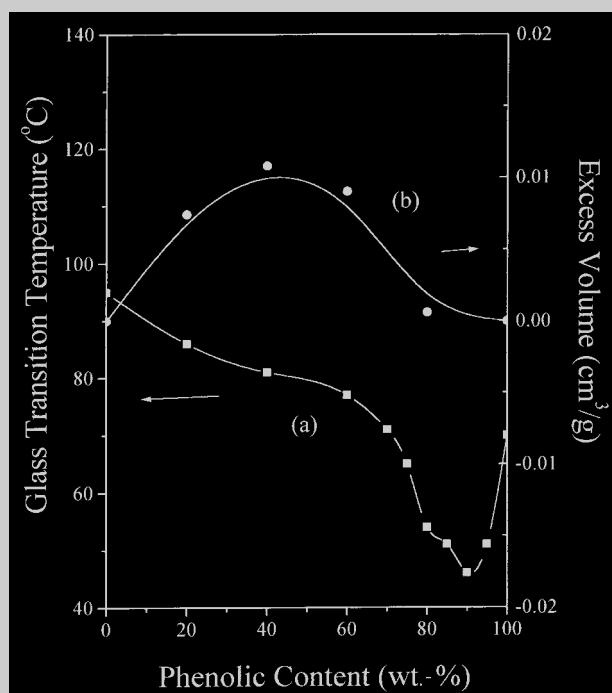


**Full Paper:** The formation of intermolecular hydrogen bonds in blends of novolac type phenolic and poly(hydroxyl ether) of bisphenol A was investigated by studying its  $T_g$  behavior, excess volume, and solid state  $^{13}\text{C}$  NMR spectra. The  $T_g$  and parameters of solid state  $^{13}\text{C}$  NMR, such as the  $T_{\text{CH}}$  and spin-lattice relaxation time in the rotating frame  $T_{1\rho}$ , indicate that the London dispersion force (entropically favored) significantly affects the intermolecular hydrogen bonding of the blend. The phenoxy chain forces opening of the intra-association of phenolic and thus creates more free OHs. This strong entropic effect reduces the total hydrogen bonding of the system, especially when one of the polymer is the minor component. This also results in the reduction of  $T_g$  and free volume expansion, reflecting in the increase of cross-polarization (C–H) time and molecular mobility within the phenolic/phenoxy blend.

Composition dependence of the glass transition temperature and excess volume of uncured phenolic/phenoxy blend throughout the whole blend composition. (a) Original glass transition temperatures  $\blacksquare$ , and (b) excess volume at 25 °C



## The solid state $^{13}\text{C}$ NMR studies of intermolecular hydrogen bonding formation in a blend of phenolic resin and poly(hydroxyl ether) of bisphenol A

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### Introduction

The phenol-formaldehyde resins are widely used in industry, because of their good heat resistance, electrical insulation, flame retardancy, and chemical resistance<sup>1–5</sup>. However, the phenolic resin is brittle and reticular in nature which limits its applications. Many approaches have been explored to improve the toughness of phenolic resins by blending with a second modifier, such as polyethylene oxide (PEO) and poly(vinyl alcohol) (PVA)<sup>6–9</sup>. On the other hand, phenoxy is capable of forming H-bonding through its OH group with appropriate polymers, and is therefore a very promising modifier for the brittle phenol. Roughly a four-fold improvement on notched

Izod impact strength has been achieved for this phenolic/phenoxy blend<sup>10</sup>. However, the structural details concerning the interaction between the phenolic and modifiers remains largely unresolved. It is still not clear concerning the correlation between the improved bulk properties and the interaction, especially the formation of H-bonding.

Previous IR studies on phenolic resin<sup>11</sup>, revealed firm evidence of the existence of strong H-bonding in several phenolic related blends, which is believed to be the driving force for the miscibility of these phenolic blends<sup>12–15</sup>. In spite of the difference in structure and dynamic motion between the phenoxy and the phenol, the specific interaction appears to be the main driving force responsible for

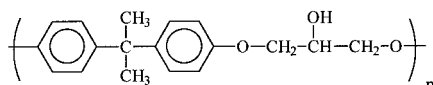
the miscibility. However, the observed improvement in physical properties cannot be accounted for solely on the basis of good miscibility.

