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Thermodynamic properties of the novolac type phenolic resin blended with poly(hydroxyl ether of bisphenol A)

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The inimitable geometry of novolac type phenolic resin (phenolic) and the strong inter-association cause the special microstructure in which the poly(hydroxyl ether of bisphenol A) (phenoxy) is sporadic in phenolic-rich region. Thermodynamic properties of the anomaly blend of phenolic and phenoxy were predicted by the Painter–Coleman Association Model. A modified method was used to obtain the equilibrium constant parameters that both polymers including self-association species, were utilised to describe the self-association and inter-association between the functional groups in the blend. The interaction of hydroxyl between phenolic and phenoxy is more competent than that of self-association of phenolic and phenoxy. The specific heat capacity (Cp) of the blend decreases with temperature, and the excess heat capacities (ΔCp) of the blend are positive and approach zero while the temperature is high enough. Enthalpy is outstripped by entropy which causes the phase separation at higher temperature. The LCST phase diagram was illustrated from the experimental results and theoretical prediction. The blend system exhibits complete miscibility within moderate temperature range from the results of thermodynamic property. © 1997 Elsevier Science Ltd.

(Keywords: thermodynamic properties; phenolic resin; phenoxy)

INTRODUCTION

Owing to its good heat resistance, electrical insulation, dimensional stability, flame resistance and chemical resistance, phenol-formaldehyde resin (phenolic resin) has been widely used in industry[1–5]. However, it is brittle in nature and limited in its applications. Many approaches have recently been proposed to improve the toughness of the phenolic resin[6–9]. Those modified phenolic blends exhibit different phase behaviours, from completely miscible to partially miscible[8,9], that influences the physical properties of phenolic resin.

The phenoxy resin, containing a hydroxyl group which has a hydrogen-bonding with other polymers, shows flexible properties and can be used as a modifier for other brittle polymers. The miscibility of the poly(hydroxyl ether of bisphenol A) (phenoxy resin) with other polymers has been investigated[10–14]. Intermolecular interactions are considered to play a key role in polymer compatibility.

Phenolic resin which contains a high density of hydroxyl group will interact with other polymers[10]. The thermodynamic properties of the phenolic resin blends that would affect the physical and mechanical properties significantly, however, have not been studied in detail yet. Recently, Coleman and Painter proposed an association model to represent the thermodynamic behaviour of polymer blends[15]. In order to account for the hydrogen-bonding interactions, a ($\Delta G_H/RT$) term is added to the Flory–Huggins equation. Painter, Coleman and coworkers have applied this model to a series of polymer blends, including poly(vinyl phenol) blended with ether- and ester- and pyridine-containing polymers[16–20]. In those cases, the hydroxyl group of poly(vinyl phenol) can provide hydrogen-bonding. However, there are some difficulties in calculating the parameters of the Painter–Coleman Association Model (PCAM) in phenolic/phenoxy blend system, since both polymers contain hydroxyl groups. The only way to measure the quantity of hydrogen-bonding is using the hydroxyl stretching band. It is difficult to separate the quantity of the 'free' hydroxyl band from each polymer in i.r. spectra. It is necessary to prescan *FT*i.r. spectrsocopy as background before the model component of polymer is added to the solution to achieve this. The self-association of polymer affects the result of prediction; it can only be predicted correctly in their rich region.

In this study, the conception of microstructure of blend was described. The PCAM is demonstrated so that it can be applied to a blend where both components contain hydroxyl groups. The low molecular weight analogue is used instead of the polymer on the *FT*i.r. test. The association equilibrium constants and enthalpies of the polymer blend were calculated from the variations of the free hydroxyl band absorption with varying model compound concentration and frequency shift in cyclohexane solution, respectively. The binary interaction model was applied to predict thermodynamic properties of the phenolic/phenoxy blend. The excess heat capacity supports the evidence of the special conformation on the phenolic/phenoxy blend system, and agrees well with the results of our previous study[21].

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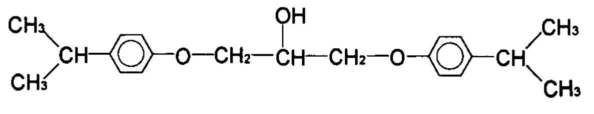
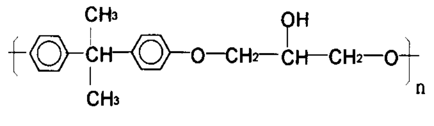
EXPERIMENTAL

Novolac type phenolic resin (phenolic) and 1,3-bis(4-(2-propyl)phenoxy)-2-propanol (IPPHP) were synthesised in this laboratory [21]. IPPHP was used as a model compound of poly(hydroxyl ether of bisphenol A) (phenoxy).



