

# The phase behaviour of novolac type phenolic resin blended with poly(adipic ester)

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(Received 16 December 1996; revised 4 April 1997; accepted 25 July 1997)

The association equilibrium constants and enthalpy of novolac type phenolic resin blend were determined. All the parameters were obtained from the results of Fourier transform infrared spectroscopy of low molecular weight analogues in dilute cyclohexane solutions. All the association parameters of novolac type phenolic resin obtained from the model compound were used to predict the miscibility window of phenolic/poly(adipic ester) blend, and that were consistently well with the actual phase behaviour. The results show that the association parameters of phenolic provide a reasonable utilization of Painter–Coleman Association model. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: hydrogen bonding strength; novolac phenolic resin; miscibility)

## INTRODUCTION

Many association models to determine the changes of the free energy and phase behaviour of binary polymer blends have been proposed<sup>1–4</sup>. The main equation of the model used is usually based on the classic Flory–Huggins relation. In order to account for the hydrogen bonding interactions, Painter, Coleman and their co-worker added a term,  $\frac{\Delta G_H}{RT}$ , to modify the classic Flory–Huggins equation<sup>1</sup>. This equation is suitable for polymer blend systems in which the inter- and intra-molecular hydrogen bonding is presented<sup>5–12</sup>.

Phenol–formaldehyde resins are used widely in industry, because of their heat resistance, electrical insulation, dimensional stability, flame and chemical resistance<sup>13–21</sup>. It is brittle and limited in its applications. Many approaches have been proposed to improve the toughness of the phenolic resin<sup>19–23</sup>. The phenolic resin blends exhibit various thermodynamic properties and different phase behaviours from complete to partial miscibility<sup>21,23</sup>. The strengths of inter- and intra-molecular interactions are considered to play a key role in the compatibility of phenolic blend. However, the details of the thermodynamic properties of phenolic are still unknown because of its inimitable molecular structure and the high density of hydroxyl group contents, this will influence the interaction with other modifiers significantly.

In this study, the association parameter of Painter–Coleman Association model (PCAM) is found for further studies of the thermodynamic properties of phenolic blends. The applicability of the model compound of novolac type phenolic resin is selected within similar analogues. The parameters of association equilibrium constant and

enthalpies are obtained from both the absorption intensity and the shift change in FTIR spectra of various model compound concentrations, respectively. The PCAM is carried out to predict the miscibility window of phenolic/poly(adipic ester) blends, and compared with the actual phase behaviour to confirm the credibility of association parameter of novolac type phenolic resin.

## EXPERIMENTAL

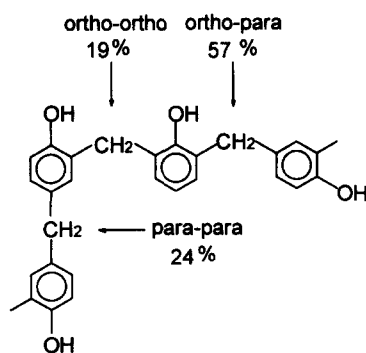
The novolac type phenolic resin was synthesized in this laboratory as described previously<sup>24</sup>. The chemical structure of novolac type phenolic resin consists of phenol rings bridge-linked randomly by methylene groups with 19% *ortho–ortho*, 57% *ortho–para*, and 24% *para–para* methylene bridges content was identified by the solution <sup>13</sup>C NMR spectrum. The phenolic resin does not contain any reactive methylol group which may cause cross-linking on heating.

The analogue of phenolic, 2,4-dimethylphenol (2,4-xyleneol), was obtained from the Lancaster Synthesis Co. USA with a purity of 97% and used as received. The cyclohexane and ethyl acetate (i.e. the analogue of poly(adipic ester)) were purchased from the Tokyo Kasei Kogyo Co. Ltd. The synthesis of poly(adipic ester) was described in previous reports<sup>25,26</sup>. All the molecular structure of polymers and model compounds are shown in Figure 1.

