

Effects of Molecular Structure of Modifiers on the Thermodynamics of Phenolic Blends: An Entropic Factor Complementing PCAM

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ABSTRACT: Different thermodynamics in phenolic blends with different polymeric modifiers, i.e., phenoxy, poly(decamethylene adipate), poly(ethylene oxide), and poly(vinyl alcohol), calculated by the Painter and Coleman association model (PCAM) are examined. The thermodynamics is calculated based upon the equilibrium constants derived experimentally from infrared spectroscopies of low molecular weight analogues with similar hydrogen-bonding formation. The discrepancies between the PCAM predictions and the experimentally observed T_g and free volume variation with blending composition are attributed to the additional entropic effects introduced by the long repeated units of modifiers. The structural characteristics and hydrogen-bonding heterogeneity as derived from solid-state NMR and IR spectra support the notion that the length and size of the modifier repeated unit are responsible for such discrepancies. These observed nonidealities can be interpreted as competition between inter- and intraassociations (ΔH_m favored), which depend on the entropy rise associated with the amount of increase of the breaking off of the self-association in phenolic and modifiers within blends. While PCAM is based on "true" miscibility, however, minor modification is required to better describe the thermodynamics for "real" blends where microdomain heterogeneity with size greater than that defined by thermodynamic criteria may be present.

Introduction

A physically homogeneous mixture can occur due to intermolecular association that provides a favorable energetic contribution to the mixing process. Many examples of miscibility and interaction strength in polymer blends have been well identified by using the Painter–Coleman association model (PCAM) in the literature.^{1–7} A variety of miscible polymer blends with strong specific interaction show an unusual compositional variation of their T_g . Previously, Painter and co-workers^{1,8} had proposed a modified classical thermodynamics theory to explain such unusual variations of T_g with numerous compositions. All these blends, driven by the strong interassociated H bonding, exhibit a "truly" homogeneous morphology. However, most miscible blends are not as ideal as those demonstrated by the PCAM. Taking phenolic blends as the example, the presence of positive and/or negative deviation in the T_g –composition curves was noticed in our previous studies.^{9–11} When polymers have an inimitable structure (i.e., phenolic, with high-density intra-hydrogen bonds) or polymeric modifiers have a longer repeating unit, this may result in less favored mixing conditions relative to those blends used in Painter and Coleman's studies. In addition, although the PCAM is based on a "true" miscibility, modification is required to better describe the thermodynamics for certain "real" blends where the microdomain heterogeneity is present with a size greater than that defined by conventional thermodynamic criteria. In this sense, the significance of current research in this area is to contribute a better understanding about, in terms of component molecular structures, the

origin of these energetic interactions, and thus, the microstructure of a polymer blend can be better predicted or controlled.

In this study, a novolac type phenolic has been used as a single hydrogen bond donor polymer that was blended with four compatible polymeric modifiers to explore the effect of the molecular structure on the variation of thermodynamics within the phenolic blend. The four modifiers are divided into two groups including the long repeated unit (e.g., phenoxy and poly(decamethylene adipate) (PDA)) and the short repeated unit (e.g., poly(ethylene oxide) (PEO) and poly(vinyl alcohol) (PVA)). In terms of functional groups of those polymeric modifiers, they represent an ester group (PDA), an ether group (PEO), and a hydroxyl group (phenoxy, PVA), all of which involve O–H \cdots O, O–H \cdots O–H, or O–H \cdots C=O types of hydrogen bonding with different repeating unit length. It is of great interest since they represent situations found in many less than ideal blend systems involving strong hydrogen-bonding interactions. Possible discrepancies with that predicted from the PCAM may be illustrated based on studying those less ideal yet strongly hydrogen-bonded blends.

The two main purposes of this study are (1) to examine the relationships of the PCAM prediction and to deduce possible factors complementing the model and (2) to gain insights into the competition between inter- and intra-H-bonding and effects of molecular structures of modifiers upon the miscibility. The general approach is summarized as follows. First, we examined the thermodynamics following the PCAM for phenolic blends based upon the equilibrium constants to describe self-association and interassociation. The equilibrium constants of phenolic blends are derived experimentally from Fourier transform infrared spectroscopies of low molecular weight analogue compounds of polymers as described previously.¹ Second, solid-state IR spectra

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Table 1. Molecular Structure, Model Compound, and T_g of Polymers Used in This Study

Material	Molecular structure	Model component	T_g (°C)
Novolak type phenolic resin (phenolic)	<p>Mn = 500, Mw = 1,200</p>	<p>2,4-xyleneol</p>	70 ± 2
Phenoxy	<p>Mn = 23,000, Mw = 48,000</p>	<p>1,3 bis-(4-(2-propyl) phenoxy)-2-propanol (IPPHP)</p>	95 ± 2
polydecamethylene adipate (PDA). x = 10	<p>m = 80</p>	<p>CH₃COC₂H₅ Ethyl Acetate</p>	-43 ± 2
Poly (ethylene oxide), (PEO)	<p>Mw=200,000</p>	<p>CH₃OCH₂CH₂OCH₃ ethylene glycol dimethyl ether (EGDME)</p>	-65
Poly (vinyl alcohol), (PVA)	<p>95% hydrolyzed, Mw=95,000</p>	<p>2,4-pentanediol</p>	81 ± 2

were used to compare the prediction of interaction from the PCAM. Then, we tried to understand the effect of those polymeric modifiers with long and short repeated units on the entropy factor in phenolic blends according to their respective T_g behaviors. Finally, solid-state NMR spectra and excess volume were then used to assess the change of H-bonding configuration by blending the phenolic with different polymeric modifiers.

The discrepancies between PCAM prediction and experimental observation were discussed in terms of the entropically favored London dispersion forces and the enthalpically favored H-bonding association. As will be revealed, the intrinsic difference in molecular structure of these polymeric modifier results in the inhomogeneous variation of H-bonding association that leads to the discrepancies with the PCAM prediction based upon "truly" miscible assumption.