The novolac analog, 2,4 dimethane phenol(2,4 xylenol) was purchased from the Lancaster synthesis Co., U.S.A. Its purity was higher than 97% and was used as received. The poly(hydroxyl ether of bisphenol A) (phenoxy resin, PKHH) was obtained from the Union Carbide Co., U.S.A., with a molecular weight Mn of 23 000. The repeated unit of phenoxy is described as follows:



Infrared spectra were obtained by using an *FT*i.r. spectrometer (Bio-Rad FTS-155, U.S.A.). In all cases, at least 16 scans with an accuracy of $2\,cm^{-1}$ were signal-averaged. For film samples, phenolic and phenoxy were mixed in THF (1% w/v) at room temperature according to the designed compositions. The mixed solution was stirred for 6–8 hr, and then allowed to evaporate slowly at room temperature for 1 day. The blend films were then dried at 50°C for 2 days and annealed at 140°C for 2 hr under vacuum. i.r. studies were carried out with the conventional NaCl disk method. For solution samples, an adequate permanently-sealed cell with NaCl windows of 0.05 mm path length (Wilmad, U.S.A.) was used. A single optical path was used for studying the self-association of 2,4 xylenol and the inter-association between 2,4 xylenol and IPPHP. All model compound solutions obeyed the Beer–Lambert law. Since the specific conformation of cyclohexane is the most suitable[10,16,22], it was used as solvent in this study. The Miscibility Guide and Phase Calculator software[15] were used to calculate the thermodynamic properties of polymer blends.

The specific heats of the pure polymers and their blends were determined by differential scanning calorimeter (d.s.c; Du-Pont, d.s.c. 2000); the external standardisation method was used. A reference baseline was recorded in an isothermal mode at 10°C for 10 min, and then the sample was heated to 190°C at a rate of 20°C/min, and then kept in an isothermal mode for 10 min at 190°C. The deflection of the d.s.c. curve was recorded during the dynamic scanning period. A ceramic disk (the external reference) and polymer specimen were scanned as aforementioned operating procedure. In all cases, aluminum pans were selected owing to them having a constant weight (within 2%). The heat capacity of the sample was obtained by an appropriate ratio of the deflections to the previously reported values of ceramic standard[23].

RESULTS AND DISCUSSION

Conception of anomaly miscibility of phenolic/phenoxy blends

In our previous study[24], the results of n.m.r. studies revealed the molecular details regarding the hydrogen-bonding interaction present in the miscible mixture of phenolic and phenoxy resin. The repartition of strong intramolecular to intermolecular interaction occurred on phenolic/phenoxy blend. The structural inhomogeneity of phenolic/phenoxy blend occurred in phenolic-rich and -poor regions due to the inimitable structure of phenolic and phenoxy. The intermolecular hydrogen-bonding component substitutes for the intramolecular interaction completely on their minor component blend regions (i.e. the self-association of phenoxy is completely converted to inter-association in the phenolic-rich region, and the self-association of phenolic has the same trend in the phenolic-poor region).

Inter-association constant (K_A)

In this work, both phenolic and phenoxy resin are self-association polymers. The phenoxy is sporadic in the phenolic-rich region which has been proven in our previous study[24]. Self-association of phenoxy effects on the blends can be neglected on this region. Similarly, self-association of phenolic can also be neglected on the phenolic-poor region. It is reasonable that the PCAM can be used in their minor regions. The interaction constant (K_A) is useful to investigate the thermodynamic properties of the blend in the phenolic-rich and phenolic-poor regions, but not in the intermediary region.

The i.r. spectra of the 2,4 xylenol and IPPHP cyclohexane solutions were used to determine the inter-association constant (K_A) between 2,4 xylenol and IPPHP. The K_A value is described as the ability of the interaction of hydrogen-bonding between phenolic unit and phenoxy unit.

In order to obtain a quantitative measurement of the actual fraction of 'free' hydroxyl of 2,4 xylenol presented in the 2,4 xylenol/IPPHP cyclohexane solution, it is necessary to prescan the IPPHP solution before the 2,4 xylenol was added to the IPPHP solution as background. (In here, the 'free' hydroxyl means the group is free from hydrogen-bonding.) This reduces the influence of the intensity of 'free' IPPHP hydroxyl on measuring the inter-association between 2,4 xylenol and IPPHP in the i.r. spectra. *Figure 1* shows 'free' hydroxyl band absorption of 2,4 xylenol on the concentration of 0.02 M 2,4 xylenol and various concentrations of IPPHP cyclohexane solution. The intensity of 'free' hydroxyl band absorption of $3620\,cm^{-1}$ is decreased with IPPHP contents.

