An Unusual, Completely Miscible, Ternary Hydrogen-Bonded Polymer Blend of Phenoxy, Phenolic, and PCL

Shiao-Wei Kuo,* Shih-Chi Chan, Hew-Der Wu, and Feng-Chih Chang

Institute of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan

Received December 21, 2004; Revised Manuscript Received March 17, 2005

ABSTRACT: We have investigated the miscibility and hydrogen-bonding behavior of ternary blends of phenoxy, phenolic, and poly(ϵ-caprolactone) (PCL) by using differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy. On the basis of DSC analyses, we observed a rare totally miscible ternary hydrogen-bonded polymer blend in the amorphous phase: all compositions of this ternary blend display a single glass transition temperature. In addition, these single glass transition temperatures can be predicted well by extending the Kwei equation from the binary polymer blend to this ternary polymer blend. The infrared spectra indicate that the intermolecular hydrogen bonding of each pair of binary components still exists in the ternary polymer blend. We used the ternary totally miscible blend to determine the interassociation equilibrium constant between the hydroxyl groups of phenolic and the hydroxyl groups of phenoxy indirectly from the fraction of hydrogen-bonded carbonyl groups of PCL. Quantitative analyses suggest that interassociation between the hydroxyl groups of phenolic and the hydroxyl groups of phenoxy is more favorable than the hydroxyl–carbonyl interassociations of either phenolic/PCL or phenoxy/PCL and the hydroxyl–hydroxyl self-association of the pure phenolic and phenoxy homopolymers at room temperature.

Introduction

Polymer blending is a convenient and attractive route for obtaining new polymeric materials, and there is considerable interest in the phenomenon of miscibility in binary polymer blends.[1–3] In contrast, ternary polymer blends have received relatively less attention because of the complexity of calculating their phase diagrams and the problems associated with experimental accuracy. Although increasing the number of polymer components does indeed lead to complications, there are several good reasons for studying the phase behavior of ternary polymer blends, especially because of their significant industrial importance. For example, Scott[4] and Tompa[5] reported ternary polymer blends in which a polymer B, miscible with each of polymers A and C, compatibilizes the immiscible binary pair A–C. Classical examples of this system include the ternary blends of poly(vinylidene fluoride) (PVDF)/poly(methyl methacrylate) (PMMA)/poly(ethyl methacrylate) (PEMA),[6] PVPh/PMMA/PEMA,[7] and SAN/PMMA/PEMA.[8] When all three binary pairs (B–A, B–C, and A–C) are individually miscible, a completely homogeneous or a closed immiscibility loop phase diagram may exist.[9] The phase separation is caused by differences in the solubility parameters and interassociation equilibrium constants of the binary systems, the so-called "$\Delta\chi$"[10] and "ΔK"[9] effects observed in ternary polymer blends such as the phenoxy/PMMA/poly(ethylene oxide) (PEO),[11] PVPh/poly(vinyl acetate) (PVAc)/PEO,[9] poly(styrene-*co*-acrylic acid)/PMMA/PEO,[12] and phenolic/PEO/PCL[13] blend systems. Totally miscible ternary polymer bends may offer unique opportunities to develop new polymer materials from a flexible combination of the three components, but only a very few ternary polymer blends have been reported to be homogeneous over their entire range of compositions. These totally miscible ternary blends include poly(epichlorohydrin) (PECH)/PMMA/

PEO,[14] PVDF/PVAc/PMMA,[15] PECH/PVAc/PMMA,[16] poly(3-hydroxybutyrate)/PEO/PECH,[17] poly(ether diphenyl ether ketone)/poly(ether ether ketone)/poly(ether imide) (PEI),[18] PEI/poly(ethylene terephthalate) (PET)/poly(butylenes terephthalate) (PBT),[19] and PCL/poly-(phenyl methacrylate)/poly(benzyl methacrylate),[20] which all possess low $\Delta\chi$ effects and hydrogen-bonding interactions between their polymer segments. As a result, they exist as totally miscible ternary polymer blend systems because the ΔK effect may be neglected. Coleman and Painter have noted[9] that only in very rare cases, such as the PVPh/PVAc/poly(methyl acrylate) (PMA) ternary blend,[9] can completely miscible ternary polymer blends exist because the $\Delta\chi$ and ΔK interactions must be so finely balanced. The chemical structures of the PVAc and PMA repeat units are isomorphous, and thus, this ternary polymer blend displays a completely homogeneous amorphous phase. We became curious about the following question: Other than isomers of two polymers, is it possible to obtain a totally miscible ternary polymer blends in which hydrogen bonding exists between the respective polymer segments?

In this paper, we report another completely miscible ternary hydrogen-bonded polymer blend: that between phenoxy, phenolic, and PCL. Phenolic and phenoxy are well-known hydrogen bond donor polymers that interact favorably with polyacrylate, polyester, polyether, and polyvinylpyridine. To the best of our knowledge, however, only a few reports exist that describe binary polymer blends incorporating these self-association polymers. We reported that the phenolic/phenoxy[21–23] and PVPh/phenoxy[24] blends are totally miscible in the amorphous phase because of the hydrogen bonds that exist between their polymer segments. In those previous studies,[21–24] we calculated the interassociation equilibrium constants between each binary blend from analyses of suitable model compounds. The interassociation equilibrium constants obtained from model compounds, however, are not exactly the same as those of the true polymer blends because of intramolecular screening and

* To whom correspondence should be addressed: e-mail kuosw@mail.nctu.edu.tw; Tel 886-3-5131512; Fax 886-3-5719507.

functional group accessibility effects[25−30] in miscible polymer blends. In our present study, we determined indirectly, for the first time, the interassociation equilibrium constant between the hydroxyl groups of phenolic and the hydroxyl groups of phenoxy from a least-squares fitting procedure based on the experimental fraction of hydrogen-bonded carbonyl groups in the phenolic/phenoxy/PCL ternary blend.