Experimental Section

Sample Preparation of Blends. The synthesis of the novolak type phenolic resin (phenolic) was described in our previous report.¹² All polymeric modifiers, model compounds, and their physical properties used in the present study are summarized in Table 1. The phenolic and the polymeric modifier were mixed in THF (1% (w/v)) at room temperature according to the designed compositions. The mixed solution was stirred for 6–8 h and then allowed to evaporate slowly at room temperature for 1 day. The blend was then dried at 50 °C for 2 days and annealed at 140 °C for 2 h under vacuum.

Infrared Spectra. The infrared spectrum was obtained by a FT-IR spectrometer (Bio-Rad FTS-155). For a film sample, the IR studies were carried out with the conventional NaCl disk method. Infrared spectra were recorded at 75/25 phenolic/modifier blend composition at 50 °C. For a solution samples, a permanently sealed cell with NaCl windows of 0.05 mm path length (Wilmad) was used to study the equilibrium constant of intermolecular interaction, K_A . Cyclohexane was used as the solvent for the obvious reason described previously.^{2,4}

Glass Transition Temperatures of Blends. The glass transition temperature (T_g) of a polymer blend was determined by a differential scanning calorimeter (Du-Pont, DSC model 2900). The scan rate was 20 °C/min ranging from –80 to 130 °C with 3–4 mg sample on a DSC sample plate, and the specimen was quickly cooled to –80 °C after the first scan. This procedure ensures a complete mixing of the polymer blend and complete removal of the residual solvent in the specimen. The T_g value was determined at the midpoint of the transition point of the heat capacity (C_p) change, and the reproducibility of T_g values was estimated to be within ± 3 °C.

Excess Volume. The specific volume was determined at 298.15 K using a pycnometer calibrated with *n*-heptane. The temperature of the water bath was kept constant to within 0.1 °C, and the measured values were found to be within ± 0.001 cm³/g from repeated measurements. The excess volume (V^E) is defined as

$$V^E = V - (\omega_a V_a^0 + \omega_b V_b^0) \quad (1)$$

where ω_i is the weight fraction of component i , V_i^0 is the specific volume of the i th pure component, and V is the specific volume of the phenolic/modifier blend.

NMR Experiments. High-resolution solid-state ¹³C NMR experiments were carried out on a Bruker DSX-300 spectrometer operating at resonance frequencies of 300.13 and 75.475 MHz for ¹H and ¹³C, respectively. The ¹³C CP/MAS spectra were measured with 3.9 μs 90° pulse angle, 3 s pulse delay time, 30 ms acquisition time, and 2048 scans. All NMR spectra were taken at 300 K with broad-band decoupling, normal cross-polarization pulse sequence, and a magic angle spinning (MAS) of 5.4 kHz.

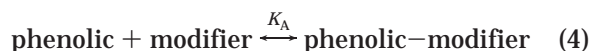
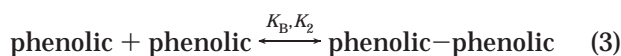
Results and Discussion

Interassociation Parameter K_A Values. The PCAM provides a direct understanding of the thermodynamics of a binary polymer blend system with H-bonding. The main Painter–Coleman association model

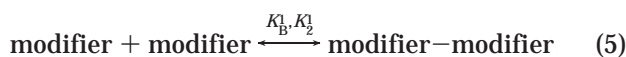
(PCAM) equation is based on the classical Flory–Huggins relation:

$$\frac{\Delta G_m}{RT} = \frac{\Phi_A}{N_A} \ln \Phi_A + \frac{\Phi_B}{N_B} \ln \Phi_B + \Phi_A \Phi_B \chi + \frac{\Delta G_H}{RT} \quad (2)$$

where Φ_A and Φ_B are the volume fractions, N_A and N_B are the degrees of polymerization of polymers A and B, and χ is the polymer–polymer interaction parameter (representing the dispersion force), which can be estimated using a group contribution method as proposed by Coleman et al.¹ Painter and Coleman have formulated an energy of mixing for the specific interaction, i.e., the H-bonding term, $\Delta G_H/RT$, based upon classical thermodynamics. By applying the PCAM, it is necessary to determine a set of equilibrium constants describing the self-association, interassociation, and other properties of thermodynamics. The self-association of phenolic involves the usual hydroxyl–hydroxyl interaction characteristics that require a minimum of two equilibrium constants, K_2 and K_B , to account for the formation of hydrogen-bonded “dimers” and “multimers”, respectively.¹ The usual interaction scheme that was considered in the PCAM-based upon competing equilibrium is described as the following:



The interassociation equilibrium parameter K_A reflects the tendency of the H-bonding association between phenolic and modifier. An additional competing equilibrium has to be considered for those modifier polymers showing strong self-association (e.g., phenoxy and PVA in this study) as follows:



where K_B , K_2 and K_B^1 , K_2^1 are self-association equilibrium constants of phenolic and modifier, respectively. All those association parameters contribute to miscibility and the competition from the variety of H-bonding existing within the phenolic blend. From previous measurements, K_2 and K_B of the phenolic are 23.29 and 52.31, respectively.¹³ To examine the effect from different modifier structures, we have selected the polymers containing hydroxyl, ester, and ether functional groups (e.g., phenoxy, PDA, poly(ethylene oxide), and poly(vinyl alcohol) resin) which are all able to form a strong H-bond with OH of the phenolic. The analogue molecules chosen to deduce the equilibrium constants are summarized in Table 1 where 2,4-xyleneol is used to model the phenolic. In this study, solutions based on the “free” (non-H-bonded) OH group absorption (2,4-xyleneol concentration 0.02 M) and the respective model compound (IPPHP, ethyl acetate, EGDME, or 2,4-pentanediol) by varying concentrations in cyclohexane were prepared for quantitative measurements. The FTIR background was obtained before the 2,4-xyleneol was added into the model compound solution. Figure 1 shows typical room-temperature IR spectra at different concentrations of EGDME mixing with 0.02 M 2,4-xyleneol in cyclohexane. The relative fraction of the “free” OH absorption is found to decrease with increasing EGDME concentration. The association constant K_a (in