Figure 2 shows 'free' hydroxyl band absorption of 2,4 xylenol and IPPHP at the concentration of 0.04 M in cyclohexane solution. The IPPHP shows two separated bands at 3610 and $3590\,cm^{-1}$. The band which appears at the higher wavenumber can be ascribed to 'free' hydrogen-bonding and the second one to intramolecular hydrogen-bonded hydroxyl. The 2,4 xylenol shows one band at $3620\,cm^{-1}$. The absorption bands of 2,4 xylenol are overlaid with that of IPPHP. The intensities of 2,4 xylenol absorption are five times high than those of IPPHP at $3620\,cm^{-1}$. When the interaction of 2,4 xylenol and IPPHP occurred, the background would change, which may affect the intensity of 2,4 xylenol in the 2,4 xylenol/IPPHP cyclohexane solution.

The intensity of 'free' hydroxyl of 2,4 xylenol must be corrected in 2,4 xylenol/IPPHP cyclohexane solution. The reason is explained as follows: in *Figure 3*, peaks (a) and (b) show the intensities of 'p' and 'q' which represent the absorption of free hydroxyl of IPPHP in neat IPPHP solution and IPPHP in 2,4 xylenol/IPPHP solution at the identical IPPHP concentration in i.r. spectra, respectively.

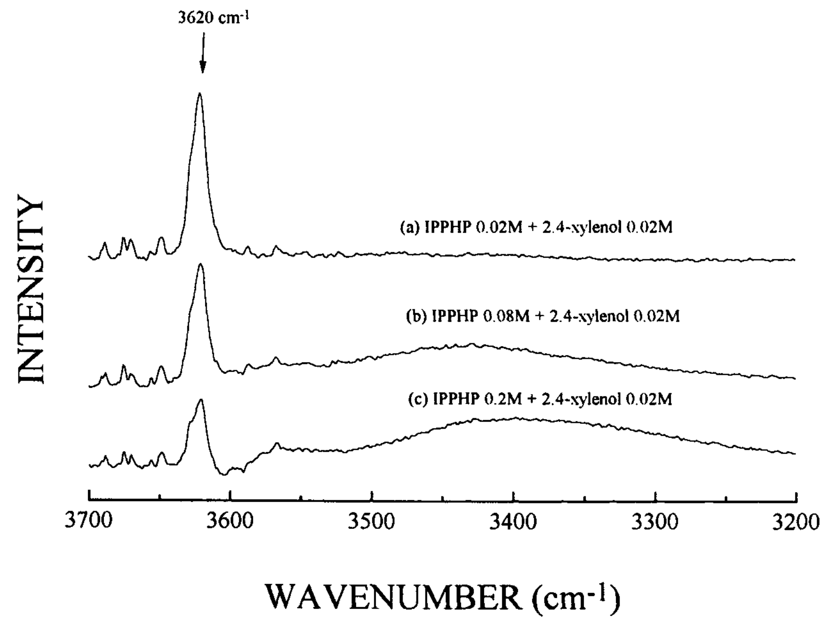


Figure 1 The 'free' hydroxyl band absorption of 2,4 xylenol at the concentration of 0.02 M 2,4 xylenol and concentrations of: (a) 0.02 M; (b) 0.08 M; and (c) 0.2 M IPPHP cyclohexane solution

Table 1 The fraction of free hydroxyl group (fm^{OH}) of 2,4 xylenol corresponding to various IPPHP cyclohexane concentrations

Conc. of IPPHP (M)	Intensity of absorption in spectra	Corrected intensity of absorption	fm^{OH}	Interaction constant *Ka*
0.04	0.022853	0.023866	0.753854	9.308572
0.08	0.017487	0.019574	0.618267	8.532039
0.10	0.01571	0.018152	0.573364	8.135074
0.20	0.009823	0.013442	0.424597	7.189562
0.25	0.008228	0.012166	0.384293	6.740758
0.40	0.006101	0.010465	0.330545	5.238609

