

Study of Hydrogen-Bonding Strength in Poly(ϵ -caprolactone) Blends by DSC and FTIR

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ABSTRACT: The hydrogen-bonding strength of poly(ϵ -caprolactone) (PCL) blends with three different well-known hydrogen-bonding donor polymers [i.e., phenolic, poly(vinyl-phenol) (PVPh), and phenoxy] was investigated with differential scanning calorimetry and Fourier transform infrared spectroscopy. All blends exhibited a single glass-transition temperature with differential scanning calorimetry, which is characteristic of a miscible system. The strength of interassociation depended on the hydrogen-bonding donor group in the order phenolic/PCL > PVPh/PCL > phenoxy/PCL, which corresponds to the q value of the Kwei equation. In addition, the interaction energy density parameter calculated from the melting depression of PCL with the Nishi–Wang equation resulted in a similar trend in terms of the hydrogen-bonding strength. Quantitative analyses on the fraction of hydrogen-bonded carbonyl groups in the molten state were made with Fourier transform infrared spectroscopy for all systems, and good correlations between thermal behaviors and infrared results were observed. © 2001 John Wiley & Sons, Inc. *J Polym Sci Part B: Polym Phys* 39: 1348–1359, 2001

Keywords: hydrogen bonding; poly(ϵ -caprolactone) (PCL); phenolic; poly(vinyl-phenol) (PVPh); phenoxy

INTRODUCTION

The miscibility and specific interaction of polymer blends have been topics of intense interest in polymer science because of the strong economic incentives arising from their potential applications. A great number of studies of miscible blends involving crystallizable polymers have been reported.^{1–4} The common component in most crystalline miscible blends is a polyester such as poly(ϵ -caprolactone) (PCL). PCL is a highly crystalline polymer that is miscible with several amorphous polymers through the formation of hydrogen bonding.^{5,6} The miscibility of

PCL blends depends on the self-association and interassociation of hydrogen-bonding donor polymers. In general, the miscibility can be simply analyzed with differential scanning calorimetry (DSC) to determine whether there are one or two glass-transition temperatures (T_g 's) of the blend. A single T_g point is an indication of full miscibility with dimensions of about 20–40 nm. However, an immiscible blend exhibits more than one T_g . Furthermore, the Kwei equation⁷ has been proposed to predict the T_g variation of a miscible blend as a function of composition, which can be interpreted in terms of specific interaction within a polymer blend.

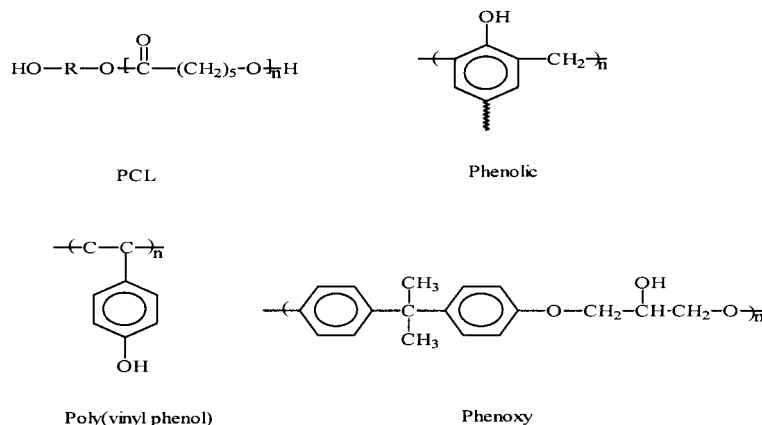
The stretching vibrations of carbonyl and hydroxyl groups have been shown to be an excellent clue to the characterization of the molecular interaction between the carbonyl group of PCL and the hydroxyl group of phenolic, poly(vinyl-phenol)

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(PVPh), and phenoxy by Fourier transform infrared (FTIR) spectroscopy.^{8–10} The average strengths of the intermolecular interactions in all blends were weaker than the corresponding self-association for the homopolymer of phenolic, PVPh, and phenoxy, according to the calculated q values based on the Kwei equation.⁷ From a thermodynamic viewpoint, the strength of the specific interaction in a blend can be described by its interaction energy density parameter B , which can be obtained from the depression in the equilibrium melting point (T_m) based on the Nishi–Wang equation.¹¹

The purpose of this study was to compare the strength of hydrogen bonding in three different hydrogen-bonding donor polymers (i.e., phenolic, PVPh, and phenoxy) and PCL.



Blend Preparation

Blends of phenolic/PCL, PVPh/PCL, and phenoxy/PCL with various compositions were prepared by solution blending. A tetrahydrofuran solution containing a 5 wt % polymer mixture was stirred for 6–8 h, and the solution was allowed to evaporate slowly at room temperature for 1 day. The film of the blend was then dried at 50 °C for 2 days to ensure total elimination of the solvent.

Characterizations

DSC

Thermal analysis was performed with a differential scanning calorimeter from DuPont (DSC-9000) with a scan rate of 20 °C/min and a temperature range of 30–150 °C. Temperature and energy calibrations were carried out with indium. The measurements were made with a 5–10-mg

EXPERIMENTAL

Materials

The PCL used in this study was TONE Polymer P-787; it was purchased from Union Carbide Corp. with a number-average molecular weight (M_n) of 80,000. The phenolic was synthesized with sulfuric acid via a condensation reaction; its M_n was 500, and its weight-average molecular weight (M_w) was 1200. Poly(vinyl phenol) (PVPh) with an M_w of 9000–10,000 was purchased from Poly-Science Inc. (United States). The phenoxy was obtained from Union Carbide with an M_n of 23,000 and an M_w of 48,000. The chemical structures of PCL, phenolic, PVPh, and phenoxy are as follows:

sample on a DSC sample cell after the sample was quickly cooled to -100 °C from the melt of the first scan. The T_g was obtained as the inflection point of the jump heat capacity with a scan rate of 20 °C/min and a temperature range of -100 to 200 °C. DSC also was used to examine the isothermal crystallization from the melt at 80 °C for 10 min; it was cooled quickly to the crystallization temperature (T_c) and then maintained at T_c for 12 h. After isothermal crystallization was completely terminated, the sample was then cooled to 0 °C and heated to 100 °C with a heating rate of 10 °C/min to measure T_m .