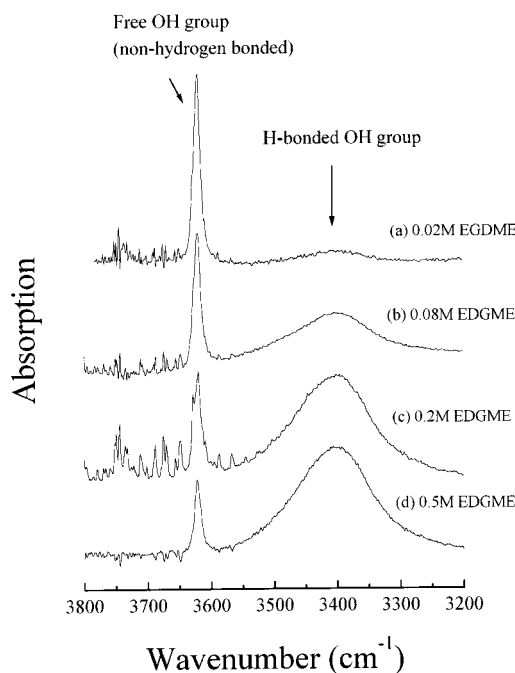


Figure 1. Infrared spectra in 3800–3200 cm^{-1} region for the various EGDME concentrations: (a) 0.02 M, (b) 0.08 M, (c) 0.2 M, and (d) 0.5 M mixed with the fixed 0.02 M 2,4-xyleneol in cyclohexane solution at 25 °C.

Table 2. Fraction of Free OH Group (f_m^{OH}) of 2,4-Xyleneol (0.02 M) Corresponding to the Various Concentration Model Compound in Cyclohexane Solution

[model] (M)	f_m^{OH}	K_a	[model] (M)	f_m^{OH}	K_a
(a) Model Compound: IPPHP ¹⁵					
0.04	0.754	9.309	0.20	0.425	7.190
0.08	0.619	8.532	0.25	0.384	6.741
0.10	0.573	8.135	0.40	0.331	5.239
(b) Model Compound: Ethyl Acetate ¹³					
0.08	0.653	7.26	0.25	0.394	6.48
0.1	0.601	7.22	0.4	0.298	6.09
0.2	0.442	6.67	0.5	0.257	5.96
(c) Model Compound: EGDME ¹⁰					
0.04	0.837	5.276	0.16	0.591	4.565
0.08	0.720	5.221	0.20	0.539	4.490
0.125	0.648	4.606	0.40	0.455	3.083
(d) Model Compound: 2,4-Pentanediol					
0.006	0.950	10.52	0.04	0.817	6.17
0.008	0.940	9.43	0.06	0.781	5.05
0.01	0.925	9.62	0.08	0.768	4.02
0.02	0.871	8.51	0.1	0.751	3.48

L mol^{-1}) is calculated from the f_m^{OH} , the fraction of the “free” OH of 2,4-xyleneol in solution, according to the method proposed by Coggeshall and Saier:¹⁴

$$K_a = \frac{1 - f_m^{\text{OH}}}{f_m^{\text{OH}}(c_A - (1 - f_m^{\text{OH}})c_B)} \quad (6)$$

where c_A and c_B are the concentrations of model compound and 2,4-xyleneol in mol L^{-1} , respectively. The K_a 's for blends with phenolic/non-self-associated modifiers blend, i.e., phenolic/PEO and phenolic/PDA, are obtained by following the PCAM prediction,¹ while the K_a 's for the modifier with self-association modifiers (e.g., phenoxy and PVA) follow the modified route as described previously.¹⁵ Table 2a–d summarizes the data of f_m^{OH} of the 2,4-xyleneol containing various concentrations of IPPHP,¹⁵ ethyl acetate,¹³ EGDME,¹⁰ and 2,4-

Table 3. Self-Association Equilibrium Parameters of Phenolic and the Intermolecular Molecular Equilibrium Constants K between Phenolic and Modifier

interaction	K (25 °C)
self-association of phenolic ¹³	
dimer formation (K_2)	23.29
multimer formation (K_B)	52.31
self-association of phenoxy ¹⁵	
dimer formation (K_2)	23.29
multimer formation (K_B)	14.40
self-association of PVA	
dimer formation (K_2)	43.12
multimer formation (K_B)	63.30
interassociation constant (K_A)	
between phenolic and phenoxy ¹⁵	114.0
between phenolic and poly(adipic ester) ¹³	89.52
between phenolic and poly(ethylene oxide) ¹⁰	67.64
between phenolic and poly(vinyl alcohol)	121.8