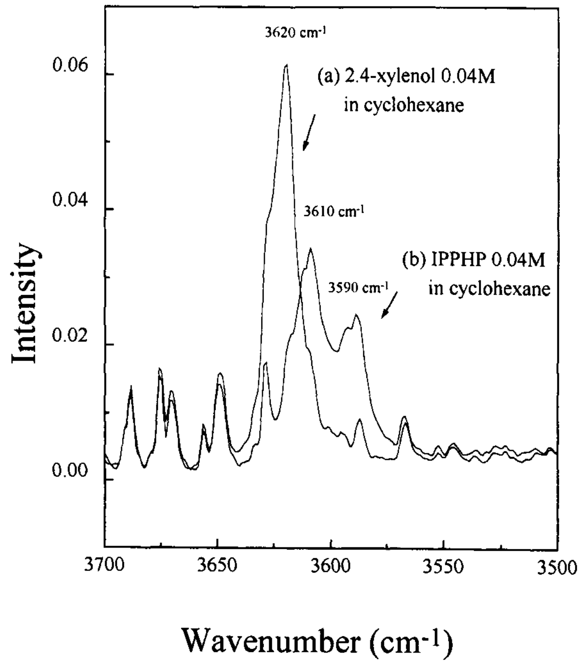


Figure 2 The 'free' hydroxyl band absorption of: (a) 2,4 xylenol; and (b) IPPHP at the concentration of 0.04 M in cyclohexane solution

The intensity 'q' can be obtained when the 2,4 xylenol is prescanned as background. Peaks (c) and (d) show the intensities of 'r' and 's' which represent the intensity of free hydroxyl in neat 2,4 xylenol solution and 2,4 xylenol in a mixture of 2,4 xylenol/IPPHP solution at the identical 2,4 xylenol concentration in i.r. spectra, respectively. The intensity of 's' is also obtained when the IPPHP is prescanned as background. The background has been changed from the intensity of 'p' to 'q', when 2,4 xylenol was added into the IPPHP solution. It is required to investigate the change in the (r − s)/(p − q) intensity ratio of 2,4 xylenol and IPPHP absorption at 3620 cm^{-1} bands when the interaction occurred. Unfortunately, this ratio can not be obtained easily due to the small difference in the relative intensity of 'free' hydroxyl in the 2,4 xylenol and IPPHP using various concentrations in i.r. spectra. Therefore, although being aware of the error source, it is considered this ratio equals 5. The correction of intensity of 2,4 xylenol on 2,4 xylenol/IPPHP solution 's' can be done by adding the value of 'p − q' [0.2(r − s)] to the value of 'S'.

Table 1 summarises the fraction of free hydroxyl group (fm^{OH}) of 2,4 xylenol corresponding to various IPPHP cyclohexane concentrations. The method proposed by Coggesthall and Saier[25,26] was used to calculate the association constant *Ka* (l mol^{-1}) from the following equation:

$$Ka = \frac{1 - fm^{OH}}{fm^{OH}(C_A - (1 - fm^{OH})C_B)} \qquad (1)$$

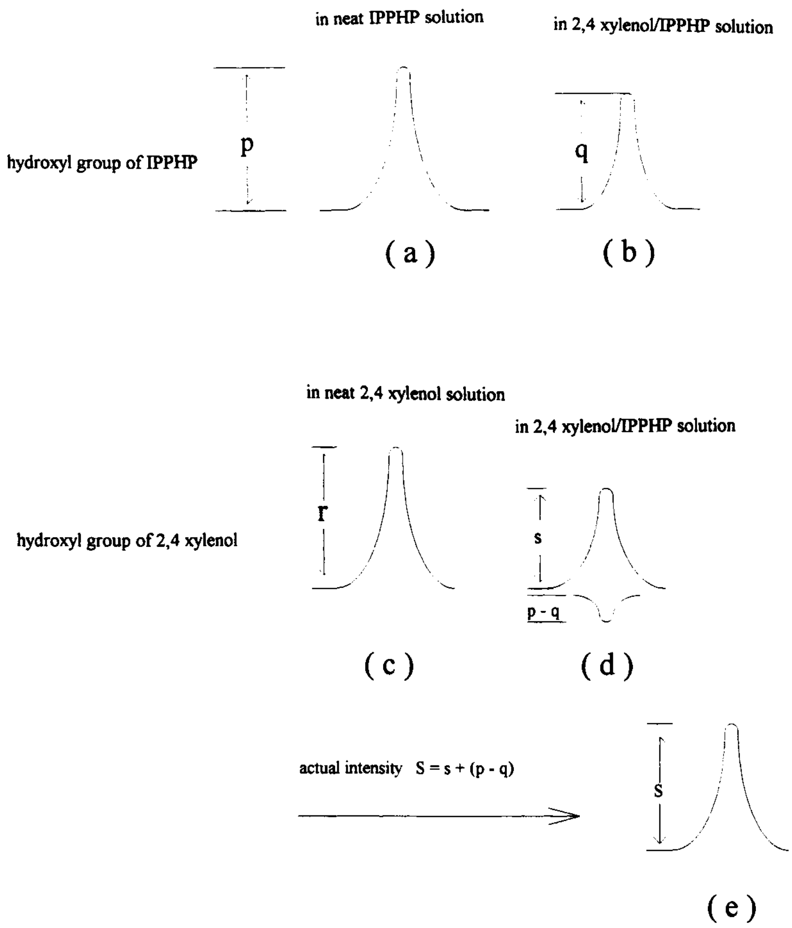


Figure 3 Schematic diagram depicting the corrected absorption of free hydroxyl of 2,4 xylenol in IPPHP/cyclohexane solution

Table 2 The chemical shift and enthalpies of self-association of phenolic and phenoxy resin, and that of inter-association between phenolic and phenoxy

Material		Chemical shift (cm^{-1})	Enthalpy (Kcal/ml)
Phenolic resin	Self-association		
	dimer formation (K_2)	−138	−4.25
	multimer formation (K_B)	−290	−6.11
Phenoxy resin	Self-association		
	dimer formation (K_2)	−100	−3.76
	multimer formation (K_B)	−144	−4.32
	Inter-association between phenolic and phenoxy (K_A)	−210	−5.12

where C_A and C_B are the concentrations of IPPHP and 2,4 xylenol in mol l^{-1}, respectively. The *Ka* value is concentration dependent. The reliable value of inter-association constant (9.45) can be obtained from the approach of zero concentration. The inter-association constant *Ka* has to be modified to become K_A by dividing the molar volume of the phenolic repeated unit (0.083 l/mole at 25°C). The equilibrium constant calculated is 114.

Enthalpies of self-association of phenolic and phenoxy resins were estimated from the observed shifts of the self-associated hydroxyl bands to the free hydroxyl bands, with the support of a correlation between band shifts and enthalpies[26]. The inter-association between 2,4 xylenol and IPPHP was investigated by taking the i.r. spectra of the 2,4 xylenol and IPPHP in cyclohexane solutions. The correlation of enthalpy (Δh) *versus* frequency shift ($\Delta\nu_{OH}$) for the hydroxyl band of 2,4 xylenol has been studied previously[27] and is expressed as follows:

$$-\Delta h\ (\text{Kcal mol}^{-1}) = 2.564 + 0.0122\Delta\nu_{OH}\ (\text{cm}^{-1}). \quad (2)$$

Table 2 summarises the chemical shift and enthalpies of self-association of phenolic and phenoxy resin, and that of inter-association between phenolic and phenoxy.

Prediction of free energy

The thermodynamic properties can be predicted for such anomaly polymer blend in spite of PCAM which does not describe both self-association polymer blend systems. The K_A value is higher than that of the self-association of phenolic and phenoxy which implies that the interaction of phenolic and phenoxy is stronger than self-association of both phenolic and phenoxy resin. It had been proven that phenoxy is sporadic in the phenolic-rich region, and phenolic is also sporadic in the phenoxy-rich region from a previous NMR study[24]. Self-association of phenoxy and phenolic can be neglected in their poor regions.

The properties and association parameter of phenolic resin and phenoxy are summarised in *Table 3* and *Table 4*,

Table 3 Properties of polymer used in this study

Polymer	Molar volume (ml/mole)	Molecular weight (g/mol)	Solubility parameter (cal/ml)$^{0.5}$	Degree of polymerization (D.P.)
Novolac type phenolic resin	84[a]	105[a]	12.05[b]	6[a]
Phenoxy resin	216[b]	284[b]	10.22[b]	80[a]

[a] Measured directly
[b] Estimated by using a group contribution method proposed by Coleman *et al.* [15]

Table 4 Association parameters of phenolic resin blended with phenoxy resin

Interaction	Dimer formation (K_2)	Multimer formation(K_B)
Self-association of phenolic	23.29	52.31
Self-association of phenoxy[a]	14.4	25.6
Inter-association with phenoxy (K_A)	114	

[a] Ref. [16]