Experimental Section

Materials. The polymers used in this study were phenolic, poly(hydroxy ether of bisphenol A) (phenoxy), and poly(ϵ-carprolactone) (PCL). The phenolic was synthesized through a condensation reaction using sulfuric acid; its average molecular weights were $M_n = 500$ and $M_w = 1200$. The phenolic resin does not contain any reactive methylol groups that are capable of causing cross-linking upon heating. The phenoxy was obtained from Union Carbide ($M_n = 23\,000$; $M_w = 48\,000$). The PCL used in this study was TONE Polymer P-787 ($M_n = 80\,000$) purchased from Union Carbide.

Preparation of Blend Samples. Ternary polymer blends of phenoxy/phenolic/PCL having various compositions were prepared by solution blending. A tetrahydrofuran (THF) solution containing 5 wt % polymer mixture was stirred for 6−8 h and then left 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 removal of the residual solvent.

Differential Scanning Calorimetry (DSC). The glass transition temperatures (T_g) of the polymer blends were determined by differential scanning calorimetry (Du-Pont, DSC model 2900). A sample (5−10 mg) was placed on the DSC cell and then heated at a scan rate of 20 °C/min within the range from 0 to 150 °C to avoid possible ester interchange known to occur above 170 °C, and then the specimen was quickly cooled to −100 °C after the first scan. The value of T_g was obtained as the midpoint of the transition point of the heat capacity (C_p) change at a scan rate of 20 °C/min over a temperature range from 0 to 150 °C.

Infrared Spectra. Infrared spectra were recorded using a Nicolet Avatar 320 FT-IR spectrometer. In all cases, at least 32 scans with an accuracy of 1 cm^{-1} were signal-averaged. Infrared spectra of polymer blend films were determined using the conventional NaCl disk method. A THF solution containing the blend (5% w/v) was cast onto a NaCl disk and dried under conditions similar to those used in the bulk preparation. The films used in this study were sufficiently thin to obey the Beer−Lambert law.

Results and Discussion

Binary Blend System. We used differential scanning calorimetry to assess the miscibility of the polymer blend by measuring the glass transition temperature of the blend composition. Figure 1 displays the values of T_g obtained using various compositions of each binary blend of phenolic/phenoxy,[23] phenolic/PCL,[31] and phenoxy/PCL.[32] All these binary compositions exhibit a single T_g, which strongly suggests that all of these compositions are miscible and possess a homogeneous phase. The dependence of T_g on the composition of these blends is presented in Figure 1; these plots fit well to the Kwei equation[33]

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

where W_1 and W_2 are the weight fractions of the components, T_{g1} and T_{g2} represent the components' glass transition temperatures, and k and q are fitting constants. The Kwei equation can apply to polymers that possess specific interactions, such as hydrogen bonds,
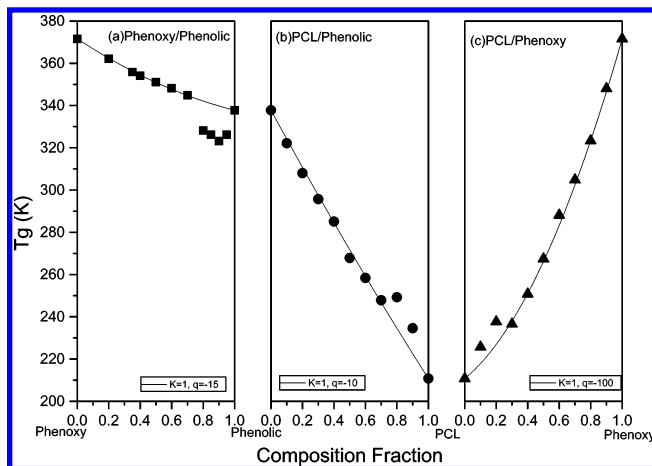

Figure 1. Plots of T_g vs composition for the individual binary blends: (a) phenolic/phenoxy, (b) phenoxy, and (c) phenolic/PCL.
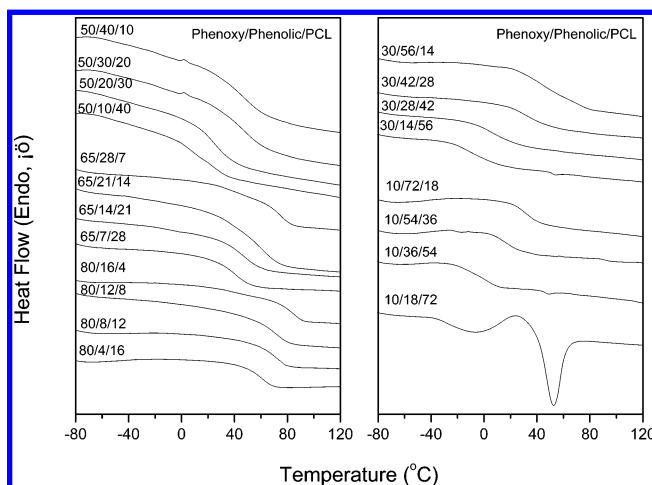

Figure 2. DSC thermograms of phenoxy/phenolic/PCL (w/w/w) blends having different compositions.

within blend systems. The parameter q corresponds to the strength of hydrogen bonding; it reflects the balance between breaking the intramolecular hydrogen bonds and forming intermolecular hydrogen bonds. Figure 1 indicates that $q = -10$ and $k = 1$ for the phenolic/PCL blend, $q = -100$ and $k = 1$ for the phenoxy/PCL blend, and $q = -15$ and $k = 1$ for the phenolic/phenoxy blend.

