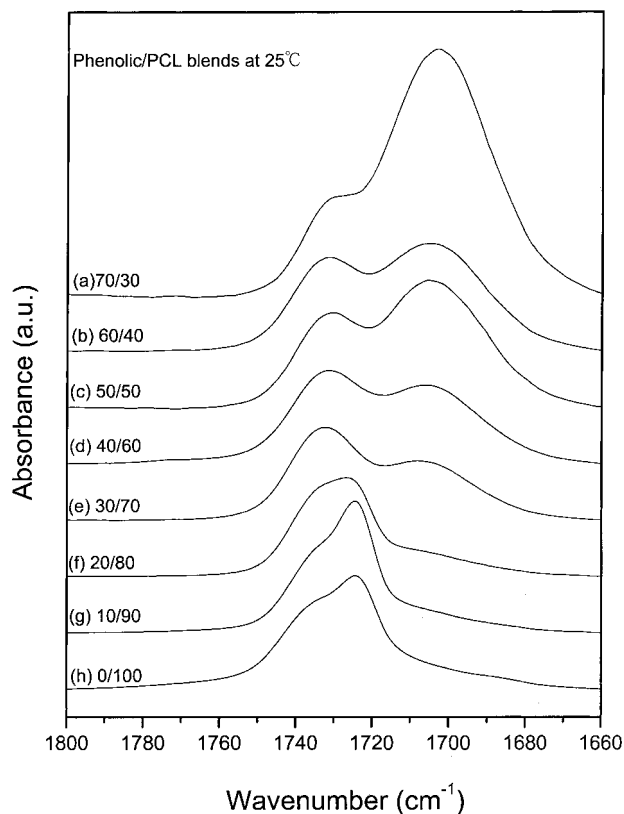


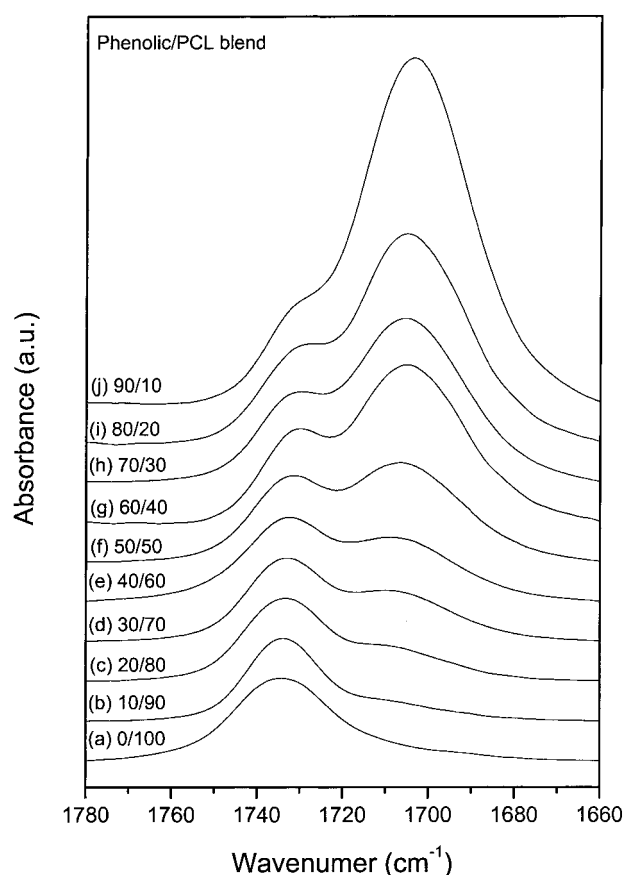
Figure 5. FTIR spectra recorded at room temperature at $1800\text{--}1660 \text{ cm}^{-1}$ region for phenolic/PCL blends: (a) 70/30 (b) 60/40 (c) 50/50 (d) 40/60 (e) 30/70 (f) 20/80 (g) 10/90 (h) 0/100.

to calculate precisely due to the three bands involved in this carbonyl stretching at room temperature.