Infrared Spectroscopy

Infrared spectroscopic measurements were recorded on a Nicolet Avatar 320 FTIR spectrophotometer, and 32 scans were collected with a spectral resolution of 1 cm^{-1} . Infrared spectra

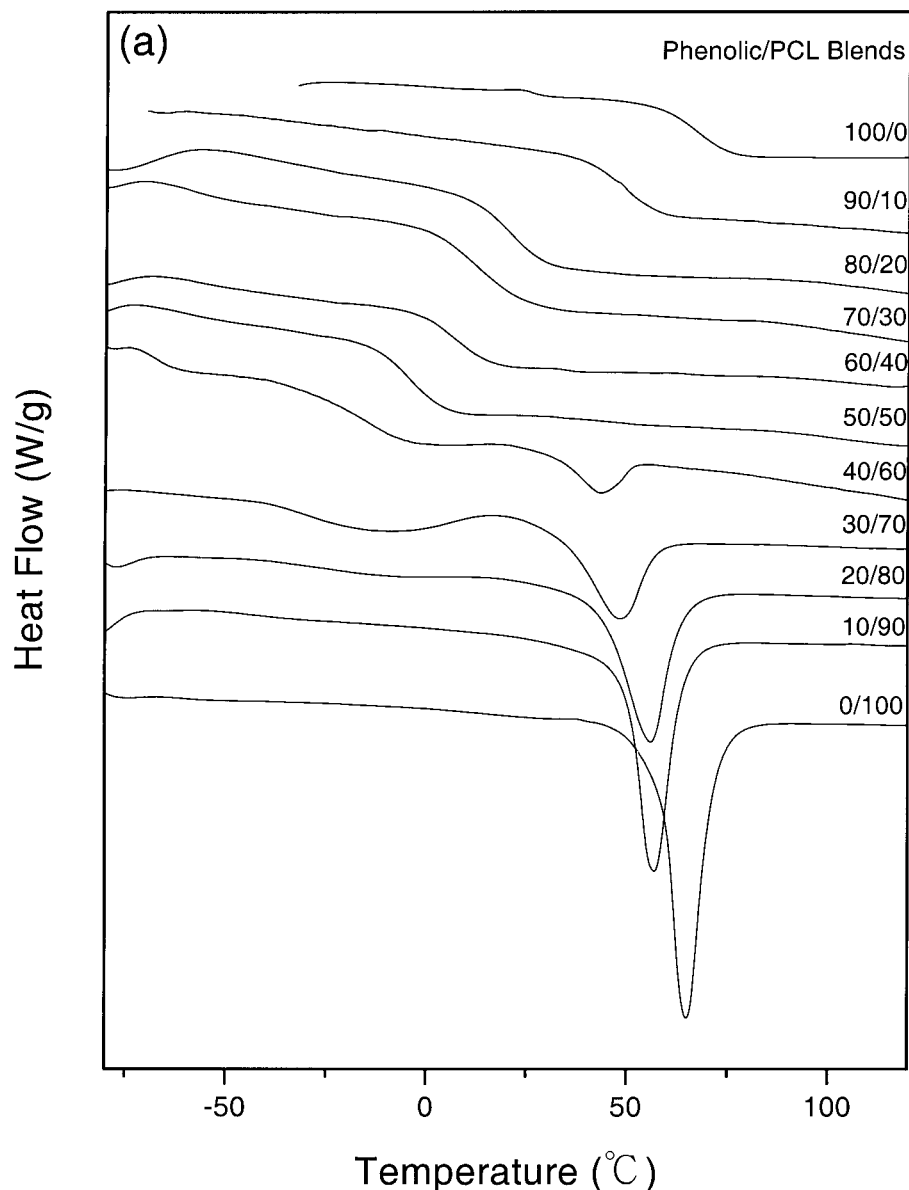


Figure 1. DSC scans of PCL blends with different compositions: (a) phenolic/PCL, (b) PVPh/PCL, and (c) phenoxy/PCL.

of polymer blend films were determined with the conventional NaCl disk method. The tetrahydrofuran solution containing the blend was cast onto a 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. Infrared spectra recorded at elevated temperatures were obtained with a cell mounted inside the temperature-controlled compartment of the spectrometer.

RESULTS AND DISCUSSION

T_g Analyses

Figure 1 displays the DSC thermograms of PCL blended with phenolic, PVPh, and phenoxy as a function of composition. The pure amorphous phenolic, PVPh, and phenoxy display one T_g at 64.6, 147.8, and 98.4 °C, respectively. T_g 's of these hydrogen-bonding donor polymers shift to lower temperatures with increasing PCL content in these blends. Meanwhile, the T_m of PCL also