The deviation in the values of T_g in Figure 1a can be interpreted as reflecting the fact that, upon blending, the self-association of phenolic is broken, with its hydroxyl groups becoming diluted within the blend. The phenoxy molecule, with its long repeating unit, provides a smaller number of potential hydrogen-bonding sites that are available to form interactions with the other blend components. The extent of forming interassociation hydrogen bonds is too small to overcome the increasing entropy due to the reduction of the number of self-associating hydrogen bonds of each polymer's hydroxyl groups.[23] The deviation of the experimental value of T_g from the Kwei equation at high PCL content in Figure 1b,c is due to the crystallization of PCL in the blends during quenching. This phenomenon indicates not only that crystallization of PCL in the blends changes the amorphous phase but also that the crystal of PCL acts as a physical cross-linking point that hinders the molecular mobility of the amorphous phase.[31]

Ternary Blend System. Thermal Analyses. Figure 2 displays the DSC thermograms of several phenolic/
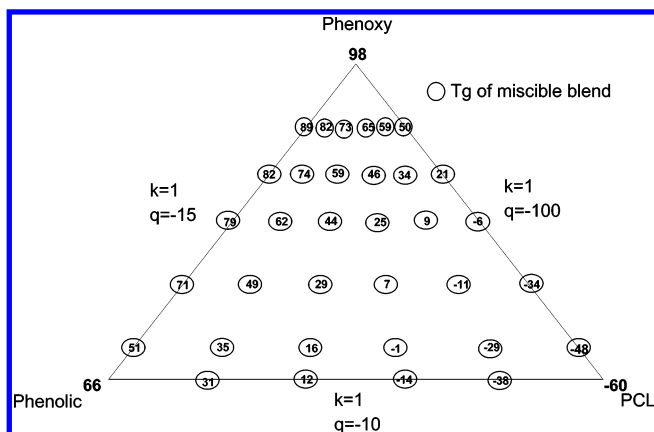
Figure 3. Ternary phase diagram of the phenoxy/phenolic/PCL system with respect to the individual values of T_g displayed in each cycle.

phenoxy/PCL ternary blends having various compositions; it reveals that each ternary blend has only a single glass transition temperature. A single value of T_g strongly suggests that the ternary polymer blend is fully miscible over its total range of compositions. On the basis of this evidence, we suggest that any phenolic/phenoxy/PCL blend composition is miscible at temperatures within the range from -80 to $+120$ °C. Figure 3 displays the phase diagram of this ternary polymer blend with respect to the value of T_g of each composition. Clearly, the value of T_g of this ternary blend increases upon increasing the phenoxy content at a constant phenolic/PCL ratio and upon increasing the phenolic content at a constant phenoxy/PCL ratio.

The well-known Fox equation[34] has been proposed to predict variations of glass transition temperatures of copolymers and blends as a function of composition:

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \tag{2}$$

where T_g is the glass transition temperature of the blend and W is the weight fraction, whose subscripts "1" and "2" indicate polymer 1 and 2, respectively. This equation is generally applied to binary blend systems that are compatible and not too strongly polar. For three-component mixing, this equation can be extended to the T_g−composition relationship

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} + \frac{W_3}{T_{g3}}$$

In addition, the weight-average values calculated from the linearity prediction has been determined in totally ternary miscible blends, such as PEO/PHB/PECH,[17] as follows:

$$T_g = W_1 T_{g1} + W_2 T_{g2} + W_3 T_{g3} \tag{3}$$

Table 1 summarizes the calculated values of T_g and those measured from the DSC analyses of each composition. It is obvious that the values of T_g calculated from the Fox equation and the linearity prediction do not fit well to the values of T_g obtained by thermal analysis; for many compositions, we observe a large negative deviation. This negative deviation between the experimental data and values calculated from the Fox equation and the linearity prediction probably arises from the ternary blend system containing some strong inter-

Table 1. Characteristics of Ternary Polymer Blends (°C)

composition phenoxy/phenolic/PCL	exptl data	prediction		
		Kwei	Fox	linear
10/0/90	−49	−53	−54	−45
10/18/72	−29	−31	−36	−22
10/36/54	−1	−7	−16	1
10/54/36	16	16	7	24
10/72/18	35	42	35	46
10/90/0	51	58	69	70
30/0/70	−34	−34	−30	−14
30/14/56	−11	−14	−15	4
30/28/42	7	7	3	22
30/42/28	29	29	24	40
30/56/14	49	49	47	57
30/70/0	71	72	75	76
50/0/50	−6	−6	−4	18
50/10/40	9	9	10	31
50/20/30	25	25	25	43
50/30/20	44	43	42	56
50/40/10	62	61	60	69
50/50/0	79	79	82	82
65/0/35	21	21	20	42
65/7/28	34	33	32	51
65/14/21	46	45	44	60
65/21/14	59	58	57	69
65/28/7	74	72	71	78
65/35/0	82	82	87	87
80/0/20	50	50	49	33
80/4/16	59	59	57	71
80/8/12	65	65	65	76
80/12/8	73	73	73	81
80/16/4	82	82	82	87
80/20/0	89	89	91	92
0/20/80	−38	−38	−44	−36
0/40/60	−14	−14	−24	−10
0/60/40	12	12	0	14
0/80/20	31	39	29	40

molecular interactions. Therefore, we extended the Kwei equation for a binary blend to describe a ternary blend such that we could predict the nature of this ternary hydrogen-bonded polymer blend system:

$$T_g = W_1 T_{g1} + W_2 T_{g2} + W_3 T_{g3} + q_{12} W_1 W_2 + q_{13} W_1 W_3 + q_{23} W_2 W_3 \tag{4}$$

where q_{ij} is the interassociation strength of each binary blend that has been calculated previously. Table 1 also summarizes the values of T_g calculated from the Kwei equation and those measured from the DSC analyses at each composition. Figure 4 indicates that the agreement between the experimental and calculated values is quite satisfactory.