For convenience, we turn our attention to the carbonyl stretching region of the phenolic/PCL blends at 75°C (above the melting temperature of PCL). Figure 6 shows the infrared spectra of the carbonyl stretching recorded at 75°C ranging from 1660 cm^{-1} to 1800 cm^{-1} for pure PCL and various phenolic/PCL blends. The carbonyl stretch-

Table 2. Curve fitting results of the phenolic/PCL blends at 75 °C.

Phenolic/PCL	Free C=O			H-bonded C=O			$fb^a)$ %
	ν cm^{-1}	$W_{1/2}^b)$ cm^{-1}	A_f %	ν cm^{-1}	$W_{1/2}^b)$ cm^{-1}	A_b %	
90/10	1733.2	13.10	8.80	1703.4	26.01	91.20	87.36
80/20	1733.4	14.49	11.55	1704.3	26.77	88.45	83.63
70/30	1734.0	15.16	15.24	1705.0	27.49	84.76	78.76
60/40	1733.0	13.61	20.33	1704.7	27.09	79.67	72.32
50/50	1734.4	16.62	28.22	1706.1	28.38	71.78	62.91
40/60	1734.4	20.78	28.55	1706.1	27.11	61.45	51.52
30/70	1734.6	17.53	50.46	1708.2	28.20	48.54	38.61
20/80	1734.6	18.30	67.80	1708.9	27.23	32.20	24.05

a) fb : fraction of hydrogen bonding.b) $W_{1/2}$: half-height width.Figure 6. FTIR spectra recorded at 75 °C at 1800–1660 cm^{-1} region for phenolic/PCL blends: (a) 0/100 (b) 10/90 (c) 20/80 (d) 30/70 (e) 40/60 (f) 50/50 (g) 60/40 (h) 70/30 (i) 80/20 (j) 90/10.

ing frequency now splits into only two bands at 1734 cm^{-1} and 1708 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 Equation (3):^[8]

$$f_b^{C=O} = \frac{A_b/1.5}{A_b/1.5 + A_f} \quad (3)$$

A_b and A_f denote peak areas corresponding to the free and the hydrogen bonded carbonyl groups, respectively. The conversion coefficient 1.5 is the ratio of these two bands according to previous infrared studies in similar system.^[8] The results from curve fitting are summarized in Table 2, indicating that the hydrogen bonded fraction of the carbonyl group increases with the increase of the phenolic content.

The hydroxyl-stretching region of the phenolic/PCL blends is also examined. Figure 7 shows the infrared spectra in the 2700 cm^{-1} to 4000 cm^{-1} of pure phenolic, pure PCL and various phenolic/PCL blends measured at 75 °C. The pure phenolic polymer is composed of two hydroxyl components, a very broad band centered at 3400 cm^{-1} is attributed to the wide distribution of the hydrogen bonded hydroxyl group and a relatively narrow band at 3525 cm^{-1} is caused by the free hydroxyl group. Figure 7 also indicates that the intensity of the free hydroxyl group (3525 cm^{-1}) decreases gradually with the increase of PCL content. Meanwhile, the broad hydrogen bonded hydroxyl band of the phenolic shifts into higher frequency with increasing PCL content at 3430 cm^{-1} . This change comes from the switch from the intramolecular hydroxyl-hydroxyl bond to the intermolecular hydroxyl-carbonyl bond, indicating that there is hydrogen-bonding interaction between the PCL carbonyl group and the hydroxyl group of phenolic. The average strength of the intermolecular interaction can be obtained by the extent of frequency difference ($\Delta\nu$) between the hydrogen bonded hydroxyl absorption and free hydroxyl absorption. This observation reveals the average strength of the hydrogen bonding between phenolic hydroxyl and PCL carbonyl. $\Delta\nu = 95 \text{ cm}^{-1}$ is obtained which is weaker than that of the self-associated hydroxyl of the phenolic ($\Delta\nu = 125 \text{ cm}^{-1}$) and this result is consistent with the negative q value obtained in the Kwei equation.