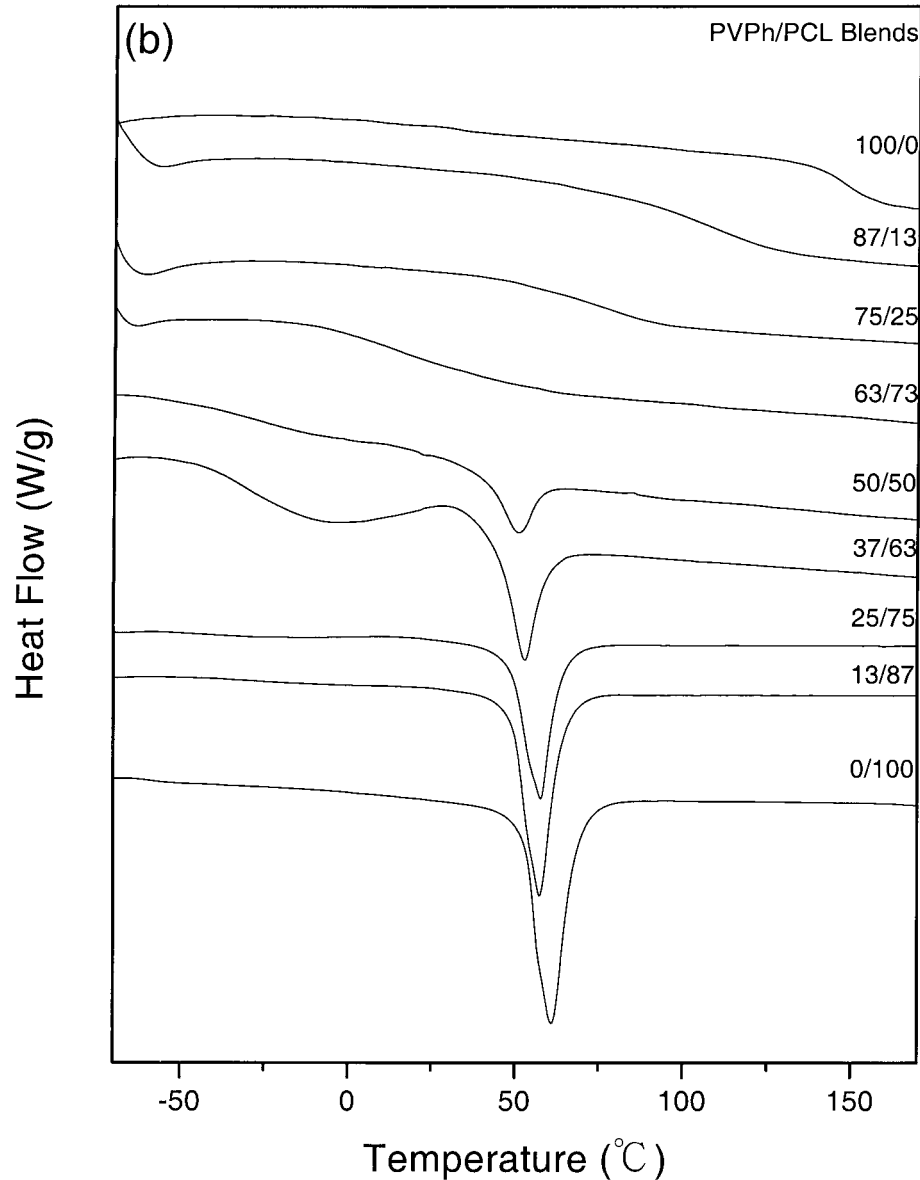


Figure 1. (Continued from the previous page)

shifts gradually to lower temperatures with an increasing content of the hydrogen-bonding donor polymer. A T_m depression is characteristic of a miscible polymer blend in the melting state; the thermodynamic equilibrium is achieved during this process. In addition, all these blends exhibit a single T_g , as shown in Figure 1, over the entire blend compositions, indicating that these blends are fully miscible in the amorphous region. The dependence of T_g on the composition of these blends is shown in Figure 2; it can be fitted well to the Kwei equation:

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

where W_1 and W_2 are weight fractions of the compositions, T_{g1} and T_{g2} represent the component T_g , and k and q are fitting constants. The Kwei equation can apply to polymer blends with specific interactions, such as hydrogen bonding in a polymer blend system. q is a parameter corresponding to the strength of hydrogen bonding, reflecting the balance between breaking the intra-hydrogen bonding and forming the interhydrogen

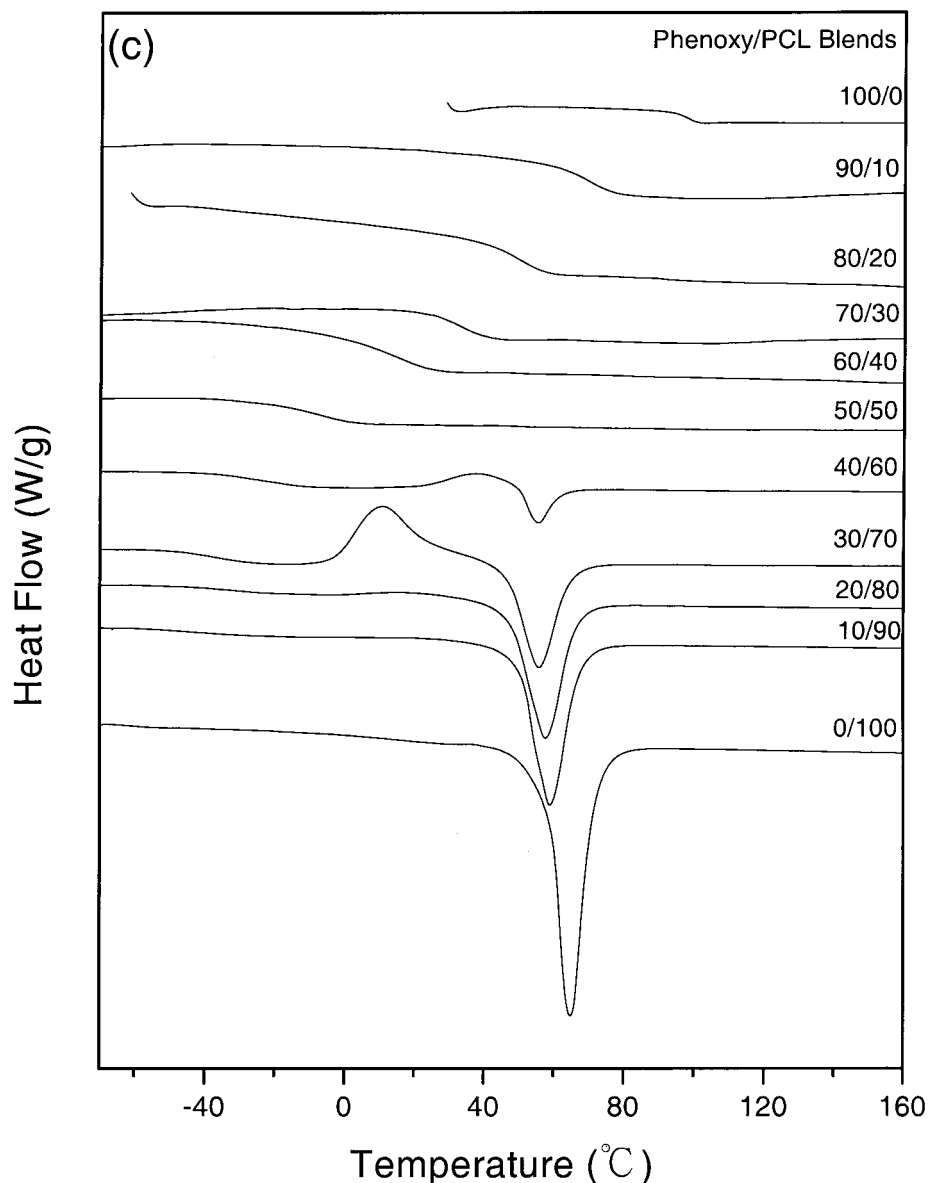


Figure 1. (Continued from the previous page)

bonding. The q value of the blend should depend on an entropy change corresponding to the change in the number of hydrogen-bonding interactions with PCL. Figure 2 shows $q = -10$ and $k = 1$ for the phenolic/PCL blend, $q = -85$ and $k = 1$ for the PVPh/PCL blend, and $q = -100$ and $k = 1$ for the phenoxy/PCL blend. All these q values are negative, indicating that the fraction of the self-associated hydrogen bonding of these donor polymers is broken to form weaker interassociated hydrogen bonding. According to the q values experimentally obtained during this study, the relative hydrogen-bonding strength is in the order phenolic/PCL > PVPh/PCL > phenoxy/PCL.