FT-IR Spectroscopic Analyses. Fourier transform infrared spectroscopy has been used widely in the study of polymer blends. This method is useful for verifying the presence of intermolecular interactions between various hydrogen bond donor and acceptor groups because of its sensitivity to hydrogen bond formation. Figure 5 displays scale-expanded infrared spectra (in the region $4000-2700$ cm^{-1}) of the hydroxyl group stretching absorptions of pure phenolic, pure phenoxy, and various phenoxy/phenolic/PCL blends having their phenoxy content fixed at 50 wt %. Pure phenolic and phenoxy present two distinct bands in the hydroxyl stretching region of the infrared spectra. We attribute the very broad bands centered at 3350 and 3400 cm^{-1} to the wide distribution of the hydrogen-bonded hydroxyl groups and the sharp bands at 3525 and 3570 cm^{-1} to the free hydroxyl groups of pure phenolic and pure phenoxy, respectively. The intensity of the signal of the free hydroxyl groups decreased upon increasing the PCL content in the phenoxy/PCL blend. Meanwhile, the signal for phenoxy's broad hydrogen-bonded hy-
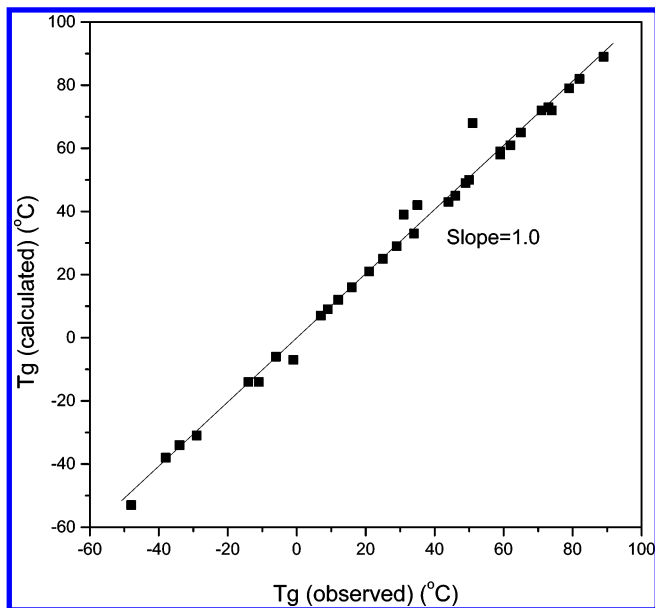
Figure 4. Relationship between the values of T_g observed by DSC (■) and those calculated using the Kwei equation (□).
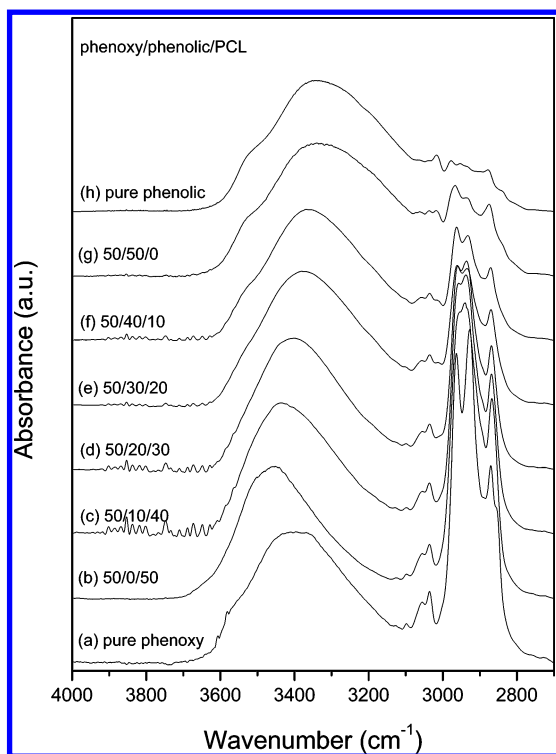

Figure 5. Infrared spectra recorded in the region 2700–3700 cm^{-1} for a series of compositions of phenoxy/phenolic/PCL (wt/wt/wt %) blends: (a) pure phenoxy, (b) 50/10/40, (c) 50/20/30, (d) 50/30/20, (e) 50/20/30, (f) 50/40/0, (g) 50/50/0, and (h) pure phenolic.

Figure 6. Infrared spectra recorded at room temperature in the range 1680–1780 cm^{-1} for phenoxyl/phenolic/PCL blends: (a) 50/0/50, (b) 50/10/40, (c) 50/20/30, (d) 50/30/20, and (e) 50/40/10.

droxyl band shifted to higher frequency upon increasing the PCL content (50 wt %) at 3430 cm^{-1}. Taking into account the interassociation and self-association equilibrium constants of the phenoxy/PCL blend, the interassociation equilibrium constant between the hydroxyl group of phenoxy and the carbonyl group of PCL ($K_A = 7$) is smaller than the self-association equilibrium constant of pure phenoxy[35] ($K_B = 25.6$). This observed change in the hydroxyl stretching region arises from switching from strong intramolecular hydroxyl–hydroxyl hydrogen bonds to weaker intermolecular hydroxyl–carbonyl hydrogen bonds. In addition, the broad
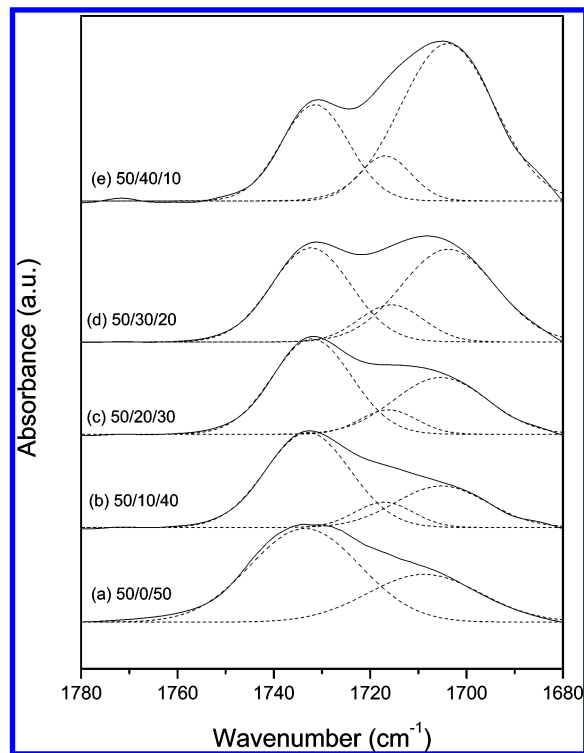
hydrogen-bonded hydroxyl band for phenolic and phenoxy shifts to a slightly lower frequency (3335 cm^{-1}) upon increasing the phenoxy content (50 wt %), which suggests that the interassociation equilibrium constant between the hydroxyl groups of phenolic and phenoxy is greater than the self-association equilibrium constants of the hydroxyl groups of the pure phenolic and pure phenoxy homopolymers. We provide further evidence in the next section.