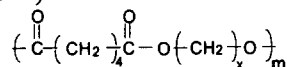
Infrared spectra were obtained on an FTIR spectrometer (Bio-Rad FTS-155, USA). In all cases, at least 16 scans with an accuracy of 2 cm<sup>-1</sup> resolution were signal-averaged. For solution samples, an adequate permanently sealed cell with NaCl windows and 0.05 mm thickness (Wilmat, USA) was used. A single optical path was used to study the self-association of 2,4-xyleneol and the inter-association between 2,4-xyleneol and ethyl acetate. All model compound solutions

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Novolac Type Phenolic Resin:



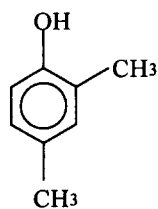
Poly (adipic ester):



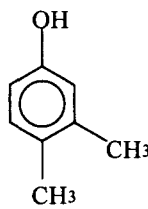
$x = 8$ , for polyoctamethylene adipate (POA)

$m \approx 80$  specific repeated units

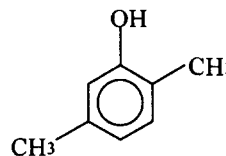
Model Compound of Novolac Type Phenolic Resin:



2,4-Xylenol



O-Xylenol



p-Xylenol

Model Compound of Poly(adipic ester):



Ethyl Acetate

Figure 1 Molecular structure of phenolic, poly(adipic ester) and their model compounds

in the absorption range obeyed the Beer–Lambert law. Cyclohexane was chosen as the solvent because the specific conformations of cyclohexane was favourable for this study<sup>5,7</sup>.

The cloud point was determined by measuring the relative intensity of light transmitted through the polymer blend film placed within the heating cell. The transmitted light intensity was measured by a photodiode. The sample, prepared as an IR sample, was introduced in the heating cell at a temperature of about 50°C below the cloud point. The temperature was then increased at a rate of 0.5°C min<sup>-1</sup>. The cloud point was taken as the onset temperature for the change in the light intensity and the reproducibility of cloud point was within ± 3°C.

The Painter–Coleman equation<sup>1</sup> was used to calculate the thermodynamic properties of polymer blends. All parameters, required to estimate the thermodynamic properties for the polymer blend by the Painter–Coleman equation<sup>1</sup>, are shown in Table 1.

RESULTS AND DISCUSSION

Determine the model compound of phenolic resin

The model compound, corresponding to the novolac type phenolic resin that consists of phenol rings bridge-linked randomly by methylene group, is chosen from various types xylenol—i.e. *o*-xylenol, *p*-xylenol and 2,4-xylenol. Those different analogues of phenolic resin are employed to explore the difference of chemical shifts on the FTIR spectrum. Figure 2 shows the chemical shift of analogues in FTIR spectra from the absorption of the hydroxyl group with and without hydrogen bonding in concentration of 0.04 M analogue cyclohexane solution. The *p*-xylenol shows two separation bands at 3491 and 3618 cm<sup>-1</sup>, *o*-xylenol shows two separation bands at 3488 and 3620 cm<sup>-1</sup>, 2,4-xylenol also shows two separation bands at 3490 and 3620 cm<sup>-1</sup>, respectively. All bands that appear at the higher wavenumber can be ascribed to ‘free’

**Table 1** Symbols used in estimating the free energy of mixing for a polymer blend by the Painter–Coleman equation<sup>1</sup>

Association interaction of polymer blend		
Association equilibrium constant	$K_2$	Self-association dimer formation of phenolic
	$K_B$	Self-association multimer formation of phenolic
	$K_A$	Inter-association between phenolic and poly(adipic ester)
Association enthalpies	$h_2$	Self-association dimer formation of phenolic
	$h_B$	Self-association multimer formation of phenolic
	$h_A$	Inter-association between phenolic and poly(adipic ester)
Characteristic parameter of polymer		
$M_w$ molecular weight	$V_m$	Volumes of the repeating unit
$\delta$ Solubility parameter	$D_p$	Degree of polymerization

(non-hydrogen bonded) hydroxyl groups and the other to hydrogen bonded hydroxyl groups. Since those chemical shifts and relative intensity show almost no difference, the 2,4-xyleneol is chosen as the model compound for novolac type phenolic resin.