Analyses of T_m Depression

The depression of T_m of a crystalline polymer blended with an amorphous polymer can reveal important information about the miscibility and polymer-polymer interaction parameter. The T_m of a miscible polymer blend is depressed because of the morphological effect and thermodynamic reasons. To eliminate the morphological effect from the T_m depression, the equilibrium temperatures for pure PCL (T_m^0) and blends (T_{m2}^0) of given compositions can be obtained from Hoffman-Weeks plots.¹² Figure 3 shows the Hoffman-Weeks plots in which T_{m2}^0 values are plotted

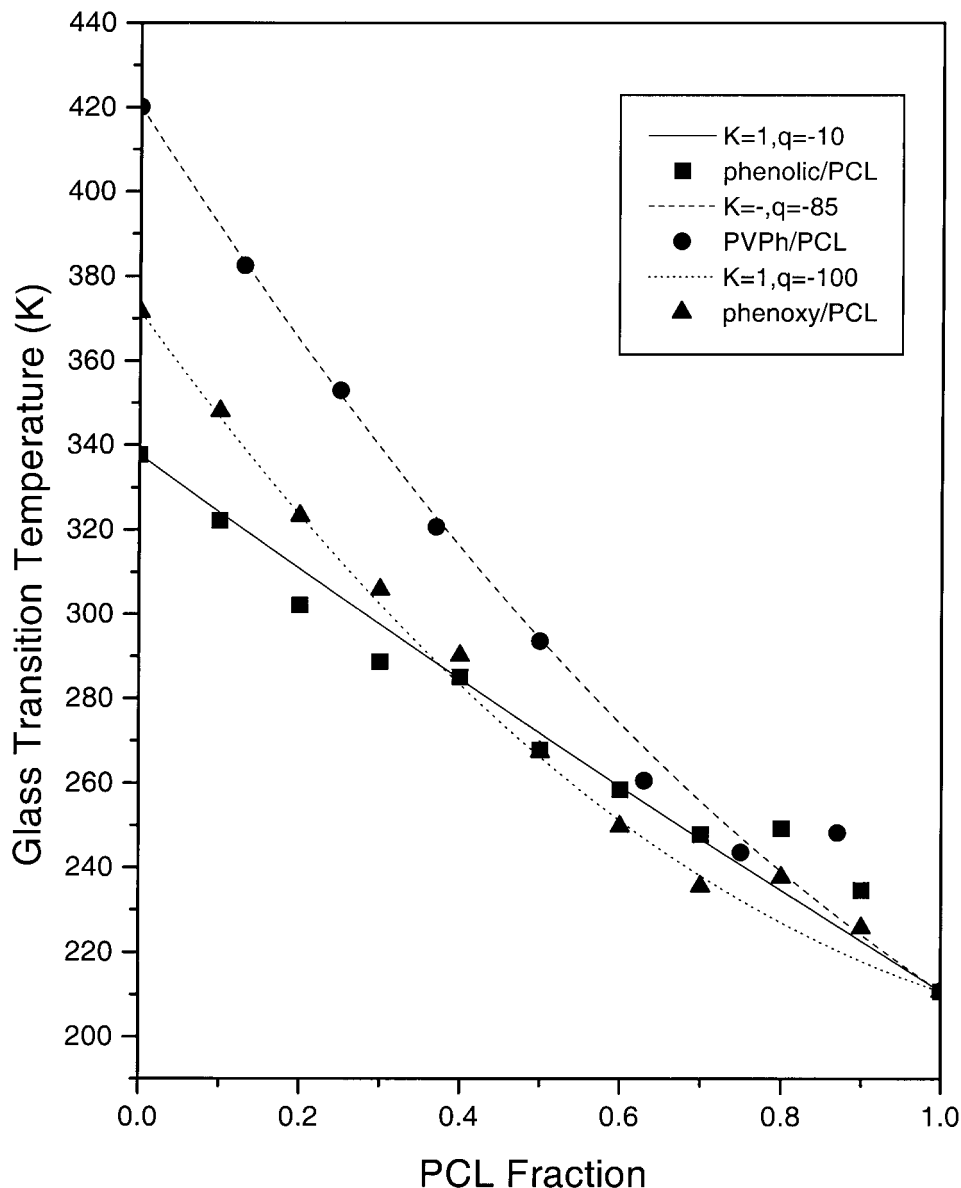


Figure 2. Experimental and theoretical predictions of T_g versus blend compositions for (a) phenolic/PCL, (b) PVPh/PCL, and (c) phenoxy/PCL.

as a function of T_c and extrapolated to obtain the equilibrium T_m 's for pure PCL and phenolic/PCL blends. The equilibrium T_m 's and volume fraction of phenolic, PVPh, and phenoxy are shown in Table I, indicating that the T_{m2}^0 values decrease with increasing phenolic, PVPh, and phenoxy contents. Generally, an immiscible or partially miscible blend typically does not show the depression of T_{m2}^0 , but T_{m2}^0 is depressed significantly with the increasing content of the amorphous polymer for a miscible blend, especially if the blend possesses a specific interaction between the components.

These results are consistent with the previously obtained T_g behavior.

The data obtained in this study were analyzed with the Nishi–Wang equation,¹¹ which is based on the Flory–Huggins theory.¹³ The T_m depression is derived as follows:

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

where $\Delta H_{2u}/V_{2u}$ is the latent heat of fusion of the 100% crystalline component per unit volume, B