In addition, Figure 5 indicates that, for the ternary blend, the band at 3430 cm^{-1} shifted to 3335 cm^{-1}, a lower wavenumber, upon increasing the phenolic/PCL ratio. This change arose from a switch from intermolecular hydroxyl–carbonyl hydrogen bonds to intermolecular hydroxyl–hydroxyl hydrogen bonds between the phenolic and phenoxy segments, which indicates that there are hydrogen-bonding interactions between the hydroxyl groups of phenoxy and phenolic resin. It also reveals that the hydroxyl–hydroxyl intermolecular interactions between the phenolic and phenoxy segments dominates in these ternary blends, and thus, it is reasonable to assign the band at 3335 cm^{-1} to the hydroxyl groups of phenolic and phenoxy segments that are hydrogen bonded to other hydroxyl groups. Coleman et al.[36] employed the frequency difference ($\Delta\nu$) between the absorptions of the hydrogen-bonded and free hydroxyl groups to determine the relative strength of different intermolecular interactions. We obtained an increase in the $\Delta\nu$ value upon increasing the phenolic/PCL ratio; this result is consistent with the result of the DSC analyses. The value of T_g of this ternary blend increased upon increasing the phenolic content because the average strength of hydrogen bonding increased.

Figure 6 displays the carbonyl stretching region (1680–1780 cm^{-1}) of these ternary blends from infrared spectra recorded at room temperature. The absorption

Table 2. Results of Curve Fitting of the Infrared Spectroscopy Data Recorded at Room Temperature for Phenoxy/Phenolic/PCL Ternary Blends

phenoxy/phenolic/PCL (wt %)	free C=O			H-bond C=O with phenoxy			H-bond C=O with phenolic			$f_b{}^a$ (%)
	ν, cm^{-1}	$W_{1/2}$, cm^{-1}	A_f, %	ν, cm^{-1}	$W_{1/2}$, cm^{-1}	A_f, %	ν, cm^{-1}	$W_{1/2}$, cm^{-1}	A_f, %	
10/18/72	1734	19	62.8	1716	12	2.8	1704	22	34.4	28.3
10/36/54	1734	18	55.0	1715	12	6.6	1703	20	38.4	35.2
10/54/36	1733	18	50.4	1715	13	9.3	1703	20	39.3	39.1
10/72/18	1733	18	34.0	1715	13	10.0	1703	20	56.0	56.4
30/14/56	1733	18	65.6	1715	11	1.7	1708	22	32.7	25.9
30/28/42	1732	19	50.0	1715	11	5.6	1704	20	44.4	40.0
30/42/28	1732	18	32.4	1715	12	20.9	1702	19	47.7	58.5
30/56/14	1732	18	22.8	1715	13	25.0	1702	19	52.2	69.3
50/10/40	1733	18	60.2	1715	13	11.1	1705	20	28.7	30.6
50/20/30	1733	18	53.0	1716	12	12.4	1705	20	34.6	37.2
50/30/20	1732	18	40.9	1716	12	13.5	1704	20	45.6	49.1
50/40/10	1732	17	27.6	1716	13	13.6	1704	20	58.8	63.6
65/7/28	1732	17	63.0	1715	12	7.0	1707	21	30.0	28.1
65/14/21	1732	18	55.8	1715	12	7.3	1706	20	36.9	34.6
65/21/14	1732	17	50.0	1715	12	7.4	1706	20	42.6	40.0
65/28/7	1732	17	48.8	1716	12	8.0	1707	20	43.2	41.1
80/4/16	1732	17	69.5	1716	12	6.2	1707	20	24.3	22.6
80/8/12	1732	17	64.2	1716	12	7.8	1707	20	28.0	27.1
80/12/8	1732	17	61.6	1715	12	8.1	1707	20	30.3	29.3
80/16/4	1732	19	60.2	1716	12	8.6	1707	19	31.2	30.6
10/0/90	1734	21	96.2	1715	28	3.8				2.5
30/0/70	1734	20	86.8	1715	28	13.2				9.2
50/0/50	1734	20	77.6	1715	28	22.4				16.1
65/0/35	1734	20	69.8	1715	29	30.2				22.3
80/0/20	1734	20	62.3	1715	29	37.7				28.7
0/20/80	1734	18	62.1				1708	28	37.9	28.9
0/40/60	1734	20	39.1				1707	28	60.9	50.9
0/60/40	1733	16	23.9				1705	27	76.1	67.9
0/80/20	1733	16	15.8				1704	27	84.2	78.0

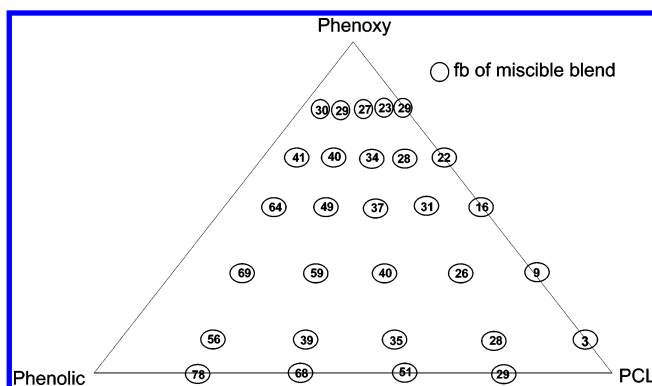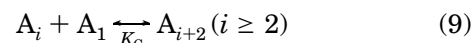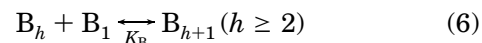^{a} f_b = fraction of hydrogen-bonded carbonyl groups.

Figure 7. Fraction of hydrogen-bonded carbonyl groups in the ternary phenoxy/phenolic/PCL blend system.