pentanediol in cyclohexane solution, respectively. The intrinsic interassociation constants, K_A 's, were obtained from the extrapolation to zero concentration of these model compounds. These values are 9.46 for IPPHP, 7.43 for ethyl acetate, 5.61 for EGDME, and 10.11 for 2,4-pentanediol. These K_A 's were modified to become K_A 's by dividing the molar volume of the phenolic repeat unit (0.083 L/mol at 25 °C). Those interassociation equilibrium constants calculated are 114 for IPPHP, 89.5 for ethyl acetate, 67.6 for EGDME, and 121 for 2,4-pentanediol, respectively. Table 3 tabulates equilibrium constants obtained from these four model compounds. Two important features are delineated. First, the self-association equilibrium constants of the phenolic, K_2 and K_B , are always lower than the intermolecular interaction equilibrium constant, K_A , in all these phenolic/modifier blends. The intensity of the H-bonded OH group increases with the addition of model compounds (0.04 M) into the 2,4-xyleneol (0.02 M) cyclohexane solution as shown in Figure 2. This result suggests that the formation of interassociated H-bonds is more favorable over the self-associated H-bonds of the phenolic. This is responsible for the main driving force for miscibility in these blends. Additionally, it means that the heterogeneity of phenolic blends is minimized because the K_A value is higher than that of K_2 and K_B .¹⁶ This result also suggests that the negative contribution to free energy from the formation of phenolic–modifier H-bonding is large enough to overcome the self-association and London dispersion force in these phenolic blend systems and thus results in miscible blends.¹⁷ Second, with regard to the H-bonding functional groups, the K_A value shows an increasing order from phenolic/PEO blend (hydroxyl–ether group, K_A = 67.64), phenolic/PDA blend (hydroxyl–carbonyl group, K_A = 89.52), to the phenolic/phenoxy and phenolic/PVA blend (hydroxyl–hydroxyl group, K_A = 114 and 121). In a variety of cyclohexane solutions containing 0.04 M model compounds and 0.02 M 2,4-xyleneol, the relative fraction of the H-bonded 2,4-xyleneol OH group also increases with the same trend, hydroxyl–ether, hydroxyl–ester, and then hydroxyl–hydroxyl. This result agrees with the general conception of the strength of the H-bonded OH group.

For modifiers showing strong self-association (e.g., phenoxy and PVA), the competition of H-bonding interaction between intermolecular and intramolecular self-association within phenolic and modifier also needs to be considered. Both K_A values of phenolic/phenoxy and phenolic/PVA blends are substantially higher than their self-association equilibrium constants. Those blends are

considered miscible where the phenoxy and PVA chains are able to penetrate into the phenolic domain.

This PCAM describes interaction of H-bonding in the forms of “monomer” (non-H-bonded species), “dimers” (H-bonded pair), and “trimers”, etc. A few critical assumptions made in this model are¹ (1) the mixing is random, and molecules A and B are of roughly equal of size and shape; (2) the free volume of the polymer blends is completely neglected; and (3) the PCAM argues on theoretical grounds that the results are valid as long as the chain is highly flexible. As will be examined in the following, despite the presence of strong hydrogen bonding, there are several discrepancies between experimental observations and PCAM predictions due to violate a portion or all of the above assumptions. In what follows, we will examine the configuration of H-bonding (from solid-state IR spectra), T_g behavior, chemical shift of solid-state NMR spectra, and excess volume within these blends. These microstructure characters are able to address more specifically the effect of the difference in modifier structures and the excess volume change in phenolic blends, which have all been considered to be identical by the PCAM.

Solid-State IR Spectra in Hydroxyl Stretching Region (3800–3200 cm^{-1}). In the pure phenolic resin, the most relevant feature in the IR spectrum is the presence of a broad band at 3800–3200 cm^{-1} as shown in Figure 3c, with corresponding OH groups in several different H-bonding configurations. The contribution from lower to higher wavenumber can be assigned as the OH groups forming H-bonds with other OH groups as trimer ($\sim 3300 \text{ cm}^{-1}$) and dimer ($\sim 3400 \text{ cm}^{-1}$), in addition to the “free” OH groups ($\sim 3590 \text{ cm}^{-1}$) as indicated in Figure 3c.¹⁸ Regardless of the high OH group content in the phenolic resin, a certain fraction of the “free” OH groups is evident. This is probably due to the intrinsic chain rigidity of the phenolic resin that tends to hinder the self-association. We will not dwell further on the OH group stretching region from the infrared spectra of these phenolic blends due to inherent difficulties in quantifying these data. It is expected that, upon mixing these modifiers with the phenolic, a portion of these “free” OH groups originating from the breaking off of the phenolic intraassociation will be consumed by the formation of interassociation between the modifiers and the phenolic because all those K_A values are substantially higher than K_2 and K_B of the phenolic in this study. The fraction of the “free” OH band relative to the H-bonded band decreases with different degrees by blending with different modifiers as shown in Figure 3. As observed in Figure 3, the trend shows that the fraction of the “free” OH ($\sim 3590 \text{ cm}^{-1}$) decreases with the increase of the H-bonded band fraction (centered at approximately $\sim 3400 \text{ cm}^{-1}$) following the order of phenolic/phenoxy, phenolic/PDA, pure phenolic, phenolic/PEO, and phenolic/PVA (all 75/25 wt %). Whether the maximum of the H-bonded OH band is shifted toward higher or lower wavenumber, the final result depends on the decrease or increase of the “free” OH group band upon blending. Compared to the pure phenolic, the relative fraction of the “free” OH group band decreases in phenolic/PEO and phenolic/PVA blends but increases in phenolic/phenoxy¹⁵ and phenolic/PDA blends. Interestingly, this order does not follow the order of K_A 's obtained from the PCAM. This observation suggests that these “free” OH groups are not completely consumed, and the redistribution of these OH groups varied

Table 4. Qualitative Description of the Molecular Structure of the Modifier

modifier	K_A (PCAM)	intramolecular H-bonding (self-association)	degree of crystallinity	molecular segmental mobility ^a	fraction of phenolic H-bonding forming
phenoxy	114	yes	amorphous	flexible (2)	increased
PDA	89.5	no	semicrystalline	relatively rigid (3)	increased
PEO	67.6	no	semicrystalline	high flexible (1)	decreased
PVA	120	yes	semicrystalline	rigid (4)	decreased

^a The ether group density is listed in increasing order in the parentheses.