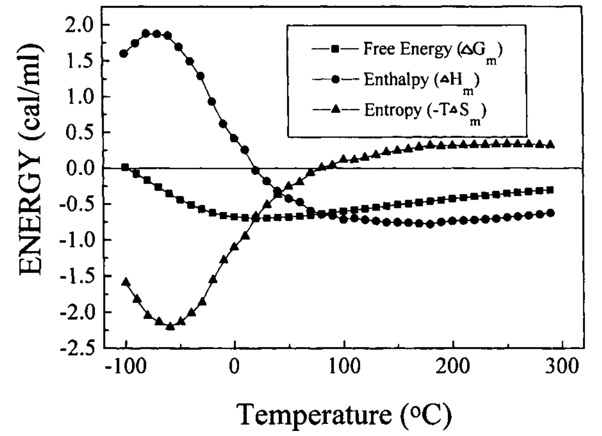


Figure 4 The total free energy (■), enthalpy (●) and entropy (▲) of mixing for 80/20 phenolic/phenoxy blends at temperatures between −100 and 300°C

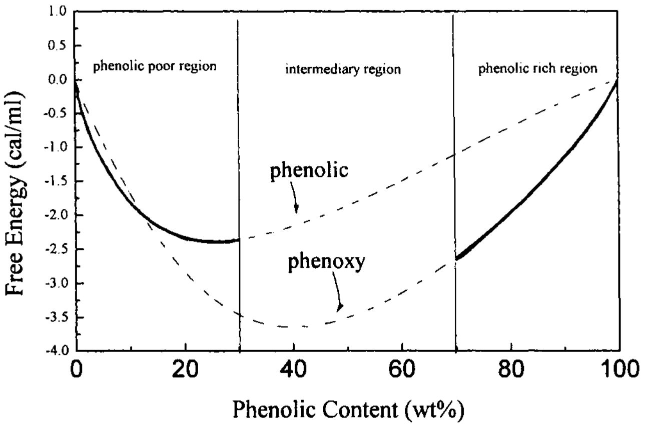


Figure 5 (a) the free energy (ΔGm) of phenolic/phenoxy blend at 25°C while the self-association of phenoxy is neglected; (b) the free energy (ΔGm) of phenolic/phenoxy blend at 25°C while the self-association of phenolic is neglected

respectively. The predicting procedure was described by the MG&PC software package[15].

As shown in *Figure 4*, the total free energy of mixing (ΔGm) for 80/20 phenolic/phenoxy (phenolic-rich region) blends at various temperatures is obtained. The calculation was based on temperatures from −100 to 300°C. The free energy of mixing is negative above −90°C, and a minimum value of 20°C is shown, which implies that the phase behaviour with both UCST and LCST would appear, since the ΔGm could be positive at lower and higher temperature from this prediction.

From the free energy of mixing (ΔGm) of the system at various temperatures, it is possible to calculate the enthalpy of the mixing (ΔHm) by using the Gibbs–Helmholtz relationship:

$$\partial(\Delta Gm/T)/\partial(1/T) = \Delta Hm \qquad (3)$$

$$\Delta Gm = \Delta Hm - T\Delta Sm. \qquad (4)$$

The enthalpy of the mixing (ΔHm) is predicted to be positive at temperatures below 20°C and negative above this temperature. The entropy of the mixing ($-$ TΔSm) is negative below − 90°C and positive above this temperature. The enthalpy term at lower temperatures and the entropy term at higher temperatures favour the polymer blend to be miscible. Prediction implies that 80/20 phenolic/phenoxy blend is miscible at moderate temperatures. The difference in solubility parameter between phenolic and phenoxy is 1.83 (cal/ml)$^{0.5}$, which is large enough to cause the phase separation in a general non-hydrogen-bonding case. Phase separation occurred at low and high temperatures only, which indicates that the interaction of the hydrogen-bonding between the phenolic and phenoxy affects the phase diagram significantly. Results show that K_A is larger than K_2 and K_B of phenolic and phenoxy, which indicates the interaction of hydrogen-bonding between phenolic and phenoxy is higher than the self-association of both polymers. From the thermodynamic point of view, the phase separation would not occur in a moderate temperature range which has been confirmed in the phenolic-rich region. Similarly, it is also completely miscible in the phenolic-poor region at moderate temperatures. The results agree well with that of n.m.r. results[24].