*Self-association constant of phenolic ( $K_2, K_b$ )*

Since the self-association ability of phenolic influences intermolecular interaction behaviour of phenolic blends significantly, it is necessary to obtain the self-association constant of phenolic for further application of PCAM for the thermodynamic of phenolic blend. The self-association of 2,4-xyleneol in cyclohexane were examined by taking FTIR

spectra of free and hydrogen-bonded hydroxyl over concentration range from 0.014 to 0.47 M at 25°C, as shown in Figure 3. In the self-association constant estimation, the intensity of ‘free’ hydroxyl group absorption decreased with the increasing of 2,4-xyleneol concentration in the solution. The absolute intensity of ‘free’ hydroxyl group at 3620 cm<sup>-1</sup> is assumed to be a measurement of free hydroxyl amount in the mixture. The frequency of associated hydroxyl band shifts to 3483 cm<sup>-1</sup> at lower 2,4-xyleneol concentration, and shifts to 3330 cm<sup>-1</sup> at higher 2,4-xyleneol concentration. The former shift is corresponding to the dimer formation of hydrogen bonding, which is favoured at lower hydroxyl concentration. The latter is corresponding to the multimer formation of hydrogen bonding, which is favoured at higher hydroxyl concentrations.

According to the PCAM, two parameters are enough for describing the self-association of phenolic, one describes the formation of dimer,  $K_2$  and the other describes the formation of higher multimer  $K_B$ <sup>1</sup>.

The Beer–Lambert law used:

$$|I/c|_{\lim c \rightarrow 0} = \epsilon \tag{1}$$

where

- $I$  = the intensity of absorption
- $\epsilon$ : absorptive coefficient
- $l$ : path length of IR cell
- $c$ : the concentration of 2,4-xyleneol in cyclohexane

$$f_m^{OH} = I/\epsilon l \tag{2}$$

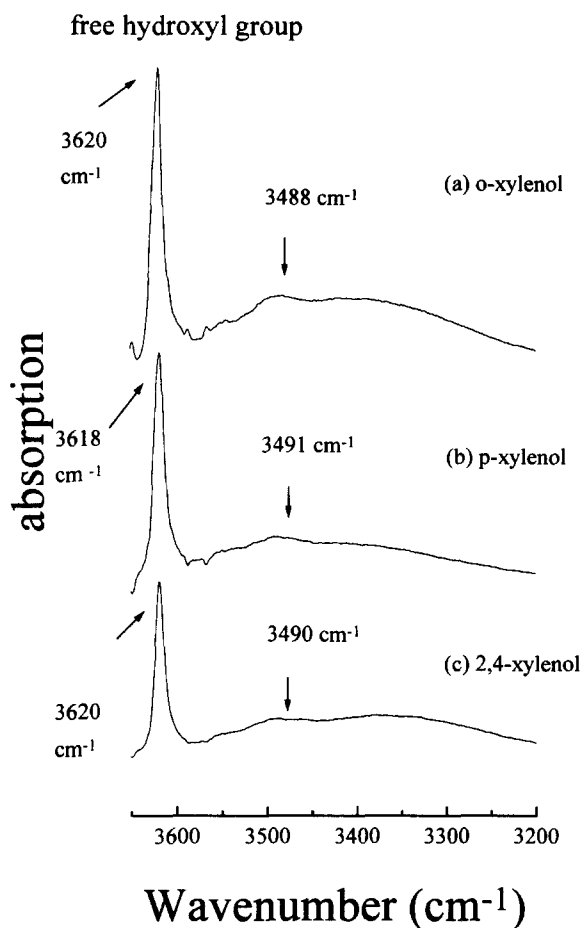
$f_m^{OH}$  is the fraction of 2,4-xyleneol that contains ‘free’ hydroxyl group within 2,4-xyleneol cyclohexane solution. The iterative least-squares fitting procedure was used to fit those data by equation (3), which related the volume fraction of free hydroxyl 2,4-xyleneol to the dimensionless equilibrium constants  $K_2$  and  $K_B$ <sup>1,5</sup>, as shown in Figure 4.