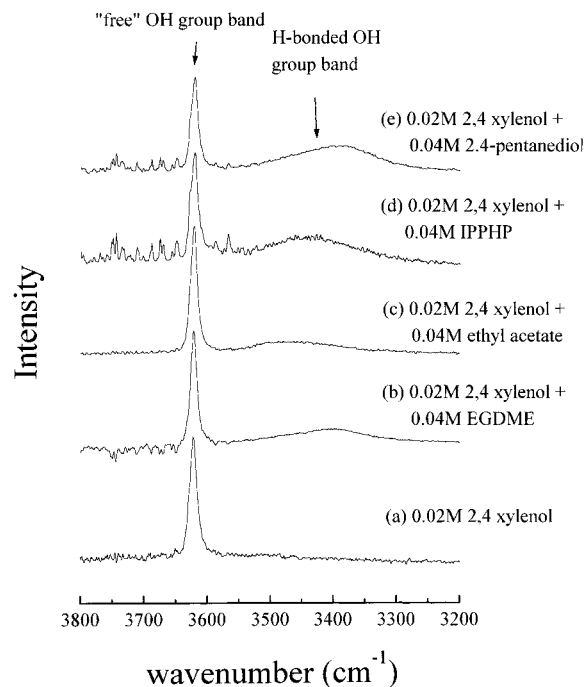


Figure 2. Infrared spectra in 3800–3200 cm^{-1} region for (a) 0.02 M 2,4-xyleneol, (b) 0.02 M 2,4-xyleneol + 0.04 M EGDME, (c) 0.02 M 2,4-xyleneol + 0.04 M ethyl acetate, (d) 0.02 M 2,4-xyleneol + 0.04 M IPPHP, and (e) 0.02 M 2,4-xyleneol + 0.04 M 2,4-pentanediol in cyclohexane solution at 25 °C.

with different modifiers, especially in the modifier with the longer repeated unit. By keeping up with the notion drawn from the model compounds, the interactions between phenolic and modifiers are strong, and the resultant blends are completely miscible. How can one rationalize the various degrees of “free” OH group fraction upon blending?

The molecular structures of modifiers were depicted in the second column of Table 1. Among all four modifiers, PEO and PVA possess a potential H-bonding site for every repeated unit of two carbons while phenoxy and PDA contain a substantially higher non-H-bonding portion per repeated unit. In phenolic/PEO and phenolic/PVA blends, the high density of those potential H-bonding sites is able to more effectively consume available “free” OH groups.

In blending with the other two modifiers, phenolic/phenoxy and phenolic/PDA blend, more nonassociation free “OH” groups are relatively created from those originally H-bonded phenolic possibly due to the entropic effect of the longer repeated unit in both phenoxy and PDA resins. It is expected that a greater fraction of these nonassociated “free” OH groups are present in these blends. Despite the rather high K_A constants, the longer segments of these non-H-bonding function groups of the modifiers (phenoxy and PDA) tend to hinder or even destroy the intraassociation of OH groups within the phenolic resin. Such a structure could lead to two

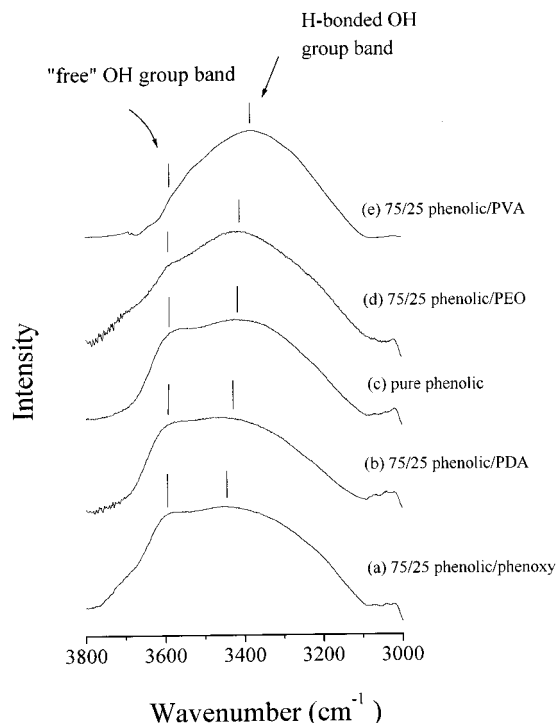
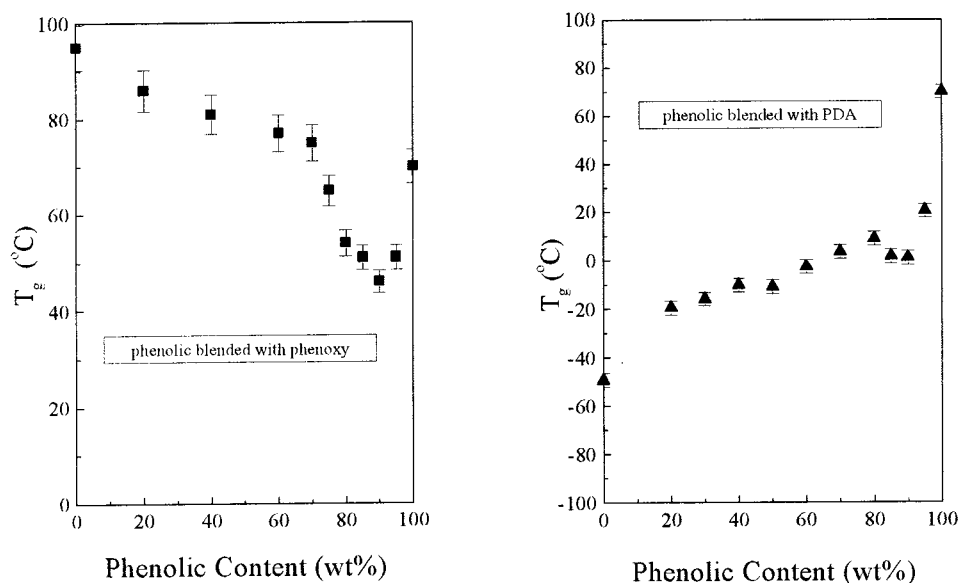


Figure 3. Infrared spectra in the 4000–3000 cm^{-1} region for pure phenolic resin and various 75/25 phenolic/modifier blends at 50 °C: (a) pure phenolic resin, (b) phenolic/phenoxy, (c) phenolic/PEO, and (d) phenolic/PVA blends.

important implications: (1) inhomogeneous H-bonding configuration in a blend leading to microdomain phase separation with size larger than the miscibility defined by conventional criteria and (2) deviation from the thermodynamics prediction by the PCAM based on the “true” miscibility. These two arguments were demonstrated by the experimental T_g s of phenolic/modifier blends.