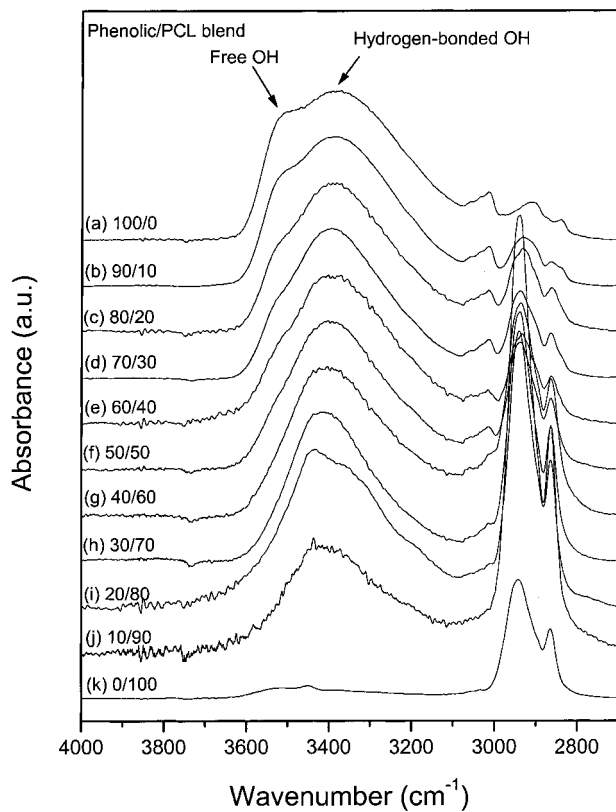
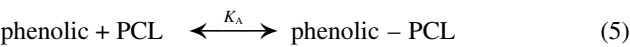
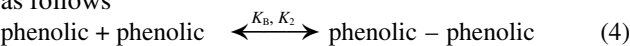


Figure 7. FTIR spectra recorded at 75 °C at 2700–4000 cm⁻¹ region for pure phenolic and various phenolic/PCL blends: (a) 100/0 (b) 90/10 (c) 80/20 (e) 70/30 (f) 60/40 (g) 50/50 (h) 40/60 (i) 30/70 (j) 20/80 (k) 10/90 (l) 0/100.

Estimation of Inter-Association Equilibrium Constant (K_A)

The typical interaction scheme that was considered in the PCAM based on the competing equilibrium is described as follows



where K_2 and K_B represent the hydrogen bonded dimer and multimer of the self-association of phenolic, respectively. The inter-association equilibrium constant K_A

Table 3. Curve fitting fraction of H-bonded carbonyl group of the phenolic/PCL blends at various temperatures.

Phenolic/PCL	75 °C	100 °C	125 °C	150 °C
90/10	87.36	85.70	83.98	81.66
80/20	83.63	82.25	80.35	77.89
70/30	78.76	77.25	75.25	72.89
60/40	72.32	70.47	68.31	65.96
50/50	62.91	61.23	59.13	56.75
40/60	51.52	49.78	47.67	45.98
30/70	38.61	36.53	35.02	34.23
20/80	24.05	23.59	22.56	21.73

reflects the extent of the hydrogen bonding between phenolic and PCL. A set of equilibrium constants, including self-association, inter-association and other thermodynamic properties must be determined in order to accurately predict a phase diagram, fraction of hydrogen bonding and free energy involving specific interactions. According to our previous and Coleman et al. studies,^[8, 14] we consider the equations are approximately

$$\Phi_B = \Phi_{B1} \left[\left(1 - \frac{K_2}{K_B} \right) + \frac{K_2}{K_B} \cdot \left[\frac{1}{(1 - K_B \Phi_{B1})^2} \right] \right] \left[1 + \frac{K_A \Phi_{0A}}{r} \right] \quad (6)$$

$$\Phi_A = \Phi_{0A} + K_A \Phi_{0A} \Phi_{B1} \left[\left(1 - \frac{K_2}{K_B} \right) + \frac{K_2}{K_B} \cdot \left[\frac{1}{(1 - K_B \Phi_{B1})^2} \right] \right] \quad (7)$$