$$f_m^{OH} = \left( \left(1 - \frac{K_2}{K_B}\right) + \frac{K_2}{K_B} \left( \frac{1}{1 + K_B \Phi_{B1}} \right)^2 \right)^{-1} \tag{3}$$

Where  $\Phi_{B1}$  is the volume fraction of free hydroxyl 2,4-xyleneol in cyclohexane solution.  $K_2$  and  $K_B$  constants were thus determined to be 15.47 and 34.73, respectively. These constants have to be scaled from the repeating unit of novolac type phenolic resin after taking the difference in the molar volumes into account. The means is described as following expression<sup>1,7</sup>.

$$K_{phenolic} \times V_{phenolic} = K_{model} \times V_{model} \tag{4}$$

The  $V_{model}$  and  $V_{phenolic}$  are 125 and 83 cm<sup>3</sup> mol<sup>-1</sup>,



**Figure 2** Infrared spectra of the free hydroxyl absorption and dimer hydrogen-bonding hydroxyl absorption of *p*-, *o*- and 2,4-xyleneol solution in concentration of 0.004 M cyclohexane. (a) *o*-xyleneol, (b) *p*-xyleneol and (c) 2,4-xyleneol

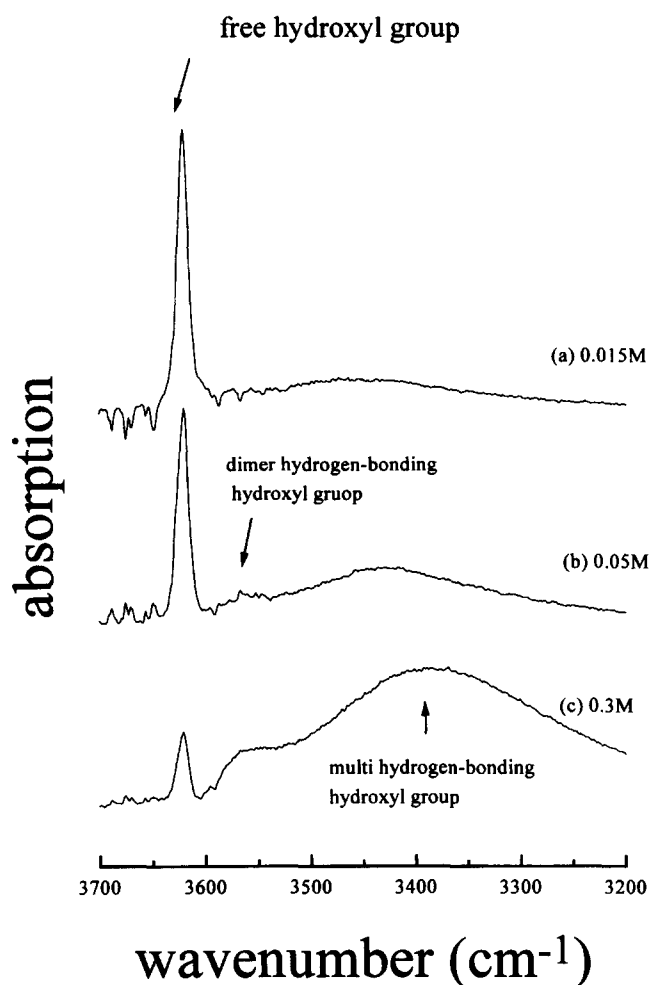


Figure 3 Infrared spectra of various concentrations of 2,4-xyleneol solution in cyclohexane. (a) 0.015 M, (b) 0.05 M and (c) 0.3 M