The T_g Behaviors of Phenolic Blends. A single glass transition temperature is commonly accepted as evidence for a fully miscible polymer blend. Those phenolic blends from all four modifiers at different compositions exhibit a single glass transition, consistent with the notion that they are all driven by the strong interassociation of H-bonding to form miscible blends. The T_g data for various phenolic/modifier compositions are listed in Figure 4 for those four modifiers. It is interesting to note that the phenolic resin blended with modifier with a longer repeating unit (i.e., phenoxy or PDA) shows a substantially negative T_g deviation in the phenolic-rich region (Figure 4a). On the contrary, the phenolic resin blended with modifier with the shorter repeating unit (i.e., PEO or PVA) shows a positive T_g deviation. Similar to the variety of the “free” OH detected by IR, the T_g deviation also exhibits different behaviors from various phenolic/modifier blends. Since K_A values of these phenolic/modifier blends were substantially greater than that of the self-association,

(a) Modifier with longer repeated unit



(b) Modifier with short repeated unit

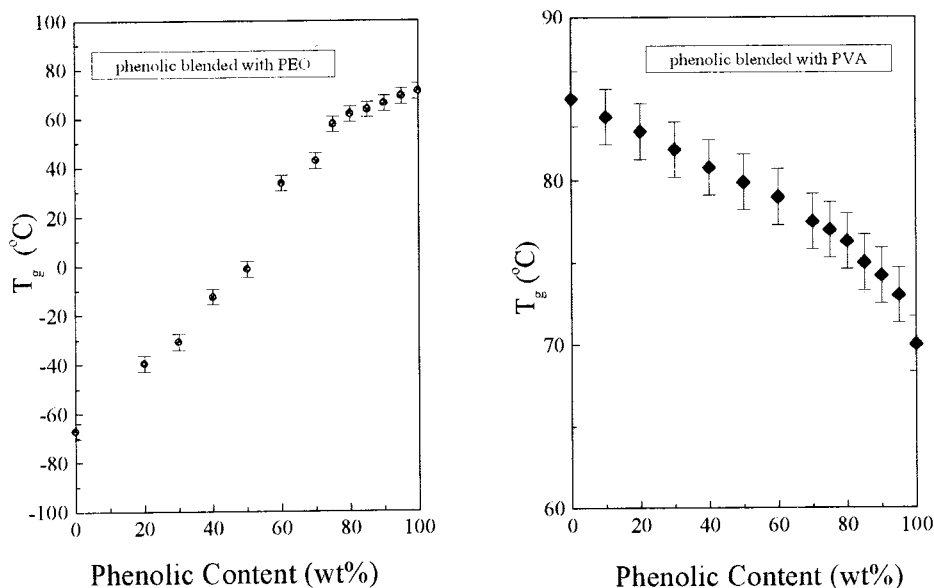


Figure 4. T_g behavior of various phenolic/modifier composition blends: (a) phenolic/phenoxy blend, (b) phenolic/PDA blend, (c) phenolic/PEO blend, and (d) phenolic/PVA blend.

it implies that these modifier chains are able to extend as far as possible in these phenolic blends. According to the argument of the PCAM, the T_g deviation is a result of entropy change corresponding to the change in the number of H-bonding interactions within these phenolic blends.¹⁹ In phenolic/PEO and phenolic/PVA blends, both PVA and PEO possess short repeating units with a higher potential H-bonding functional group density and a higher K_A value that tend to form a higher density of intermolecular H-bonding with the phenolic. This higher density of intermolecular H-bonding not only overcomes the energy of self-association upon blending but also reduces the entropy of the phenolic blend. As a result, the framework of these blends becomes stiffer, and the observed positive T_g deviation is therefore expected. These two cases are similar to examples given by the PCAM in their original publications.²⁻⁷ On the other hand, both phenoxy and PDA molecules with the long repeating unit provide a relatively smaller

number of potential H-bonding sites to form less intermolecular H-bonds with the phenolic. The reduction in entropy by forming a phenolic-modifier interaction for those modifiers with the long repeating unit is not great enough to overcome the entropy increase associated with the breaking off of the self-association of the phenolic. The long repeating unit length and the low density of the potential H-bonding sites induces the additional entropy factor ($-T\Delta S_m$). As a result, it will elevate the entropy upon blending and thus result in substantial T_g reduction in these phenolic blends. The variations of the entropic change ($-T\Delta S_m$) upon blending with short and long repeating units as a function of composition were schematically demonstrated in Figure 5, in which the entropic change of the phenolic/modifier with the long repeating unit blend is greater (further away from zero) than that of phenolic/modifier with the short repeating unit blends.

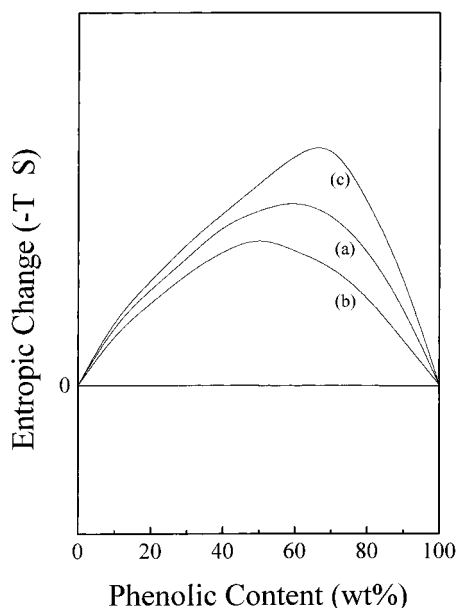


Figure 5. Variation of the entropic change ($-T\Delta S_m$) upon blending with short and long repeated unit as a function of composition: (a) PCAM predicted, (b) upon blending with short repeated unit, and (c) upon blending with long repeated unit.