where Φ_A and Φ_B are volume fractions of non-self associated species A and self associated species B, respectively. Φ_{0A} and Φ_{B1} are the corresponding volume fractions of isolated PCL and phenolic segment, respectively. r is the ratio of molar volumes, V_A/V_B . Self-association equilibrium constants, K_B and K_2 , describe the formation of multimers and dimers, respectively. Finally, the K_A is the equilibrium constant describing the association of A with B. In addition, K_B and K_2 are 52.31 and 23.29 at 25 °C of the phenolic,^[15] respectively. Table 3 summarizes the fractions of hydrogen bonded carbonyl group of the PCL at various temperatures and compositions of phenolic/PCL blends. In order to calculate the inter-association constants (K_A), the methodology of a least square method has been widely detailed in our previous and Coleman et al. studies.^[8, 14] The experimental values show excellent agreement with the predicted values for the hydrogen bonded carbonyl at 75 °C as shown in Figure 8. Table 4 lists the self-association and inter-association constants at various temperatures. Therefore, it is possible to calculate the inter-association enthalpy in this temperature range based on the Van't-Hoff expression and can be extended to room temperature. A value of -4.62 kcal/mol

Table 4. Equilibrium constants of hydrogen bond formation for phenolic/PCL blend.

Temperature °C	Phenolic self-association Equilibrium constant K_2	K_B	Inter-association K_A
75	8.59	11.88	38.51
100	5.77	6.57	23.92
125	4.07	3.91	16.44
150	2.99	2.48	11.72

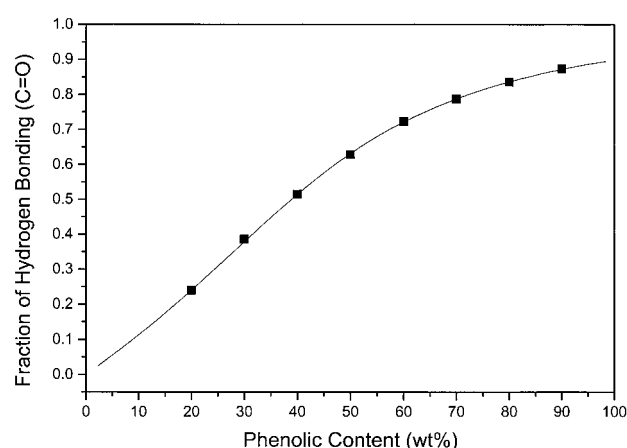


Figure 8. Fraction of the hydrogen-bonded carbonyl group versus composition: (■) FT-IR data and (—) theoretical values from polymer blend calculated at 75 °C.

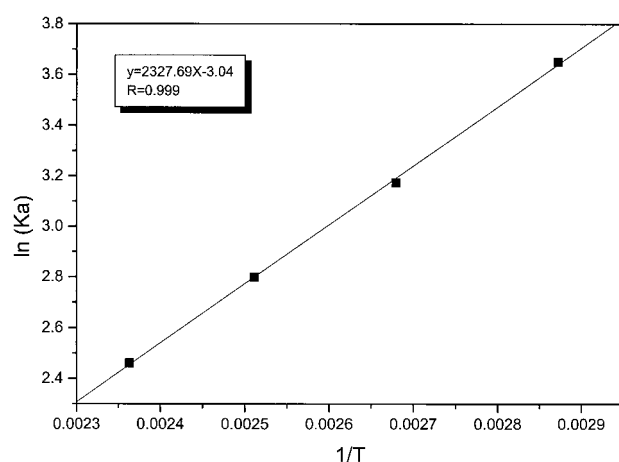


Figure 9. Van't Hoff plot for the determination of the inter-association enthalpy for phenolic/PCL blend.

is obtained from the slope in Figure 9 for the inter-association enthalpy of the phenolic/PCL blend. The inter-association constant of 116.83 was obtained by extrapo-