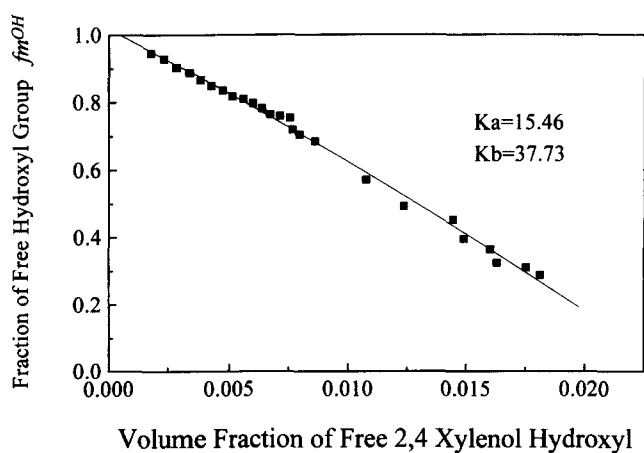


Figure 4 Results of iterative least-square fitting to volume fraction of free 2,4-xyleneol hydroxyl versus fraction of free hydroxyl group in cyclohexane

respectively<sup>26</sup>. The actual  $K_2$  and  $K_B$  equilibrium constants are modified to be 23.29 and 52.31, respectively.

#### Estimation of the association enthalpy of phenolic blend

The thermodynamic behaviour of phenolic blend is also affected by the inter- and intra-association enthalpy. As described in previous reports<sup>27</sup>, the association enthalpies,  $\Delta h_m$  can be estimated indirectly based on the frequency shift in the IR spectrum of 2,4-xyleneol with various bases, and the

correlation between chemical shift  $\Delta\nu$  and association enthalpies  $\Delta h_m$  for these bases with different small hydrogen bonded donors was established previously. The 0.02 M 2,4-xyleneol cyclohexane solution is mixed with various 0.1 M small molecules based cyclohexane solution—i.e. ethyl acetate, 1,4-dioxane, tetrahydrofuran and pyridine to measure the change of the IR frequency shift. As shown in Figure 5, the IR frequency shift of hydrogen bonded hydroxyl of ethyl acetate is  $3475\text{ cm}^{-1}$  and enthalpy is  $-4.11\text{ kcal mol}^{-1}$ , dioxane is  $3364\text{ cm}^{-1}$  and  $-5.38\text{ kcal mol}^{-1}$ , tetrahydrofuran is  $3352\text{ cm}^{-1}$  and  $-6.53\text{ kcal mol}^{-1}$ , pyridine is  $3176\text{ cm}^{-1}$  and  $-7.8\text{ kcal mol}^{-1}$ , respectively.

Those experimental results provide correlation between enthalpy and frequency shift for the hydroxyl band of 2,4-xyleneol. The results can be expressed as the following equation:

$$-\Delta h (\text{kcal mol}^{-1}) = 2.564 + 0.0122\Delta\nu_{\text{OH}} (\text{cm}^{-1}) \quad (5)$$