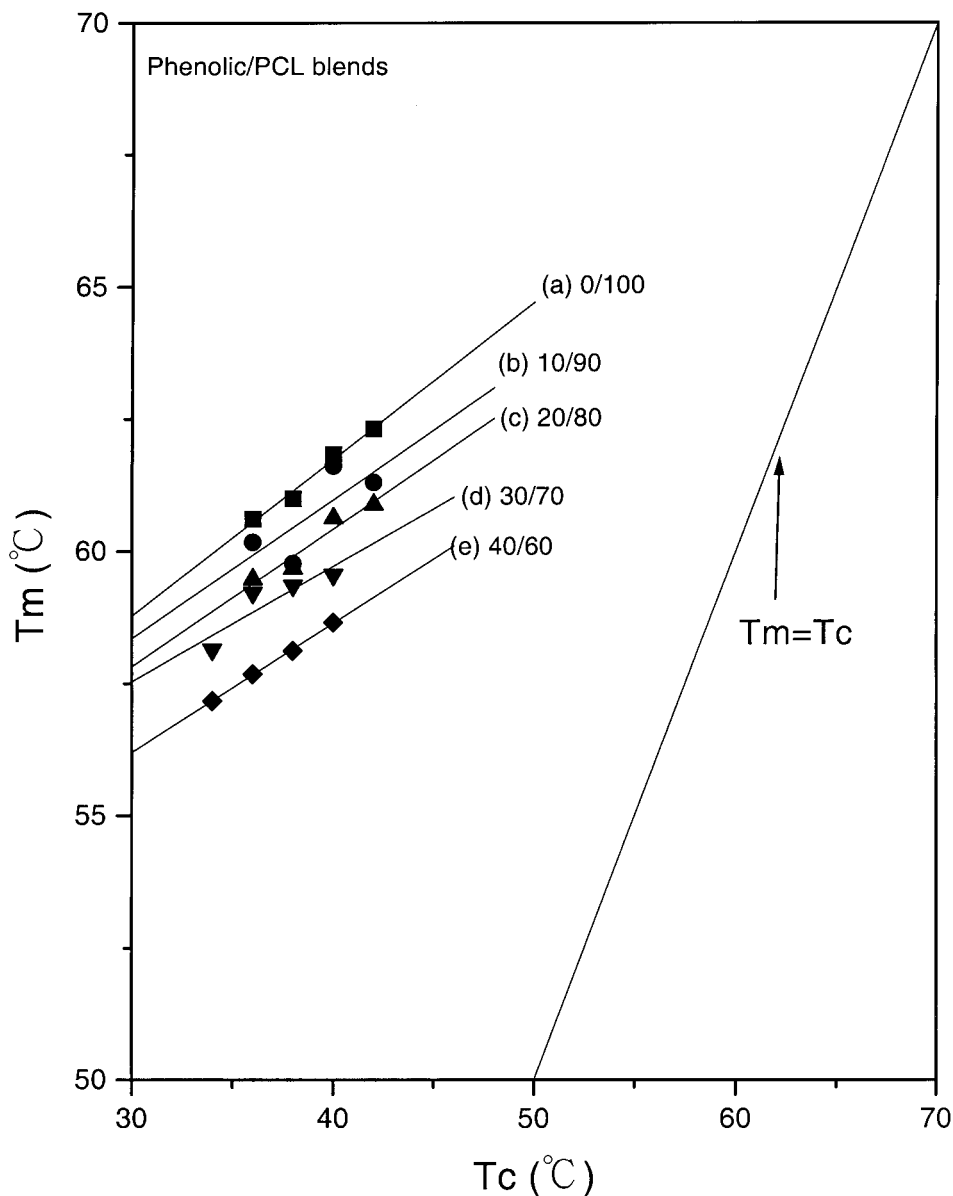


Figure 3. Hoffman-Weeks plots for phenolic/PCL.

denotes the interaction energy density between blend components, and Φ_1 is the volume fraction of the amorphous component. Figure 4 shows that the T_m depressions (ΔT_m) for phenolic/PCL, PVPh/PCL, and phenoxy/PCL blends increase linearly with Φ_1^2 . These weight fractions were converted into volume fractions, with the molar volume of monomeric units determined by the group contribution method.¹⁴ With eq 2, $V_{2u} = 106.9 \text{ cm}^3/\text{mol}$,¹⁴ and $\Delta H_{2u} = 3690 \text{ cal/mol}$,⁶ B values were calculated from slopes shown in Figure 4. The calculated B values are as follows:

$$B = -12.51 \text{ cal/cm}^3 \text{ for phenolic/PCL}$$

$$B = -9.82 \text{ cal/cm}^3 \text{ for PVPh/PCL}$$

$$B = -7.55 \text{ cal/cm}^3 \text{ for phenoxy/PCL}$$

The negative B values from these three systems provide the evidence that these systems are miscible in the melt. This result is consistent with the result of the glass-transition behavior. According to the q and B values of these three blend systems, the corresponding hydrogen-bonding strengths can be measured. Therefore, we can conclude that the relative strength of hydrogen bonding of the three hydrogen-bonding donor

Table I. Equilibrium T_m 's for PCL Blended with Phenolic, PVPh, and Phenoxy with Different Values of Φ_1

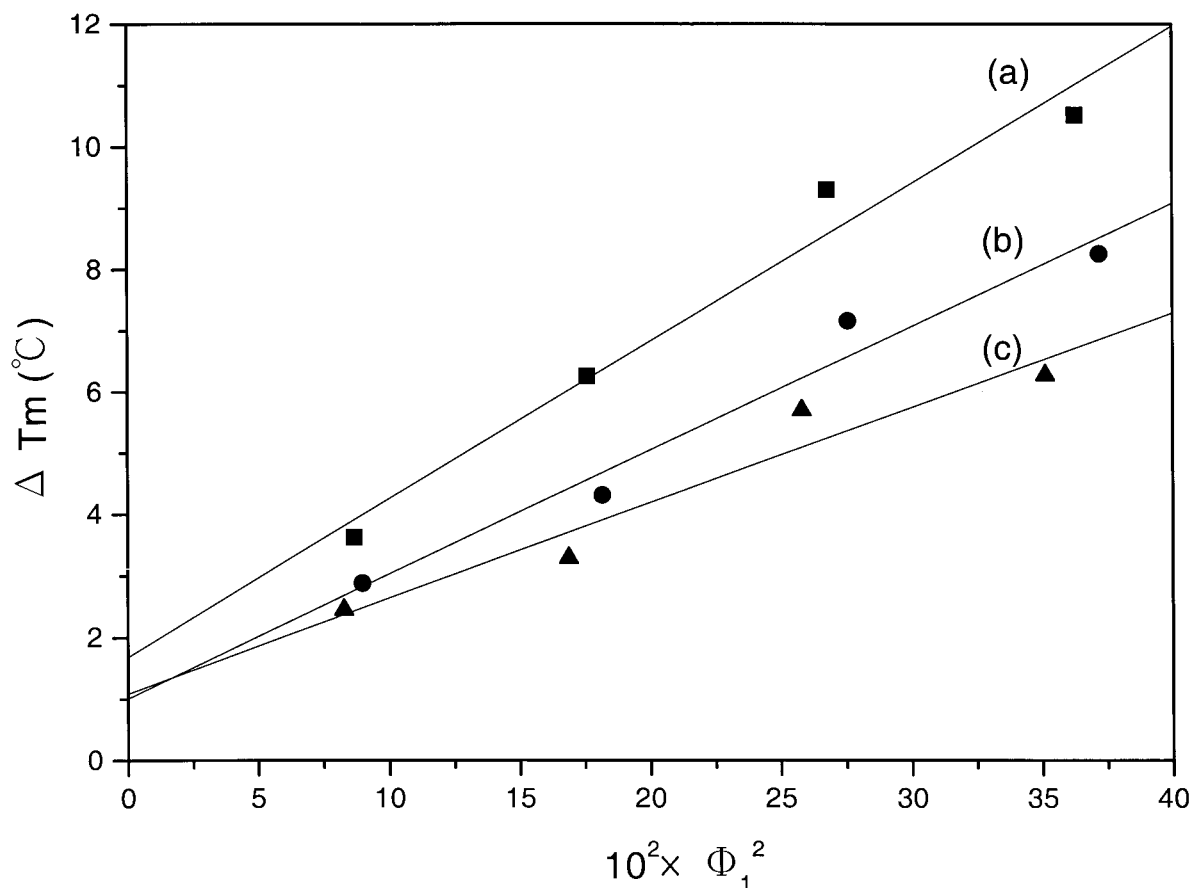
Blend	Phenolic		PVPh		Phenoxy	
	Φ_1	T_{m2} (°C)	Φ_1	T_{m2} (°C)	Φ_1	T_{m2} (°C)
0/100	0	70.9	0	70.9	0	70.9
10/90	0.086	67.3	0.089	68.1	0.082	68.5
20/80	0.175	64.6	0.181	66.6	0.168	67.6
30/70	0.267	61.6	0.275	63.2	0.258	65.2
40/60	0.362	60.4	0.371	62.7	0.351	64.7

polymers with PCL is in the order phenolic > PVPh > phenoxy.