Figure 5(a) shows the free energy (ΔGm) of phenolic/phenoxy blend at 25°C while the self-association of phenoxy is neglected. The solid line of curve (a) can be considered as an actual result in the phenolic-rich region. *Figure 5*(b) shows the simulation of the free energy of phenolic/phenoxy blend at 25°C while the self-association of phenolic is neglected. The solid line of curve (b) also can be considered as an actual result in the phenolic-poor region. Both curves (a) and (b) show the same tendency and the lowest point appears at the phenolic-poor region. Solid lines of both curves are negative and imply it is completely miscible in those regions at 25°C. There are not only inter-associations between phenolic and phenoxy, but also both self-association of phenolic and phenoxy present on the intermediary region. The PCAM can not be used to predict the thermodynamic properties of both self-association polymer systems on this region. The free energy of mixture is still ambiguous on the intermediary region from the PCAM. It can be concluded the free energy is negative in the intermediary stage in spite of both curves not being taken as actual results in the intermediary region from *Figure 5*(a) and *Figure 5*(b).

Excess heat capacity (ΔCp)

In order to check the results from the PCAM predictions, measuring the enthalpy of mixing is a direct method. However, the calorimetric measurement of ΔHm in polymer blend is very difficult due to the viscoelastic character of the polymer. A compressible version of binary mixtures with a specific interaction model has been proposed by Issac *et al.*[28]. They derived a mathematical model to prove the excess heat capacities (ΔCp) data which can be used to study the thermodynamics of polymer blends. Although the experiment which studies the variation of ΔHm with temperature, $\Delta Cp = (\partial \Delta Hm)/(\partial T)p$ is difficult, it is possible. The excess heat capacities (ΔCp) for polymer blends can be obtained by carefully using the differential scanning calorimeter, and the reproducibility of Cp values was obtained within ± 0.01 cal/g K. The quantity is given by the excess specific heat of the polymer blend[29].

$$\frac{\partial(\Delta Hm)}{\partial(T)} = \rho\Delta Cp = \rho(Cp - \omega_A Cp_A - \omega_B Cp_B) \qquad (5)$$

where ρ is density, ω_i the weight fractions, and Cp_i the heat capacities of the pure components.

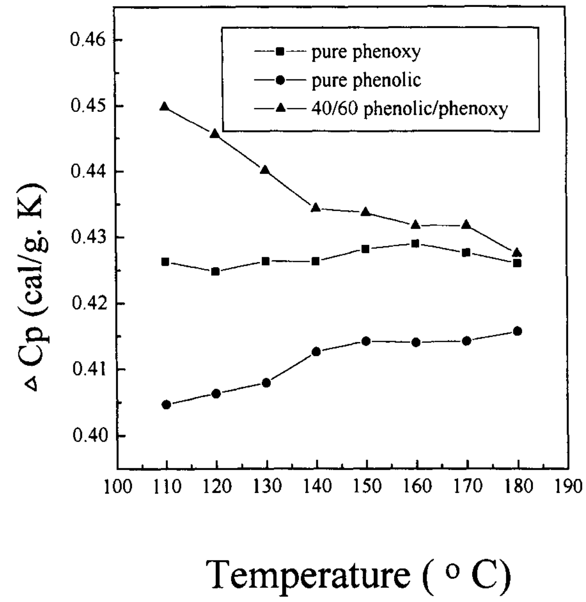


Figure 6 Specific heats of pure phenoxy (■), phenolic (•) and 40/60 phenolic/phenoxy blend (▲) in the temperature range of 110~180°C

Figure 6 shows the specific heats (Cp) of pure components and of 40/60 phenolic/phenoxy blend in the temperature range of 110~180°C, where both pure compounds and their blends are in the liquid state. The specific heat of pure component increased slightly with temperature and although it is necessary to consider the important experimental error inherent to these measurements, it agrees with the Eyring hole model[30]. In general, polymers have higher specific heat capacity at higher temperatures, since the motion of the molecule chain increases with temperature. On the contrary, the specific heat capacity (Cp) of the blend decreases with an increase in temperature. There are some reasons which cause the decrease of heat capacity.

The evolution of the excess heat capacity (ΔCp) has been presented in *Table 5*. The excess heat capacity decreases slightly with temperature for various phenolic/phenoxy blends.

It is obvious that if polymers interact favourably they would be miscible. The physical interactions between two polymers are determined by solubility parameter (χ, random term) and hydrogen-bonding interaction [($\Delta G_H/RT$), non-random term]. The solubility parameter contributes to cohesive energy density as Painter–Coleman described[15]. The hydrogen-bonding interactions show a 'directional-specific' interaction. In general, a positive value of excess heat capacity is that the polymer blend interaction is dominated by the 'directional-specific' (non-random term) nature, a negative value of excess heat capacity is dominated by the cohesive energy and only dispersion force existed (random term) in the blend[31]. Excess heat capacities of phenolic/phenoxy blend would approach zero while the temperature is high enough, and the phase separation would only occur if dispersion force existed.