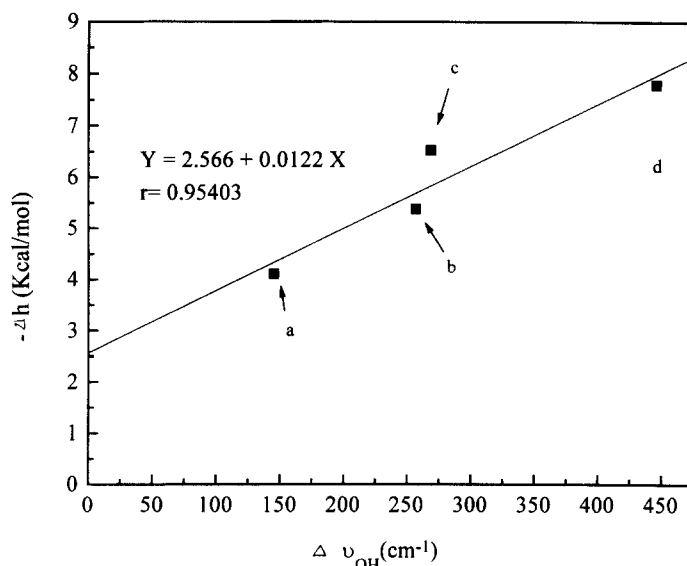
The chemical shifts of dimer and multimer of hydrogen bonded hydroxyl of 2,4-xyleneol are  $137\text{ cm}^{-1}$  and  $290\text{ cm}^{-1}$ , respectively. Substituting the chemical shift into equation (5), the enthalpies of dimer and multimer hydrogen bonding of 2,4-xyleneol are given to be  $-4.25$  and  $-6.11\text{ kcal mol}^{-1}$ , respectively.

#### Estimation of inter-association parameters between phenolic and modifier

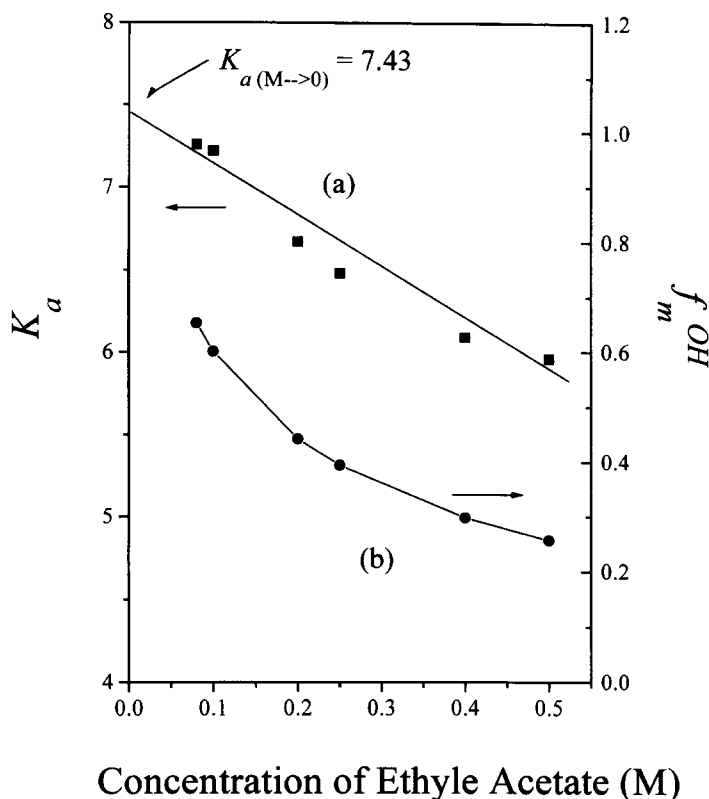
In order to check the credibility of association parameter of phenolic used in PCAM, the poly(adipic ester) is as modifier to blend with phenolic. The ethyl acetate contained the carbonyl group is used as the model compound of poly(adipic ester). Inter-association constant  $K_A$  of PCAM described the ability of hydrogen bonding interaction between phenolic and poly(adipic ester) unit. In this study, the 'free' hydroxyl band absorption at constant 2,4-xyleneol concentration of 0.02 M and various ethyl acetate concentrations in cyclohexane are used for quantitative measurement. It is necessary to prescan FTIR before the 2,4-xyleneol is added into the various concentrations of ethyl acetate solution as background. The method proposed by Coggeshall and Saier<sup>28</sup> involved the calculation of an association constant  $K_a$  (in  $\text{L mol}^{-1}$ ) from the following equation:

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

Where  $c_A$  and  $c_B$  are the concentrations of ethyl acetate and 2,4-xyleneol in  $\text{mol L}^{-1}$ , respectively. Figure 6 shows the  $fm^{\text{OH}}$  and  $K_a$  of 2,4-xyleneol for various concentrations of ethyl acetate cyclohexane solution. The  $K_a$  value is concentration-dependent. The reliable value of inter-association constant  $K_a$  ( $= 7.43$ ) can be obtained from the extrapolation of zero ethyl acetate concentration. The inter-association constant  $K_a$  has to be modified to become  $K_A$  by dividing the molar volume of the repeating unit of phenolic ( $= 0.0831\text{ mol}^{-1}$  at  $25^\circ\text{C}$ ). Thus the equilibrium constant  $K_A$  of 89.52 is obtained. The properties of pure polymer, equilibrium constant and enthalpy of phenolic and poly(adipic ester) are summarized in Table 2, except the degree of polymerization and molar volume of phenolic resin are measured directly, the rest of the polymer properties can be estimated by the Painter-Coleman equation<sup>1</sup>.



**Figure 5** Enthalpies and spectral chemical shifts of 2,4-xylenol with various basic compounds (a) ethyl acetate, (b) 1,6-dioxane, (c) tetrahydrofuran and (d) pyridine



**Figure 6**  $K_a$  and  $f_m^{OH}$  versus various acetate concentrations in cyclohexane solution (a)  $K_a$  and (b)  $f_m^{OH}$

#### Calculation of phase diagram of miscibility window

There is no distinction between the specific repeating unit of polymer that contains  $n$  methylene groups and the average specific repeated unit if a copolymer containing the same number of methylene per ester group in the Painter-Coleman equation. The theoretical prediction of the miscibility window was calculated at 120°C for phenolic/poly(adipic ester) blend and the result was presented in Figure 7. The  $x$ -axis is the weight fraction of phenolic resin in the blends, and the  $y$ -axis is the number of methylene groups per carbonyl group. The numbers of repeating units

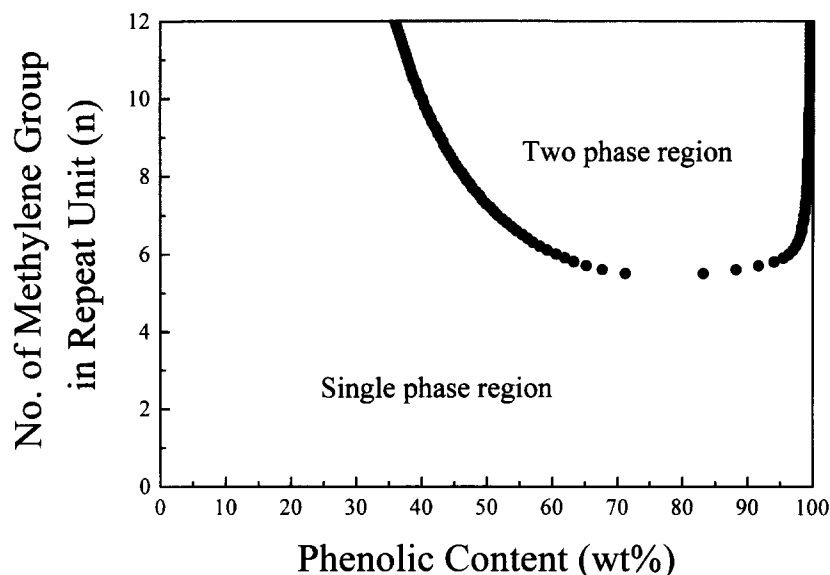
are 80 and 7 for poly(adipic ester) and phenolic resin, respectively. The phenolic resin is predicted to be completely miscible with amorphous poly(adipic ester) containing 0–5 methylene group per specific repeated unit. As shown in Figure 7, the family of poly(adipic ester) was predicted to be partially immiscible when more than six methylene groups were added to the poly(adipic ester) specific repeated unit at 120°C.