FTIR Analyses

Infrared spectroscopy is able to provide positive information on specific interactions between polymers, both qualitatively and quantitatively. The hydroxyl-stretching range in the infrared spec-

trum is sensitive to the hydrogen-bonding formation. Figure 5 illustrates the infrared spectra in the range 2700–4000 cm^{-1} of phenolic/PCL, PVPh/PCL, and phenoxy/PCL blends measured at 75 °C. Pure phenolic, PVPh, and phenoxy show two distinct bands in the hydroxyl-stretching region of the infrared spectra. A very broad band centered at 3400, 3375, and 3420 cm^{-1} can be attributed to the wide distribution of the hydro-


Figure 4. Plots of the equilibrium T_m depression versus the square of the volume of the fraction of (a) phenolic, (b) PVPh, and (c) phenoxy.

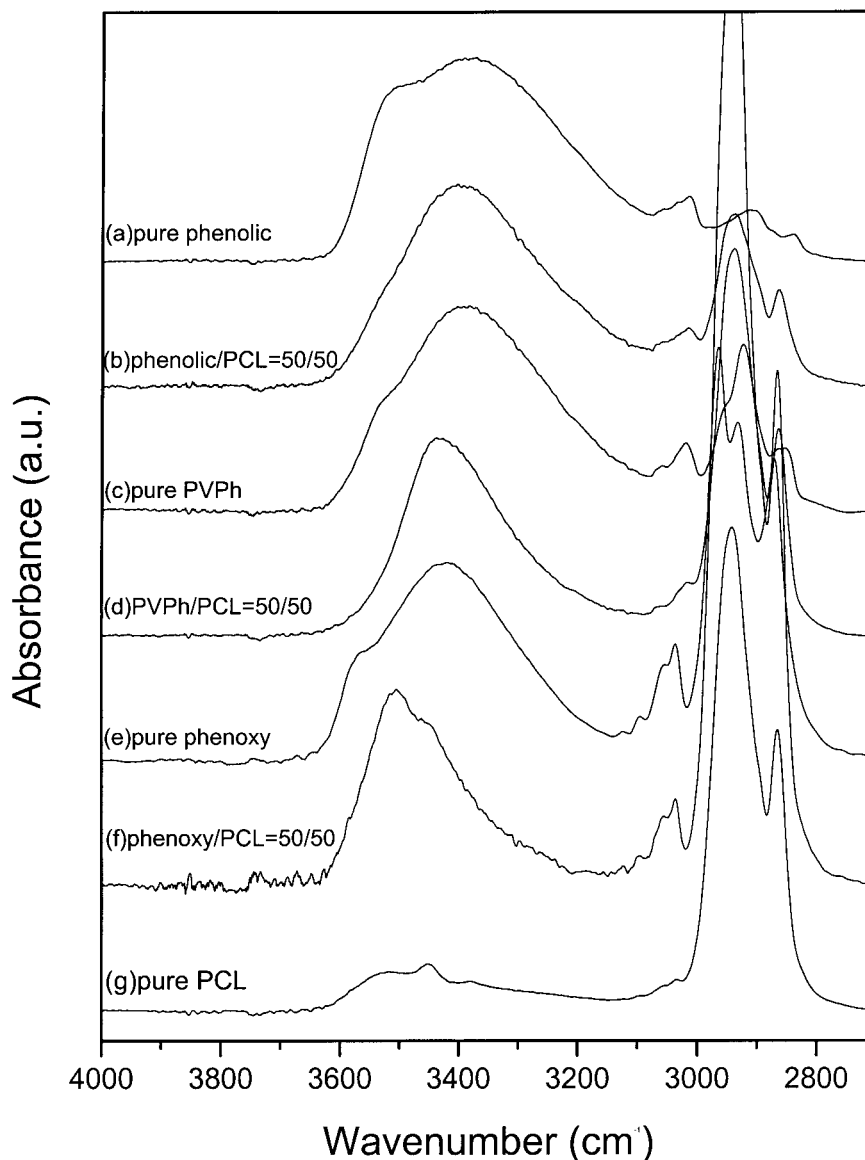


Figure 5. FTIR spectra recorded at 75 °C in the 2700–4000-cm⁻¹ region for phenolic/PCL blends: (a) pure phenolic, (b) 50/0 phenolic/PCL, (c) pure PVPh, (d) 50/50 PVPh/PCL, (e) pure phenoxy, (f) 50/50 phenoxy/PCL, and (g) pure PCL.

gen-bonded hydroxyl group, and a sharp band at 3525, 3525, and 3570 cm⁻¹ is caused by the free hydroxyl group for pure phenolic, PVPh, and phenoxy, respectively. The intensity of the free hydroxyl group decreases with the increasing PCL content, as would be expected. Meanwhile, this broad hydrogen-bonded hydroxyl band shifts to a higher frequency with increasing PCL content (50 wt %) at 3430, 3440, and 3525 cm⁻¹ for phenolic, PVPh, and phenoxy, respectively. All these observed changes result from switching from the strong intramolecular hydroxyl–hydroxyl bond to

the weak intermolecular hydroxyl–carbonyl bond. Coleman et al.¹⁰ used the frequency difference ($\Delta\nu$) between the hydrogen-bonded hydroxyl absorption and free hydroxyl absorption to investigate the average strength of the intermolecular interaction. In this study, the average strength of the hydrogen bonding between the carbonyl group of PCL and the hydroxyl group of the three hydroxyl-containing polymers are in the order phenolic/PCL ($\Delta\nu = 95$ cm⁻¹) > PVPh/PCL ($\Delta\nu = 85$ cm⁻¹) > phenoxy/PCL ($\Delta\nu = 45$ cm⁻¹). In addition, $\Delta\nu$ between the interassociation hydrogen-