For phenolic/phenoxy and phenolic/PDA blends, the negative T_g deviation is less in the phenolic-poor region than in the phenolic-rich region as shown in Figure 4a,b. The observed asymmetry of the T_g deviation versus composition is due to different changes in entropy upon mixing. The special characteristics of the phenolic is the presence of an extremely high OH group density and the formation of high density of the intraassociated H-bonds, resulting in lower entropy as well as higher T_g relative to other polymers. Hence, the entropy change of the phenolic upon blending is greater in the phenolic-rich region. In addition, the entropy of these modifiers is not as changeable as the phenolic resin; therefore, the T_g deviation is less pronounced in the phenolic-poor region. The plausible explanation of such discrepancies can be traced back to both the negative T_g derivation and the substantially lower value in the phenolic-rich region, which are not expected based upon the PCAM predication. Since a single T_g was observed for all these phenolic/modifier blends, the inhomogeneous structure in microdomains is expected to be smaller than that defined by DSC criteria.

These microstructure characteristics can be further examined by solid-state NMR special chemical shifts and free volume expansion/contraction techniques that was described in the following section.

Solid-State ^{13}C CP/MAS NMR Spectra. Typical ^{13}C CP/MAS NMR spectra of the hydroxyl-substituted (α) carbon of the phenolic in pure phenolic resin and various phenolic/modifier = 80/20 blends were depicted in Figure 6, where a variety of α carbon chemical shifts was shown. This variety is related to its H-bonding strength, which produces a small perturbation to the magnetic shielding on the nucleus and results in downfield chemical shift (deshielding) compared to the ones without H-bonding.²⁰ Normally the alteration of the ^{13}C chemical shift, for example the α carbon in phenolic, reflects the varying strength of H-bonding and thus the change of enthalpy. The peak location of the ^{13}C resonance is the averaged values of those H-bonded and non-H-bonded moieties. Therefore, the change in this

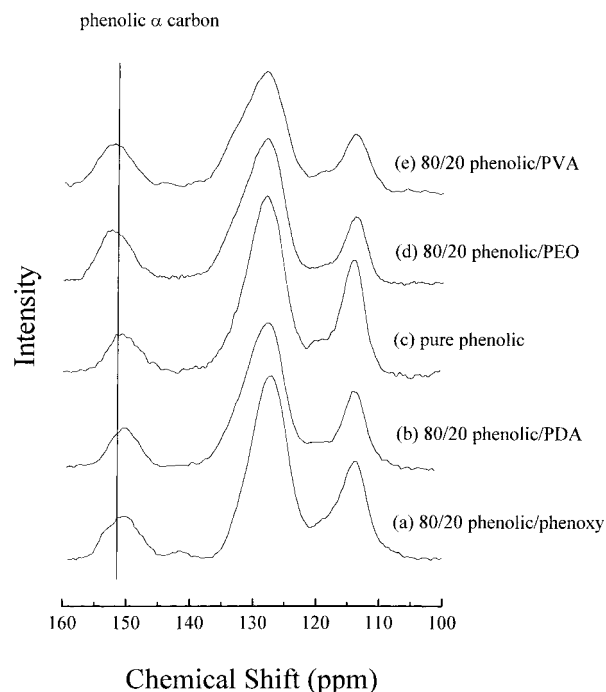


Figure 6. Typical solid-state ^{13}C CP/MAS NMR spectra of the hydroxyl-substituted (α) carbon of phenolic in pure phenolic resin and various phenolic/modifier blends: (a) phenolic/phenoxy, (b) phenolic/PDA, (c) pure phenolic resin, (d) phenolic/PEO, and (e) phenolic/PVA blends.

shift can be considered as the change in the "free" OH fraction, instead of the variation of the H-bonding strength. The α carbon resonance in pure phenolic is at 151.2 ppm. This same resonance in phenolic/phenoxy and phenolic/PDA blends (80/20) shifts upfield, and that in phenolic/PEO and phenolic/PVA blends occurs downfield relative to the reference shift. In phenolic/phenoxy and phenolic/PDA blends with the longer repeating unit, the upfield resonance indicates less density of the hydrogen-bonded OHs. On the contrary, the resonance downfield occurring in phenolic/PEO and phenolic/PVA blends suggests that more hydroxyl are hydrogen-bonded relative to the pure phenolic. These results are consistent with the IR measurements and suggest that phenolic/PEO and phenolic/PVA blends possess higher inter- H-bonding interaction than that for phenolic/phenoxy and phenolic/PDA blends.