The purpose of the study is to understand the source of intermolecular H-bonding from a microstructure characteristic viewpoint. High-resolution solid-state NMR spectroscopy is a convenient tool to investigate molecular dynamics and molecular structures of polymer blends<sup>9, 16–18</sup>. The NMR parameters e.g. chemical shifts, relaxation time ( $T_{CH}$ ,  $T_{1\rho}^H$ ), can directly reveal polymer microstructures and molecular mobility. The molecular interaction of phenolic/phenoxy blends will be further discussed based on their  $T_g$  behavior, excess volume, and the solid state NMR parameters.

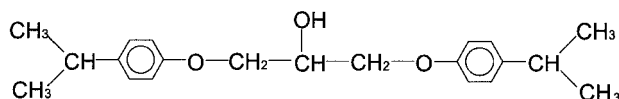
## Experimental part

### Chemicals

The synthesis of the novolac type phenolic resin (phenolic) was described in our previous report<sup>12</sup>. The poly(hydroxyl ether) of bisphenol A (Phenoxy resin, PKHH) was obtained from the Union Carbide Co. with a  $\bar{M}_n$  and  $\bar{M}_w$  of 23,000 and 48,000, respectively. The repeated phenoxy unit is depicted as follow:



Phenolic/phenoxy blends were prepared by simultaneously dissolving both polymers in THF (1 % w/v) at room temperature according to the designed compositions. The mixture was stirred for 6–8 h, and the solution allowed evaporating slowly at room temperature for one day. The blend was then dried at 50 °C for 2 days and annealed at 140 °C for an additional 2 h under vacuum. 3-bis[4-(2-Propyl)phenoxy]-2-propanol (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) (purity >97 %) was purchased from the Lancaster synthesis Co. (USA) and used as received.

### Infrared spectra

Infrared spectra were obtained using a FT-IR spectrometer (Bio-Rad FTS-155, USA). The interaction among model components in THF solution was shown by recording 16 scans with an accuracy of 2  $\text{cm}^{-1}$  in an adequate permanently sealed cell with NaCl windows (path length; 0.05mm).

### Differential scanning calorimetry (DSC)

Glass transition temperatures ( $T_g$ ) of polymer blend films are determined by differential scanning calorimeter (Du-Pont,

DSC Model 2900). The scan rate is 20 °C/min ranging from 10 to 130 °C using 3–4 mg of sample on the DSC sample plate after the specimen is quickly cooled to room temperature following the first scan. This procedure is adopted to ensure a complete mixing of the polymer mixture and the complete removal of the residual solvent and water from the specimen. The  $T_g$  values were determined at the midpoint of the transition point of the heat capacity ( $C_p$ ) change, and the reproducibility of  $T_g$  values is estimated to be within  $\pm 2$  °C.

### Specific volume

Specific volumes are determined at 25 °C using a pycnometer calibrated with *n*-heptane. The temperature of the water bath is kept constant to within  $\pm 0.1$  °C and the measured values are found to be accurate within  $\pm 0.001$   $\text{cm}^3/\text{g}$  from repeated measurements.

### NMR experiments

High-resolution solid-state  $^{13}\text{C}$  NMR experiments are carried out on a Bruker DSX-300 spectrometer operating at resonance frequencies of 300.13 and 75.475 MHz for  $^1\text{H}$  and  $^{13}\text{C}$ , respectively. The  $^{13}\text{C}$  CP-MAS spectra are measured with 3.9  $\mu\text{s}$  90° pulse width; 3s pulse delay time; 30 ms acquisition time; spectral width, 200 ppm; and 2048 scans. The C=O carbon of the glycine at 176.04 ppm is taken as the secondary reference of the  $^{13}\text{C}$  chemical shift. The efficiency of cross-polarization ( $T_{CH}$ ) is measured by carbon signal intensity versus variable contact time ( $\tau_c$ ) ranging from 0.2 to 18 ms. Proton spin-lattice relaxation times in rotating frame ( $T_{1\rho}^H$ ) is measured via carbon signal intensity using a 90°- $\tau$ -spin lock pulse sequence prior to the cross-polarization. The delay time ( $\tau$ ) ranges from 0.1 to 16 ms. All NMR spectra are taken at temperature of 300 K with broad band decoupling, normal cross-polarization pulse sequence and a magic angle sample (MAS) spinning frequency of 5.4 kHz.