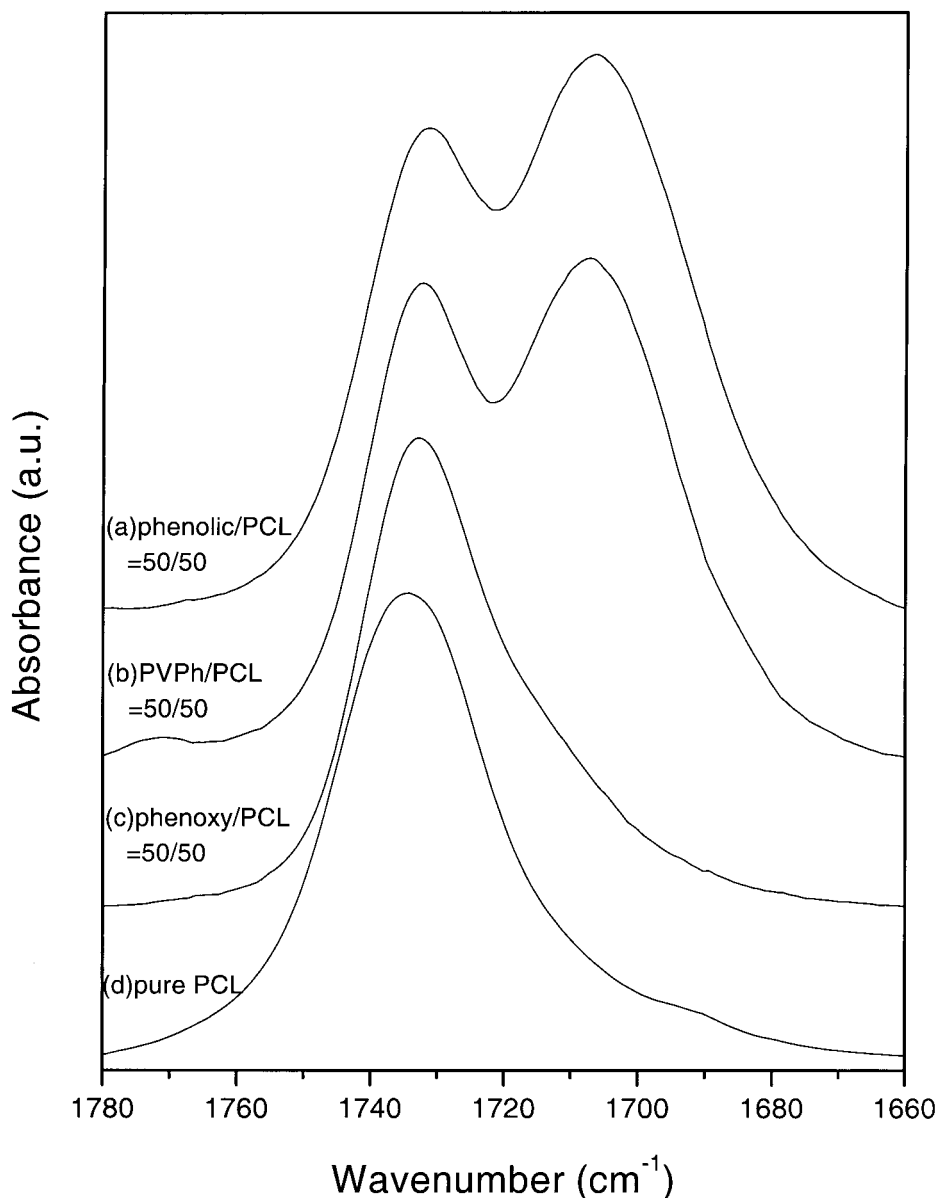


Figure 6. FTIR spectra recorded at 75 °C in the 1780–1660- cm^{-1} region for phenolic blends: (a) 50/50 phenolic/PCL, (b) 50/50 PVPh/PCL, (c) 50/50 phenoxy/PCL, and (d) pure PCL.

bonding absorption of the hydroxyl–carbonyl group and the self-association hydrogen-bonding absorption of hydroxyl–hydroxyl group is -30 , -65 , and -105 cm^{-1} for phenolic/PCL, PVPh/PCL, and phenoxy/PCL blends, respectively. All these negative values indicate that the hydroxyl–carbonyl interassociation is relatively weaker than the self-association of hydroxyl–hydroxyl. These results are consistent with the negative q values obtained with the Kwei equation.

Besides the hydroxyl-stretching region, the carbonyl stretching is also sensitive to hydrogen-

bonding formation. As a result, we now focus on the carbonyl-stretching region. According to our previous study,¹⁵ the carbonyl stretching in infrared spectra of PCL blends recorded at room temperature is rather complicated because PCL is a semicrystalline polymer. Therefore, we conducted FTIR measurements at 75 °C (above the PCL T_m) to avoid complications caused by PCL crystallization. Figure 6 shows the infrared spectra of the carbonyl stretching recorded at 75 °C ranging from 1660 to 1800 cm^{-1} for pure PCL and 50/50 phenolic/PCL, 50/50 PVPh/PCL, and 50/50 phe-

Table II. Fraction of the Hydrogen-Bonded Carbonyl Group for PCL Blended with Phenolic, PVPh, and Phenoxy with Different Compositions at 75 °C

Phenolic/ PCL	Free C=O			Hydrogen-Bonded C=O			
	ν (cm ⁻¹)	$W_{1/2}$ (cm ⁻¹)	A_f (%)	ν (cm ⁻¹)	$W_{1/2}$ (cm ⁻¹)	A_b (%)	f_b (%)
90/10	1733.2	13.1	8.8	1703.4	26.0	91.2	87.3
80/20	1733.4	14.4	11.5	1704.3	26.7	88.5	83.6
70/30	1734.0	15.1	15.2	1705.0	27.4	84.8	78.7
60/40	1733.0	13.6	20.3	1704.7	27.0	79.7	72.3
50/50	1734.4	16.6	28.2	1706.1	28.3	71.8	62.9
40/60	1734.4	20.7	28.5	1706.1	27.1	61.5	51.5
30/70	1734.6	17.5	50.4	1708.2	28.2	48.6	38.6
20/80	1734.6	18.3	67.8	1708.9	27.2	32.2	24.1

PVPh/ PCL	Free C=O			Hydrogen-Bonded C=O			
	ν (cm ⁻¹)	$W_{1/2}$ (cm ⁻¹)	A_f (%)	ν (cm ⁻¹)	$W_{1/2}$ (cm ⁻¹)	A_b (%)	f_b (%)
87/13	1734.5	14.3	15.1	1704.8	26.4	84.9	78.9
75/25	1733.9	15.1	21.3	1706.9	22.5	78.7	71.0
63/37	1734.4	14.7	30.0	1707.3	24.9	70.0	60.8
50/50	1734.4	15.4	39.1	1707.1	26.5	60.9	50.9
40/60	1735.2	18.6	47.4	1709.0	26.8	52.6	42.5
30/70	1735.6	20.1	56.8	1708.2	27.5	43.2	33.6
20/80	1735.2	20.8	71.6	1707.1	27.0	28.4	20.9