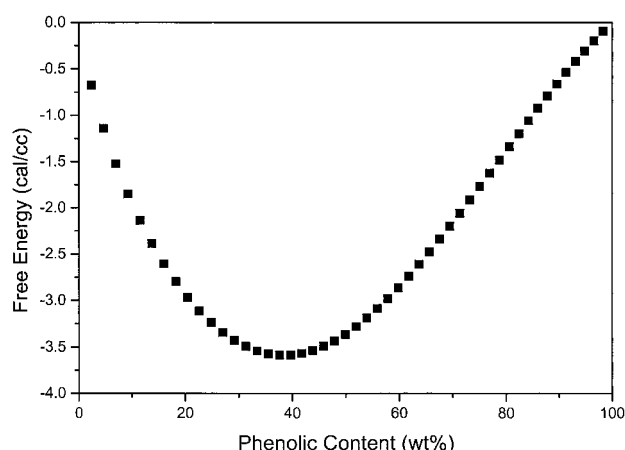


Figure 10. Calculated the free energy of mixing against phenolic/PCL blend composition at 100 °C.

lating to 25 °C from this representation. Table 5 lists all the parameters required by the Painter-Coleman association model to estimate thermodynamic properties for this polymer blend.

Prediction of Free Energy

Figure 10 shows that the predicted free energy at 100 °C is negative for all compositions. The free energy approaches a minimum of -3.5 cal/cc when the phenolic content is around 40 wt.-%. Consequently, we confirm that the phenolic/PCL is miscible due to the negative free energy and the positive second derivative of weight fraction.

Calculation of the Miscibility Window of the Phase Diagram

Figure 11 shows the theoretically predicted miscibility window for phenolic/PCL blends. The x-axis is the weight fraction of phenolic in the blend and the y-axis is

Table 5. Summary of the self-association and inter-association parameters of phenolic/PCL 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 PCL		116.83	−4.62	
Polymer	$\frac{\text{Molar volume}}{\text{ml/mol}}$	$\frac{\text{Molecular weight}}{\text{g/mol}}$	$\frac{\text{Solubility parameter}}{(\text{cal/ml})^{0.5}}$	Degree of Polymerization
Phenolic ^{a)}	84	105	12.05	6
PCL ^{b)}	106.9	114.16	9.21	714

^{a)} See ref.^[15]

^{b)} Estimated by using a group contribution method proposed by Coleman et al.^[8]

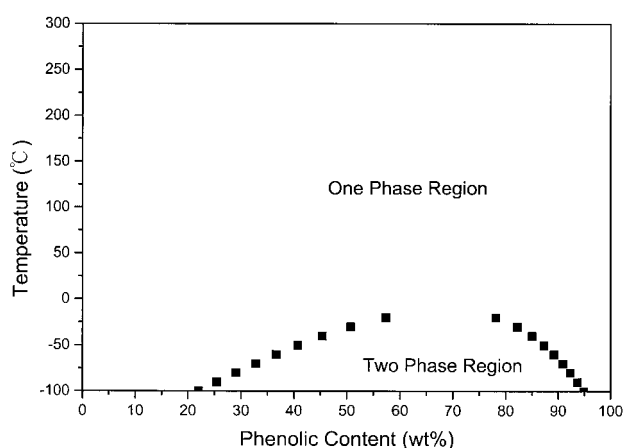


Figure 11. The calculated phase diagram (■) of the phenolic/PCL blend according to PCAM.

the temperature. The theoretical spinodal phase diagram is calculated from -100°C to 300°C . The two phase region are calculated for blends below -25°C which define an area of immiscibility in the phase diagram. This phenomenon indicates that this system are theoretically completely miscible over a temperature range of -25 to 300°C .

Conclusions

The PCL is totally miscible with phenolic in the amorphous phase over entire compositions due to the hydrogen bonding between the phenolic hydroxyl group and the PCL carbonyl group. The Kwei equation can accurately predict T_g 's from the experimental results. FTIR studies provide positive evidence of the hydrogen bonding between the phenolic hydroxyl group and the PCL carbonyl group. In addition, the hydroxyl stretching spectra are able to explain the Kwei equation. Moreover, the inter-association constant based on PCAM can be obtained by employing the fraction of hydrogen bonding with all compositions at various temperatures. The inter-association constant for the phenolic/PCL blend is higher than

the self-association constant, suggesting that the tendency toward hydrogen bonding of the phenolic and PCL dominate the intra-hydrogen bonding of the phenolic resin in the mixture. According to the PCAM, the theoretical phase diagram are miscible over a range of -25 to 300°C based on our experimental blend of composition.

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