## Result and discussion

### Evidence of hydrogen bonding between phenolic and phenoxy

Fig. 1 shows “free” OH band absorption of the 2,4 xylenol on concentration of 0.02 M 2,4 xylenol and various concentrations of IPPHP cyclohexane solutions<sup>11</sup>. The intensity of ‘free’ OH band absorption of 3620  $\text{cm}^{-1}$  is decreased, while the band corresponding to the H-bonded emerges gradually with IPPHP contents. This provides strong evidence that there is strong H-bonding between phenolic and phenoxy.

### $T_g$ s and excess volumes of phenolic/phenoxy blends

Fig. 2 shows the measured glass transition temperature ( $T_g$ s) and excess volumes throughout the whole composition range. The presence of single glass transition temperature for all phenolic/phenoxy compositions is consis-

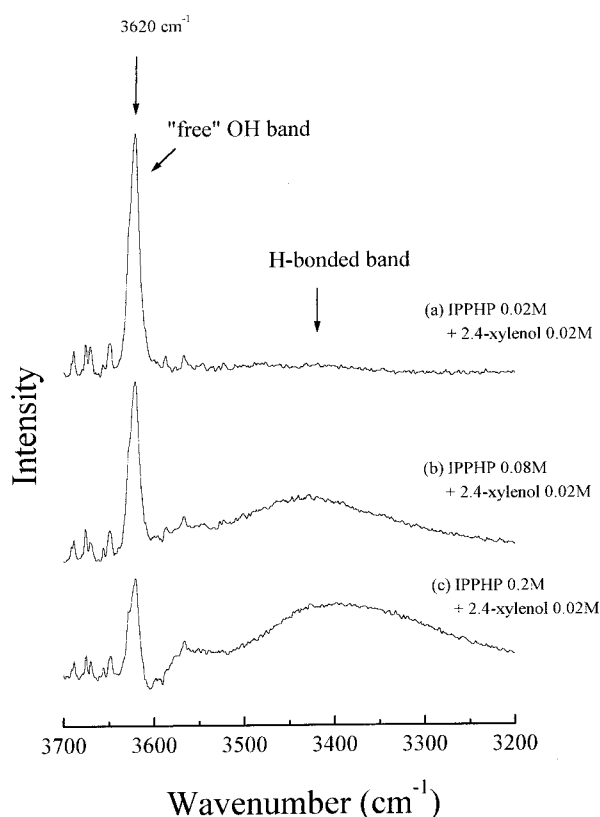


Fig. 1. The evidence hydrogen bonding between phenolic/phenoxy blend: the “free” OH band absorption of 2,4 xyleneol at concentration of 0.02 M 2,4 xyleneol and concentrations of (a) 0.02 M, (b) 0.08 M, and (c) 0.2 M IPPHP cyclohexane solution

tent with the thermodynamic criteria of a miscible blend. The glass transition temperatures of pure phenoxy and pure phenolic are at  $95 \pm 2$  and  $70 \pm 2$  °C, respectively. Both parent polymers have rather high  $T_g$  which are presumably due to their high density of intra-H-bonding. The phenolic resin is amorphous and relatively rigid, while the phenoxy resin is also amorphous but rather flexible. The  $T_g$  derivation is negative throughout the whole composition range, and the minimum of  $T_g$  appears at phenolic/phenoxy = 90/10 composition as shown in Fig. 2a.  $T_g$  deviation is a result of entropy change corresponding to the change in the number of H-bonding interactions<sup>19</sup>. The reduction of the number of H-bonding interaction associate with the entropy increases significantly upon blending.

The excess volume of a polymer blend has been conveniently used to understand the characterization of a polymer mixture<sup>20</sup>. Without considering the mixing effect, an additive relationship is expected of this truly miscible mixture<sup>21</sup>.

$$V_0 = (\phi_1/\rho_1) + (\phi_2/\rho_2) \quad (1)$$

where the  $\phi_i$  is the weight fraction of the components in the blend, and  $\rho_i$  the densities of pure state of polymers. The