Phenoxy/ PCL	Free C=O			Hydrogen-Bonded C=O			
	ν (cm ⁻¹)	$W_{1/2}$ (cm ⁻¹)	A_f (%)	ν (cm ⁻¹)	$W_{1/2}$ (cm ⁻¹)	A_b (%)	f_b (%)
90/10	1734.1	21.0	61.5	1715.1	30.1	38.5	29.4
80/20	1734.2	20.5	66.0	1715.0	30.1	34.0	25.5
70/30	1734.6	19.6	71.0	1715.1	29.4	29.0	21.4
60/40	1734.5	19.7	75.1	1715.2	28.8	24.9	18.1
50/50	1735.1	19.7	78.3	1715.1	28.8	21.7	15.6
40/60	1735.0	20.4	82.3	1715.1	28.0	17.7	12.5
30/70	1734.9	19.7	85.8	1715.2	28.0	14.2	9.9
20/80	1734.8	21.0	88.6	1715.2	28.1	11.4	7.9

noxy/PCL blends. All these carbonyl-stretching frequencies split into two bands, which can be fitted well to the Gaussian function. Absorption at 1734 cm⁻¹ corresponds to the free carbonyl group, whereas the hydrogen-bonded carbonyl group is at 1705, 1706, and 1715 cm⁻¹, corresponding to phenolic, PVPh, and phenoxy, respectively. The fraction of the hydrogen-bonded carbonyl group can be calculated with the following equation:¹⁴

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

A_f and A_b are peak areas corresponding to the free and hydrogen-bonded carbonyl groups, respec-

tively. The conversion coefficient 1.5 is the ratio of these two bands, the free and hydrogen-bonded carbonyl groups, in an ester group.¹⁴ Results from curve fitting are summarized in Table II, indicating that the hydrogen-bonded fraction of the carbonyl group increases with the increasing content of these hydrogen-bonding donor polymers. Figure 7 shows the hydrogen-bonded fraction of the carbonyl group versus the PCL content with phenolic, PVPh, and phenoxy, indicating that the phenolic/PCL blend has a greater fraction of hydrogen-bonding formation. This result is also consistent with the B values based on the Nishi-Wang equation and q values from the Kwei equation.

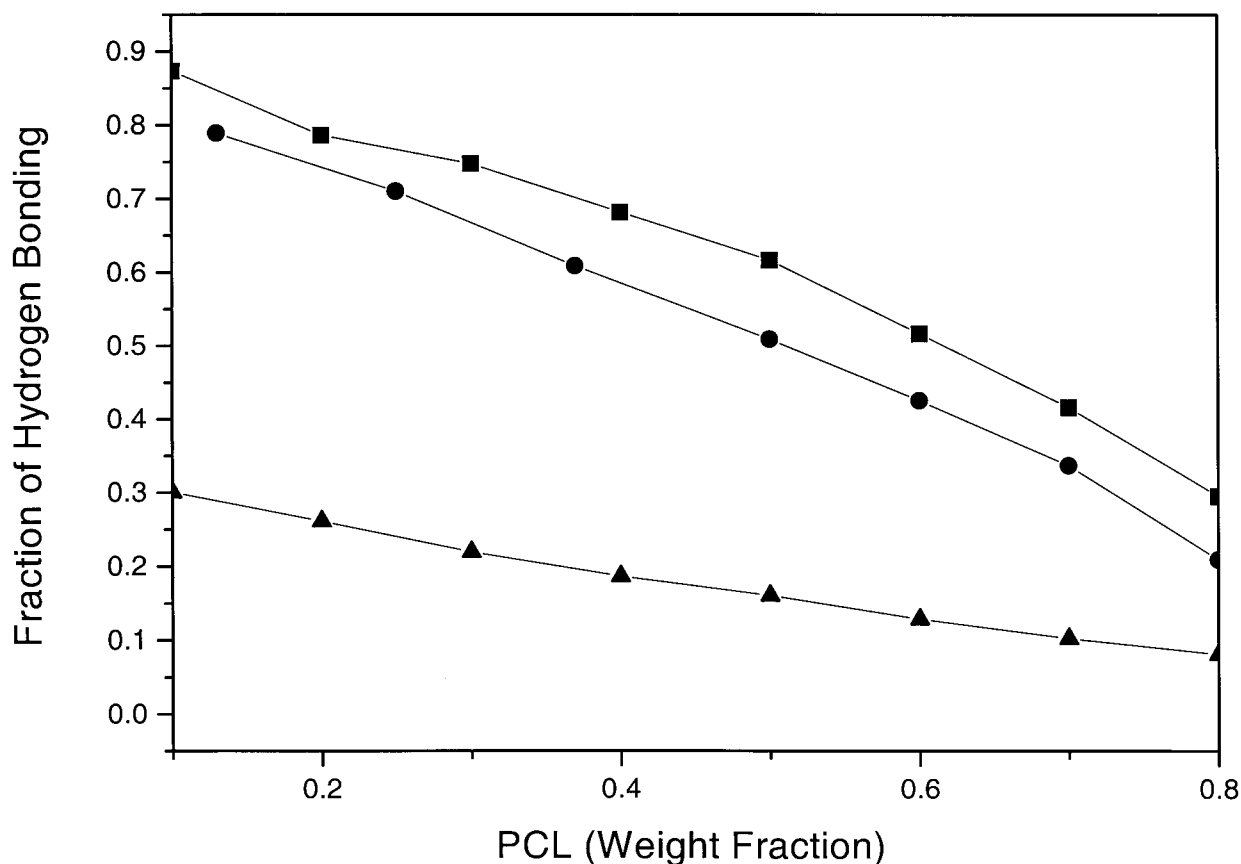


Figure 7. Relation of the hydrogen-bonded fraction of the carbonyl group within various PCL blend systems: (■) phenolic/PCL, (●) PVPh/PCL, and (▲) phenoxy/PCL.

CONCLUSIONS

PCL is fully miscible with phenolic, PVPh, and phenoxy in the amorphous phase over entire compositions by DSC because of hydrogen-bonding formation between the hydroxyl group and the PCL carbonyl group. The Kwei equation can accurately predict T_g 's according to the experimental results, and the strengths of hydrogen bonding were in the order phenolic > PVPh > phenoxy. FTIR studies provide positive evidence of hydrogen bonding between the hydroxyl group from these hydrogen-bonding donor polymers and the PCL carbonyl group. FTIR also gives the relative strengths of hydrogen bonding for these three hydroxyl-containing polymers in the order phenolic > PVPh > phenoxy.

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