Excess Volume. The excess volume has been derived on the basis of thermodynamics of a polymer blend which is intended to describe free volume change of polymer blends.^{21,22} Figure 7 shows the representative results of excess volume of various compositions for phenolic/phenoxy and phenolic/PEO blends. On the basis of the fact that the K_A value of the phenolic/phenoxy blend is almost twice as large as that of the phenolic/PEO blend, the interaction in the former is expected to be stronger than in the latter and greater free volume contraction is also expected. However, experimental results of these two blends exhibited completely opposite excess volume behavior, i.e., contraction (negative deviation) in phenolic/PEO blend, and expansion (positive deviation) in phenolic/phenoxy blend. The higher K_A value of the phenolic/phenoxy blend tends to better cohere with both polymer components through strong intermolecular H-bonding and should result in volume contraction. The increase in free volume by the reduced H-bonding density of this phenolic/phenoxy blend is more than the free volume decreased by the

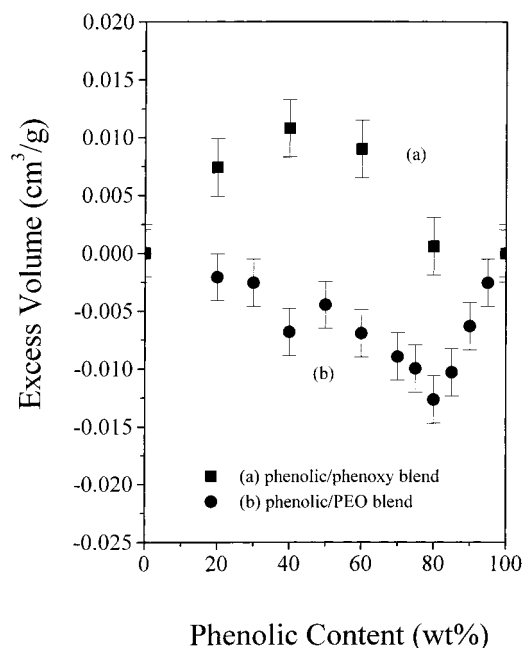


Figure 7. Representative results of excess volume for various (a) phenolic/phenoxy (■) and (b) phenolic/PEO (●) blends.

higher K_A value and thus leads to overall free volume expansion. On the other hand, the phenolic/PEO blend with shorter repeated unit of the PEO gives higher H-bonding density and results in volume contraction as would be expected. The more favored entropic effect from the longer repeating unit segment hinders the opportunity of forming H-bonding to those vicious "free" hydroxyls and thus favors free volume increases. As mentioned previously, this factor gives a positive entropic contribution to the Gibbs free energy of a blend (e.g., the term $\Phi_A\Phi_B\chi$ in eq 2 to be positive) which is not been considered in the original PCAM. This result agrees well with the results concluded from IR quantification and NMR chemical shifts.

The excess volume result provides a clear contrast between ideal and real blends. Therefore, it is necessary to consider the structure of the modifier in deducing phenolic blend properties.

Ramification

One may consider H-bonding as a physical cross-linking that drives the miscibility with strong intermolecular H-bonding in phenolic blends. The main factor influencing the miscibility is the strength of association that includes both inter- and intraassociations. However, the strong interassociation effect dominates for all blends due to the relatively high K_A values. Therefore, the influence of intraassociation in phenoxy and PVA are considered to be weak in these blends.

When the phenolic is blended with modifier with the longer repeating units, i.e., phenoxy and PDA, the increasing entropic factor of the modifier competes with H-bonding (enthalpy favored) and thus hinders the contacts within itself and with unlike units of the modifier chains. Some H-bonded OHs of phenolic are set to be "free" due to insufficient functional group of modifier is available to interact with those linkages. The change of physical interaction has the net effect of expanding the free volume and decreases the H-bonding concentration in the H-bonded "cross-link" network. The free volume expansion as well as T_g reduction is indeed

being observed. The increasing " χ " effect gives a positive contribution to the entropic factor and raises the total Gibbs free energy in the phenolic blend.

In the highly H-bonded modifiers with short repeating units such as PEO and PVA, these OHs are more effectively bonded. The effect of molecular structure is less pronounced for a modifier with a short repeating unit, where the entropic effect becomes less important. A free volume contraction resulting from the dominating interassociation is observed. In this case, the total Gibbs free energy is governed by the reduction of enthalpy from the H-bonding in a manner similar to that described by the PCAM prediction.

In the composition-dependent T_g , PEO shows an S-shaped relation and the PVA gives positive deviation. Both blends show behavior consistent with the scope described by the PCAM. For blends with phenoxy and PDA, double-dip curves with negative deviation are found in the T_g deviation, which are not expected on the basis of the PCAM prediction of a "true" miscible blend. The discrepancy can be attributed to the appreciable entropic effect of the modifier, which was not considered in the original PCAM model. Therefore, it is necessary to include these structural factors to the physical interaction " χ " (which is influenced by the entropic effects) together with the H-bonding (the enthalpic effects) in considering the thermodynamics in blends.

Conclusions

The current study has demonstrated different thermodynamic behaviors of phenolic blends with various polymeric modifiers. The competition between enthalpic and entropic effects is discussed through using PCAM, T_g behavior, solid-state IR, solid-state NMR, and free volume techniques. The discrepancies between the experimental observations and the thermodynamic prediction may come from the entropy change of the modifier that creates more free hydroxyls and leads to microdomain heterogeneity. This hypothesis is supported by the evidence from solid-state IR, T_g behavior, solid-state NMR, and excess volume. The observed negative T_g deviation and free volume expansion after blending can be attributed to the additional entropy increment by introducing the longer repeating units of the modifier. The modifier structure, with favorable entropic effect, can create microdomain heterogeneity with a scale small than that expected of a miscible blend on the basis of general DSC criteria. This heterogeneity in this system is not enough to produce multiple T_g 's.

The PCAM model is able to provide a general prediction of thermodynamics and T_g behavior for a "true" miscible blend. These microscopic structure variations in blends, such as various H-bonding configurations, can be deduced from solid-state IR, solid-state NMR, and free volume, which will complement deficiencies of the PCAM derived thermodynamics. Taking the factor of molecular structure into consideration, the understanding of phenolic blend thermodynamics predicted from the PCAM can be more accurate.

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- (18) In the phenolic/phenoxy blend, both free OH group absorption intensities in their parents are weaker than in 75/25 phenolic/phenoxy blend. On the contrary, both free OH group absorption intensities in pure phenolic and PVA are stronger than their blend. The effect of OH group of modifier on IR spectrum can be neglected for qualitative description of the interaction presents within phenolic rich region.
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