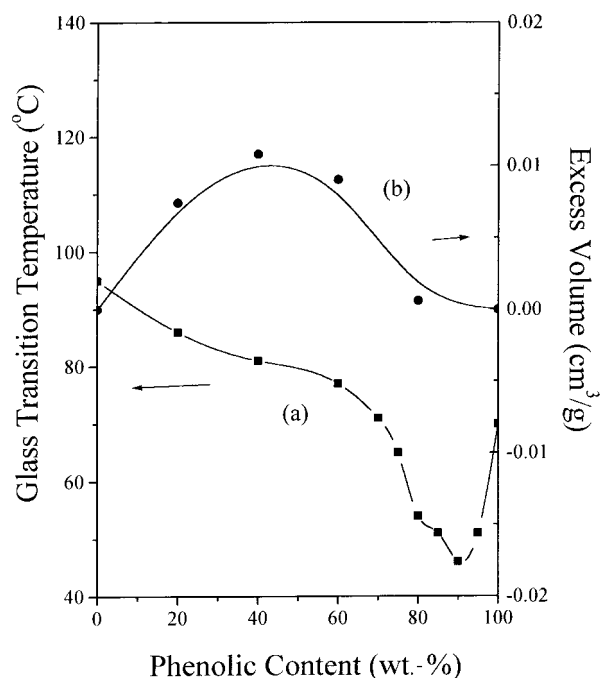


Fig. 2. Composition dependence of the glass transition temperature and excess volume of uncured phenolic/phenoxy blend throughout the whole blend composition. (a) Original glass transition temperatures ■, and (b) excess volume at 25 °C

excess volume,  $\Delta V$  shown in Fig. 2b is taken as the difference between the actual specific volume of the blend and its  $V_0$ . Apparently, the excess volume exhibits a positive deviation. However, considering the strong H-bonding favoring the phenolic/phenoxy miscibility<sup>11</sup>, the compact polymer mixture should result in negative excess volume. Both experimental volume expansion and reduced  $T_g$  are contradictory to the strong inter-association. It is inferred that the molecular structure of components plays an important role on causing the unexpected composition dependent  $T_g$  behavior and the excess volume.

The  $T_g$  behavior and excess volume describe both inter-association and London dispersion between component polymers. It is assumed that the relatively long repeating unit length of the polymer provides an additional entropy factor in this mixture. In order to provide evidence in supporting this presumption that accounts the detailed molecular structure for the intermolecular H-bonding configuration, high-resolution solid state NMR methodologies have been carried out including  $^{13}\text{C}$  chemical shifts; CP-MAS cross-polarization dynamics; and proton spin-lattice relaxation in rotating frame relaxation time ( $T_{1\rho}^H$ ). The H-bonding configuration of a blend reveals the picture of the thermodynamics that will be discussed later.

### $^{13}\text{C}$ CP/MAS NMR spectra

Fig. 3 shows the typical  $^{13}\text{C}$  CP-MAS NMR spectra of the phenoxy, uncured phenolic, and uncured blends with var-

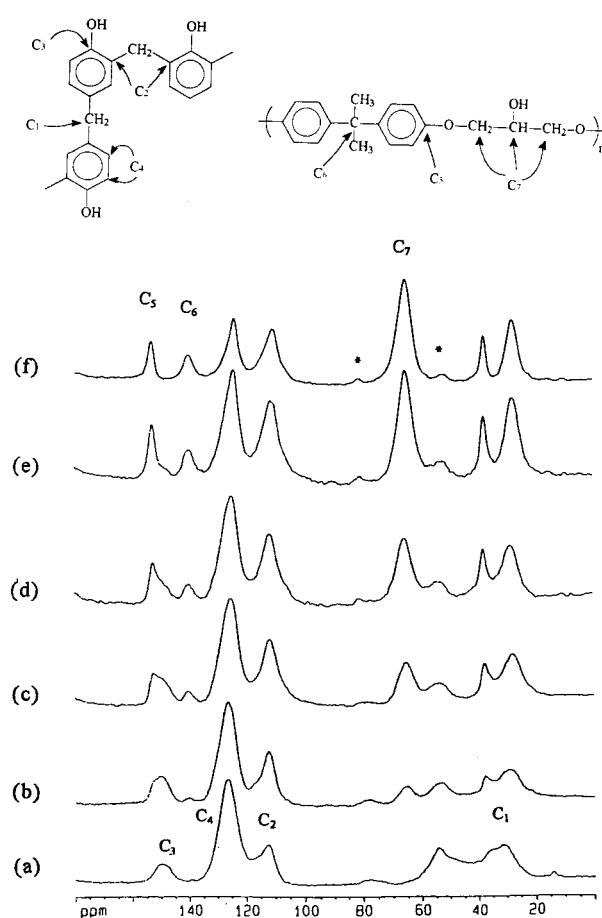


Fig. 3. The  $^{13}\text{C}$  CP/MAS spectra of novolac type phenolic resin (phenolic), phenoxy and phenolic/phenoxy blends. (a) 100/0, (b) 80/20, (c) 60/40, (d) 40/60, (e) 20/80, and (f) 0/100. (\* : side band)