In Figure 8, the spinodal line for the phenolic/POA is calculated over the temperature range from 50 to 150°C. The immiscible region is shown in the phenolic-rich region. The fraction of carbonyl group affects on the phase

**Table 2** The properties of pure polymers, equilibrium constant and enthalpy of phenolic and poly(adipic ester)

Polymer	Molar volume (/(mL mol <sup>-1</sup> ))	Molecular weight (/(g mol <sup>-1</sup> ))	Solubility parameter (/(calories /mL <sup>-1</sup> )) <sup>0.5</sup>	Polymer <i>D<sub>p</sub></i>
Novolac type phenolic resin	84 <sup>a</sup>	105 <sup>a</sup>		
((CH <sub>2</sub> ) <sub>6</sub> CO <sub>2</sub> ) <sub>n</sub>	118.6	128.19	9.19	80 <sup>a</sup>
CH <sub>2</sub>	16.5	14.03	8.00	-
COO	19.6	44.01	15.20	-
Interaction	Equilibrium constant <i>K</i> (25°C)		Enthalpy $\Delta h$ (/(kcal mol <sup>-1</sup> ))	
<b>Self-association</b>				
dimer formation		23.29( <i>K</i> <sub>2</sub> )		-4.246( <i>h</i> <sub>2</sub> )
multimer formation		52.31( <i>K</i> <sub>B</sub> )		-6.110( <i>h</i> <sub>B</sub> )
<b>Inter-association with poly(adipic ester)</b>				
		89.52( <i>K</i> <sub>A</sub> )		-4.11( <i>h</i> <sub>A</sub> )

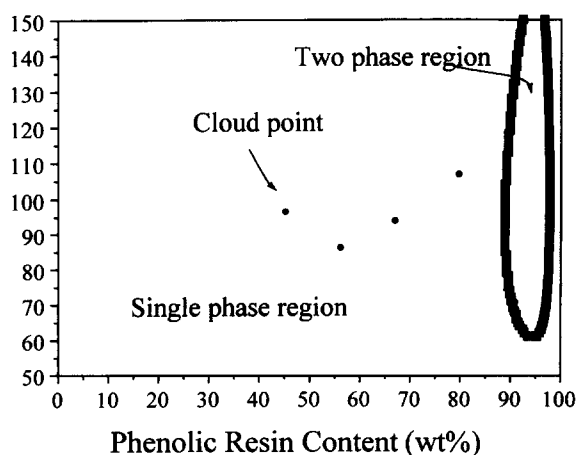
<sup>a</sup>measured directly



**Figure 7** The theoretical predictions of the miscibility window for phenolic/poly(adipic ester) at 120°C

diagrams significantly, the immiscible region appears when the POA (*n* = 6) blended with phenolic. Cloud points were observed in the phenolic rich region in POA, which supported the validity of the Painter–Coleman equation prediction though some quantitative disagreement was observed.

Although, there are some assumptions in the association model and the inherent errors in the determination of equilibrium constants, enthalpy, solubility parameter, and the molar volume of polymer, the predicted phase diagram and degree of hydrogen bonding still agree quite well with the actual behaviour.



**Figure 8** the calculated spinodal phase diagram (solid line) of phenolic/POA (*n* = 6) blend and actual phase behavior of phenolic/POA (●)

## CONCLUSIONS

The intramolecular hydrogen bonding present within the phenolic resin leads to improvement in the miscibility of phenolic blend. It is reasonable that the intermolecular hydrogen bonding (between hydroxyl and carbonyl) is higher than intramolecular hydrogen bonding (between hydroxyl and hydroxyl), as shown in results of the equilibrium constant of inter-association *K<sub>A</sub>* is higher than equilibrium constant of self-association (*K<sub>2</sub>* and *K<sub>B</sub>*).

When more than six methylene groups are contained in the specific repeating unit, it was predicted the phase separation occurred at 120°C. All the association parameters of phenolic used in PCAM mirror the real phase behaviour of phenolic blend at moderate temperature.

## ACKNOWLEDGEMENTS

This research was financially supported by the National

Science Council, Taiwan, Republic of China, under the Contract No. NSC-85-2216-E-007-007

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