These types of phase diagram are shown to be the consequence of the competition between the entropically favoured dispersion forces and the enthalpically favoured hydrogen-bonding interaction. In the phenoxy/phenolic blend system, there is a strong hydrogen-bonding (directional-specific) interaction between the hydrogen group of phenoxy and phenolic resin at the moderate temperature region. The hydrogen-bond affects the interaction significantly. However, the hydrogen-bonding would be destroyed gradually with a temperature increase[21], and no longer play a key role on intramolecular interaction whereas the dispersion force is more competent on the intramolecular interaction. The miscibility of the blend is reduced, and the

Table 5 The excess heat capacity (ΔCp, cal·g^{-1}·K^{-1}) of various phenoxy/phenolic blends (wt%) 20/80, 40/60, 60/40 *versus* temperature

Phenolic/phenoxy (wt%)	Temperature (°C)								
	100	110	120	130	140	150	160	170	180
20/80	0.02499	0.02361	0.02253	0.02105	0.02034	0.01536	0.01645	0.01403	0.005
40/60	0.03550	0.03211	0.02827	0.02107	0.01541	0.01107	0.0099	0.0094	0.0056
60/40	0.03548	0.03262	0.03226	0.0289	0.02872	0.02616	0.02416	0.02231	0.0261

LCST behaviour may occur in the system within the higher temperature range.

As predicted by PCAM (as shown in *Figure 4*), the enthalpy increased and the entropy decreased over 160°C. Both enthalpy and entropy decreased in absolute value as a function of temperature. But the enthalpy part decreased more in absolute value. This behaviour results in LCST behaviour, the entropy is more competent than enthalpy to cause the phase separation at the higher temperature range. *Table 5* demonstrates how the excess heat capacity slightly decreases with temperature, in excellent agreement with the results of prediction and experiment[21]. The results also agree with theoretical prediction proposed by ten Brinke *et al.*[31]

The excess heat capacity of the phenolic/phenoxy blend shows a positive value in a whole range of blends at 100°C, which implies the interaction of phenolic/phenoxy trends is dominated by hydrogen-bonding, and is completely miscible at this temperature. The composition dependence seems somewhat unsystemmetrical, and the highest value appeared at the system with 80 wt% phenolic. The lowest Tg and the highest amount of the free hydrogen group were also found at 80 wt% phenolic in our previous study[21]. The phenoxy chain hindered the interaction of hydrogen-bonding of phenolic and decreased the amount of hydrogen-bonding in the blend. The higher ΔCp value indicates that molecular motion increased and the random term is more favourable[31], and the number of the favourable 'directional-specific' interactions (the non-random term) is reduced at the identical temperature. In this study, the favourable 'directional-specific' interactions are reduced by the phenoxy chain. The change of density of hydrogen-bonding is not affected by temperature only, but also by the conformation of the polymer.

Although, the PCAM does not take the conformation of polymer into account, there are many studies published already which proved that the model can be used to study the miscibility of polymer blend well[15-20]. In this case the PCAM can predict the phenolic/phenoxy blends well.

CONCLUSIONS

The properties of thermodynamics of phenolic/phenoxy blends are predicted by PCAM in this study. It is reasonable that PCAM is used in their minor regions. The intermolecular association between phenolic resin and phenoxy is more competent than that of self-association of their neat polymers due to strong intermolecular hydrogen-bonding at moderate temperatures. The blend system is completely miscible for a wide temperature range. Hydrogen-bonding is decreased with the increase of temperature, and no longer plays a key role in intramolecular interaction whereas the dispersion force predominated at a higher temperature. When the directional-specific interaction is reduced with increasing temperature, the entropy causes phase separation more than that in the enthalpy at a higher temperature. Phase separation would occur at a higher temperature.

The phenoxy chain hindered the intramolecular hydrogen-bonding of phenolic, and reduced the density of hydrogen-bonding in the polymer blend system. Increasing the temperature is not the only way to reduce the hydrogen-bonding of the polymer blend, but the conformation affects the interaction of hydrogen-bonding. When the directional specific interaction is reduced, the molecular motion of phenolic is increased. The molecular motion of phenolic/phenoxy is more mobile due to the decrease of hydrogen-bonding at the identical temperature. The phenoxy is a good modifier for phenolic resin.

ACKNOWLEDGEMENTS

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