at 1734 cm^{-1} represents the free carbonyl group, while the signals of the hydrogen-bonded carbonyl groups appear at 1705 and 1715 cm^{-1}, corresponding to bonding to phenolic and phenoxy, respectively. Figure 6 indicates that the carbonyl stretching frequencies split into the three main bands fit well to a Gaussian function. The fraction of hydrogen-bonded carbonyl groups can be calculated by using an appropriate absorptivity ratio ($a_R = a_{HB}/a_F = 1.5$), which has been discussed previously.[37] Table 2 summarizes the results from curve fitting; Figure 7 displays the fraction of hydrogen-bonded carbonyl groups in this ternary polymer blend. Clearly, these results indicate that the fraction of hydrogen-bonded carbonyl groups increases upon increasing the relative ratio of phenolic to PCL. In addition, the fraction of PCL that is hydrogen bonded at a high phenolic content in this ternary blend system is lower than that present in the binary phenolic/PCL polymer blend, which indicates that hydrogen bonding exists between the phenoxy and phenolic segments. In other words, the PCL carbonyl units compete with the hydroxyl groups of phenoxy in forming hydrogen bonds to

the hydroxyl groups of the phenolic resin. Furthermore, the fraction of PCL that is hydrogen bonded at a low phenolic content in this ternary blend system is higher than that observed in the binary polymer blend of phenolic/PCL because hydrogen bonding also exists between the carbonyl groups of the PCL and the hydroxyl groups of phenoxy. Therefore, the complicated intermolecular hydrogen-bonding interactions that exist in this ternary polymer blend system behaves like a network and the phenolic resin is oligomeric, so they do get some help from the entropy of mixing. Even though different hydrogen-bonding strengths exist in each binary blend, the ternary blend remains completely miscible. Again, we conclude here that if intermolecular hydrogen bonding exists between each pair of binary components in a ternary blend, a completely miscible ternary blend may be obtained, as in this phenolic/phenoxy/PCL system.

Interassociation Equilibrium Constant (K_A) between Phenolic and Phenoxy Segments. The original Painter−Coleman association model[37] is incapable of estimating the thermodynamic properties of a blend containing two self-associating polymers. Therefore, in this study we extended the original PCAM to estimate the thermodynamic properties of such a blend. The equilibria can be described as follows:

$$B_1 + B_1 \underset{K_2}{\rightleftharpoons} B_2 \tag{5}$$

$$B_h + B_1 \underset{K_B}{\rightleftharpoons} B_{h+1} \, (h \geq 2) \tag{6}$$

$$B_h + A_i \underset{K_A}{\rightleftharpoons} B_h + A_i \tag{7}$$

$$A_1 + A_1 \underset{K_{C2}}{\rightleftharpoons} A_2 \tag{8}$$

$$A_i + A_1 \underset{K_C}{\rightleftharpoons} A_{i+2} \, (i \geq 2) \tag{9}$$

$$K_2 = \frac{\Phi_{B_2}}{2\Phi_{B_1}\Phi_{B_1}} \tag{10}$$

$$K_B = \frac{\Phi_{B_{h+1}}}{\Phi_{B_h}\Phi_{A_i}}\frac{h}{h+1} \tag{11}$$

$$K_A = \frac{\Phi_{B_hA_i}}{\Phi_{B_h}\Phi_{A_i}}\frac{hir}{h+ir} \tag{12}$$

$$K_{C2} = \frac{\Phi_{A_{i+1}}}{2\Phi_{A_1}\Phi_{A_1}} \tag{13}$$

$$K_C = \frac{\Phi_{A_{i+1}}}{\Phi_{A_1}\Phi_{A_1}}\frac{i}{i+1} \tag{14}$$

The terms K_2 and K_B are the self-association constants for dimer and multimer formation, respectively, of B; K_A is the interassociation constant for the interaction between A_i and B_h; K_{C2} and K_C are the self-association constants for dimer and multimer formation, respectively, of A; $r = V_A/V_B$ is the ratio of the segmental molar volumes; Φ_{B_h} is the volume fraction of the chains of length h, and Φ_{A_i} is the volume fraction of the chains of length i at any instant in time.

The stoichiometric relationships are obtained readily from material balance considerations. The total volume fractions of all of the A and B units present in the mixture are given by

$$\Phi_{B_h} = \Phi_{B_1} + \sum_{h=2}^{\infty}\Phi_{B_h} + \sum_{h=1}^{\infty}\Phi_{B_hA_i}\left(\frac{h}{h+ir}\right) \tag{15}$$

$$\Phi_A = \Phi_{A_1} + \sum_{h=2}^{\infty}\Phi_{A_h} + \sum_{h=1}^{\infty}\Phi_{B_hA_i}\left(\frac{ir}{h+ir}\right) \tag{16}$$

Therefore, the total volume fractions of these two self-associating polymers (A and B) can be extended as follows:

$$\Phi_B = \Phi_{B_1}\left[\left(1-\frac{K_2}{K_B}\right)+\frac{K_2}{K_B}\left(\frac{1}{(1-K_B\Phi_{B_1})^2}\right)\right]\left[1+\frac{K_A\Phi_{A_1}}{r_A}\right] \tag{17}$$

$$\Phi_A = $$
$$\Phi_{A_1}\left[\left(1-\frac{K_{C_2}}{K_C}\right)+\frac{K_{C_2}}{K_C}\left(\frac{1}{(1-K_C\Phi_{A_1})^2}\right)\right]\left[1+\frac{K_A\Phi_{B_1}}{r_B}\right] \tag{18}$$

These results for Φ_A and Φ_B are similar to those for one self-associating polymer and one nonself-associating polymer, which can be expressed as follows:

$$\Phi_B = \Phi_{B_1}\left[\left(1-\frac{K_2}{K_B}\right)+\frac{K_2}{K_B}\left(\frac{1}{(1-K_B\Phi_{B_1})^2}\right)\right]\left[1+\frac{K_A\Phi_{A_1}}{r}\right] \tag{19}$$

$$\Phi_A = \Phi_{0A} + K_A\Phi_{0A}\Phi_{B_1}\left[\left(1-\frac{K_2}{K_B}\right)+\frac{K_2}{K_B}\left(\frac{1}{(1-K_B\Phi_{B_1})}\right)\right] \tag{20}$$

In our ternary hydrogen-bonded blend system, the hydrogen bonding between the phenolic hydroxyl group and the PCL carbonyl group and between the phenoxy hydroxyl group and the PCL carbonyl group is represented by

$$B_h + C_1 \overset{K_D}{\rightleftharpoons} B_hC \tag{21}$$

$$A_i + C_1 \overset{K_E}{\rightleftharpoons} A_iC \tag{22}$$

These six equilibrium constants can be expressed as follows in terms of volume fractions:

$$\Phi_B = \Phi_{B1}\Gamma_2\left[1+\frac{K_A\Phi_{A1}}{r_A}+\frac{K_D\Phi_{C1}}{r_C}\right] \tag{23}$$

$$\Phi_A = \Phi_{A1}\Gamma_4\left[1+\frac{K_A\Phi_{B1}}{r_B}+\frac{K_E\Phi_{C1}}{r_D}\right] \tag{24}$$

$$\Phi_C = \Phi_{C1}[1 + K_D\Phi_{B1}\Gamma_1 + K_E\Phi_{A1}\Gamma_3] \tag{25}$$

where

$$\Gamma_1 = \left(1-\frac{K_2}{K_B}\right)+\frac{K_2}{K_B}\left(\frac{1}{(1-K_B\Phi_{B1})}\right) \tag{26}$$

$$\Gamma_2 = \left(1-\frac{K_2}{K_B}\right)+\frac{K_2}{K_B}\left(\frac{1}{(1-K_B\Phi_{B1})^2}\right) \tag{27}$$

$$\Gamma_3 = \left(1-\frac{K_{C2}}{K_C}\right)+\frac{K_{C2}}{K_C}\left(\frac{1}{(1-K_C\Phi_{A1})}\right) \tag{28}$$

$$\Gamma_4 = \left(1-\frac{K_{C2}}{K_C}\right)+\frac{K_{C2}}{K_C}\left(\frac{1}{(1-K_C\Phi_{A1})^2}\right) \tag{29}$$

Φ_B, Φ_A, and Φ_C are the volume fractions of the repeat units in the blend, Φ_{B1}, Φ_{A1}, and Φ_{C1} are the volume fractions of isolated units in the blend, and $r_A = V_A/V_B$, $r_B = V_B/V_A$, $r_C = V_C/V_B$, and $r_D = V_C/V_A$ are the ratios of the segmental molar volumes. The values of the self-association constants of phenolic ($K_2 = 23.3$ and $K_B = 53.3$)[23] and the self-association constant of phenoxy ($K_{C2} = 14.4$ and $K_C = 25.6$)[35] and the interassociation constants for phenolic and PCL ($K_D = 116.8$)[31] and phenoxy and PCL ($K_E = 7$)[35] have been determined previously. Equations 23–25 are too complicated to determine the interassociation equilibrium constant (K_A) between the hydroxyl groups of phenolic and phenoxy. For convenience, we take into account the fact that, for the interassociation and self-association in phenolic/PCL and phenoxy/PCL blends, the value of K_E of the phenoxy/PCL blend is considerably smaller than the value of K_D of the phenolic/PCL blend and that the value of K_C for pure phenoxy is also smaller than that of K_B for pure phenolic. Therefore, we may ignore the hydrogen bonding of the phenoxy/PCL blend and of pure phenoxy. Equations 23–25 simplify as follows:

$$\Phi_B = \Phi_{B1}\Gamma_2\left[1+\frac{K_A\Phi_{A1}}{r_A}+\frac{K_D\Phi_{C1}}{r_C}\right] \tag{30}$$

$$\Phi_A = \Phi_{A1}[1 + K_A\Phi_{B1}\Gamma_1] \tag{31}$$

$$\Phi_C = \Phi_{C1}[1 + K_D\Phi_{B1}\Gamma_1] \tag{32}$$

Table 3. Self-Association and Interassociation Equilibrium Constants and Thermodynamic Parameters for Phenolic/PCL, Phenoxy/PCL, and Phenolic/Phenoxy Blends at 25 °C[a]

polymer	V	M_w	δ	DP	equilib constant		enthalpy (kcal/mol)	
					K_2	K_B	h_2	h_B
phenolic[b]	84	105	12.05	6	23.3	52.3	−4.1	−6.1
phenoxy[c]	216	284	10.22	80	14.4	25.6	−2.5	−3.4
PCL[d]	107	114	9.21	714				
					K_A		h_A	
phenolic/PCL[e]					116.8		−4.6	
phenoxy/PCL[c]					7.0		−2.0	
phenolic/phenoxy					230.0		−5.1[b]	

[a] V = molar volume (mL/mol), M_w = molecular weight (g/mol), δ = solubility parameter (cal/mL)$^{1/2}$, DP = degree of polymerization, K_2 = dimer self-association equilibrium constant, K_B = multimer self-association equilibrium constant, K_A = interassociation equilibrium constant, h_2 = enthalpy of dimer self-association formation, h_B = enthalpy of multimer self-association formation, and h_A = enthalpy of interassociation formation. [b] Reference 23. [c] Reference 35. [d] Reference 37. [e] Reference 31.

Equations 30−32 are capable of describing both the PVPh/PMA/PEO and phenolic/PEO/PCL blend systems. The value of the interassociation constant K_A may be determined indirectly from a least-squares fitting procedure of the fraction of hydrogen-bonded carbonyl groups obtained experimentally for the present ternary polymer blend. If the equilibrium constants (K_2, K_B, K_C), segment molar volumes, and fractions of hydrogen-bonded carbonyl groups are known, the value of K_A can be calculated from eqs 26, 27, and 30−32 by using a least-squares fit based on the fraction of hydrogen-bonded carbonyl group obtained experimentally. To minimize errors in this calculation, we considered the blend containing a relatively low phenoxy content (10 wt %) so that we could ignore the effect of hydrogen bonding between the phenoxy hydroxyl groups and the PCL carbonyl groups. Figure 7 indicates that only 3% of the carbonyl groups are hydrogen bonded in the phenoxy/PCL (10/90) blend. We obtained a value for K_A of 230.0 for the phenolic/phenoxy blend at room temperature. The value of K_A calculated from the ternary blend is higher than that obtained for the model compound. The same trend also has been found in previous studies of PVPh/PVAc/PEO and phenolic/PEO/PCL blend systems. Table 3 lists all of the parameters required by the Painter−Coleman association model to estimate the thermodynamic properties of this ternary phenolic/phenoxy/PCL blend; the data imply that the interassociation equilibrium constant for hydroxyl−hydroxyl interactions of phenolic/phenoxy is indeed greater than the interassociation equilibrium constants for the hydroxyl−carbonyl interactions of phenolic/PCL and phenoxy/PCL blends and the self-association constants of pure phenolic and pure phenoxy at room temperature. Here, we need to emphasize that Painter et al. proposed two self-associating polymers,[37] which also can be handled using approach first developed by Boris Veytsman[38] recently. We will extend this treatment for ternary blend systems in the future.

Conclusions

We have investigated the phase behavior and hydrogen bonding present within a ternary blend of phenolic, phenoxy, and PCL by using DSC and FTIR spectroscopic analyses. On the bais of DSC analysis, we observed that this unusual, completely miscible, ternary hydrogen-bonded blend possesses a single glass transition temperature over its entire range of compositions. Infrared spectra indicated that intermolecular hydrogen bonding exists within this ternary polymer blend. In addition, we calculated the interassociation equilibrium constant for the interactions between the hydroxyl groups of phenolic and phenoxy. Even though different intermolecular hydrogen-bonding strengths exist in each binary blend, the ternary blend remains completely miscible because the intermolecular hydrogen bonds that exist within the individual binary blends create a networklike structure.

References and Notes

(1) Utracki, L. A. *Polymer Alloys and Blends;* Hanser Publishers: Munich, 1989.
(2) Bonner, J. G.; Hope, P. S. In *Polymer Blends and Alloys*; Folkes, M. J., Hope, P. S., Eds.; Blackie: Glasgow, UK, 1993; p 46.
(3) Paul, D. R. In *Polymers Blends*; Paul, D. R., Newman, S., Eds.; Academic Press: New York, 1978; Vol. II, p 35.
(4) Scott, R. L. *J. Chem. Phys.* **1949**, *17*, 279.
(5) Tompa, H. *Trans. Faraday Soc.* **1949**, *45*, 1140.
(6) Kwei, T. K.; Frisch, H. L. Radigan, W.; Vogel, S. *Macromolecules* **1977**, *10*, 157.
(7) Pomposo, J. A.; Cortazar, M.; Calahorra, E. *Macromolecules* **1994**, *27*, 252.
(8) Fowler, M. E.; Barlow, J. W.; Paul, D. R. *Polymer* **1987**, *28*, 1177.
(9) Zhang, H.; Bhagwagar, D. E.; Graf, J. F.; Painter, P. C.; Coleman, M. M. *Polymer* **1994**, *35*, 5379.
(10) Patterson, D. *Polym. Eng. Sci.* **1982**, *22*, 64.
(11) Hong, B. K.; Kim, J. K. Jo, W. H.; Lee, S. C. *Polymer* **1997**, *38*, 4373.
(12) Jo, W. H.; Kwon, Y. K.; Kwon, I. H. *Macromolecules* **1991**, *24*, 4708.
(13) Kuo, S. W.; Lin, C. L.; Chang, F. C. *Macromolecules* **2002**, *35*, 278.
(14) Min, K. E.; Chiou, J. S.; Barlow, J. W.; Paul, D. R. *Polymer* **1987**, *28*, 172.
(15) Guo, Q. P. *Eur. Polym. J.* **1996**, *32*, 1409.
(16) Guo, Q. P. *Eur. Polym. J.* **1990**, *26*, 1329.
(17) Goh, S. H.; Ni, X. *Polymer* **1999**, *40*, 5733.
(18) Yau, S. N.; Woo, E. M. *Macromol. Rapid Commun.* **1996**, *17*, 615.
(19) Woo, E. M.; Tseng, Y. C. *Macromol. Chem. Phys.* **2000**, *201*, 1877.
(20) Lee, S. C.; Woo, E. M. *J. Polym. Sci., Polym. Phys.* **2002**, *40*, 747.
(21) Wu, H. D.; Ma, C. C. M.; Chu, P. P. *Polymer* **1997**, *38*, 5419.
(22) Wu, H. D.; Ma, C. C. M.; Chang, F. C. *Macromol. Chem. Phys.* **2000**, *201*, 1121.
(23) Wu, H. D.; Chu, P. P.; Ma, C. C. M.; Chang, F. C. *Macromolecules* **1999**, *32*, 3097.
(24) Kuo, S. W.; Wu, H. D.; Lin, C. L.; Chang, F. C. *J. Polym. Res.* **2003**, *10*, 87.
(25) Painter, P. C.; Veytsman, B.; Kumar, S.; Shenoy, S.; Graf, J. F.; Xu, Y.; Coleman, M. M. *Macromolecules* **1997**, *30*, 932.

(26) Coleman, M. M.; Pehlert, G. J.; Painter, P. C. *Macromolecules* **1996**, *29*, 6820.

(27) Pehlert, G. J.; Painter, P. C.; Veytsman, B.; Coleman, M. M. *Macromolecules* **1997**, *30*, 3671.

(28) Pehlert, G. J.; Painter, P. C.; Coleman, M. M. *Macromolecules* **1998**, *31*, 8423.

(29) Coleman, M. M.; Guigley, K. S.; Painter, P. C. *Macromol. Chem. Phys.* **1999**, *200*, 1167.

(30) Painter, P. C.; Coleman, M. M. *Polymer Blends*; Paul, D. R., Ed.; John Wiley & Sons: New York, 2000; Vol. 1.

(31) Kuo, S. W.; Chang, F. C. *Macromol. Chem. Phys.* **2001**, *202*, 3112.

(32) Kuo, S. W.; Huang, C. F.; Chang, F. C., *J. Polym. Sci., Polym. Phys. Ed.* **2001**, *39*, 1348.

(33) Kwei, T. *J. Polym. Sci., Polym. Lett. Ed.* **1984**, *22*, 307.

(34) Fox, T. G. *J. Appl. Bull. Am. Phys. Soc.* **1956**, *1*, 123.

(35) Iriarte, M.; Alberdi, M.; Shenoy, S. L.; Iruin, J. J. *Macromolecules* **1999**, *32*, 2661.

(36) Moskala, E. J.; Varnell, D. F.; Coleman, M. M. *Polymer* **1985**, *26*, 228.

(37) Coleman, M. M.; Graf, J. F.; Painter, P. C. *Specific Interactions and the Miscibility of Polymer Blends*; Technomic Publishing: Lancaster, PA, 1991.

(38) Park, Y.; Veytsman, B.; Coleman, M.; Painter, P. C. *Macromolecules*, in press.

(39) Veytsman, B. *J. Phys. Chem.* **1993**, *97*, 7144.

MA047371A