Tab. 1. The chemical shifts of phenolic and phenoxy in NMR spectrum, and symbol used in text

Component	Chemical shift	Description	Symbol in text
Phenolic	31 ppm	methylene	C <sub>1</sub>
	112 ppm	ortho-substituted in phenol ring	C <sub>2</sub>
	150 ppm	hydroxyl-substituted in phenol ring	C <sub>3</sub>
Phenoxy	126 ppm	other carbon in phenol ring	C <sub>4</sub>
	153 ppm	ether-substituted in phenol ring	C <sub>5</sub>
	139 ppm	quaternary carbon in phenol ring	C <sub>6</sub>
	66 ppm	ether carbon and hydroxyl carbon	C <sub>7</sub>

ious compositions. The main peak assignments for phenolic and phenoxy are summarized in Tab. 1. The electron-donated carbon produces small perturbations to the magnetic shield on the nucleus and results in a downfield chemical shift as compared to the ones without the H-bonding interaction<sup>9)</sup>. On the contrary, the electron-accepted carbon tends to shift upfield. Fig. 4 shows the chemical

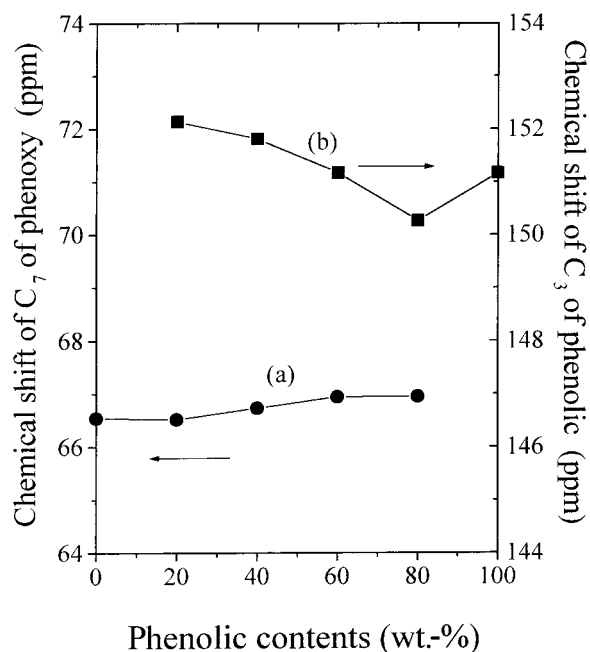


Fig. 4. The chemical shift variation with composition for (a) C<sub>3</sub> of hydroxyl-substituted carbon in phenolic rings of the phenolic ■, and (b) C<sub>7</sub> of the phenoxy ●

shifts of the OH-substituted carbon in the phenolic rings (C<sub>3</sub>, ~150 ppm) and in the phenoxy (C<sub>7</sub>, ~66 ppm) for various compositions of blends. The C<sub>3</sub> resonance of the pure phenolic (151.2 ppm) shifts upfield initially and then shifts downfield gradually from a composition of phenolic/phenoxy = 80/20 and with increasing phenoxy content. The upfield shift of the averaged location implies a more non-bonded fraction of the OH-substituted carbon (C<sub>3</sub>) relative to that of the pure phenolic at a phenoxy content of less than 20 wt.-%. The subsequent downfield shift means an increase in the H-bonded fraction or a decrease in the “free” OH when the phenoxy content is greater than 20 wt.-% with more phenoxy content. On the other hand, the C<sub>7</sub> resonance of the pure phenoxy (66.5 ppm) shifts downfield gradually with increasing phenolic content. This change suggests an increase in intermolecular H-bonding of phenoxy upon blending with phenolic.

Judging from Fig. 1, there is a strong H-bonding present in the phenolic/phenoxy blend. However, the molecular structure of the components would affect the amount of H-bonding of blend, and thus the related molecular dynamics. From the above results, one may conclude that more “free” OHs are present in phenolic-rich blends. These chemical shifts suggest that the phenoxy chains penetrate and separate the intra-association of the phenolic molecules. As the quantity of the phenoxy added increases continuously, the formation intermolecular H-bonding increases and the free OHs are reduced, as shown from the  $T_g$  behavior and NMR chemical shift.

Therefore, due to the reduction of H-bonding in the phenolic-rich region, the increasing polymer segmental

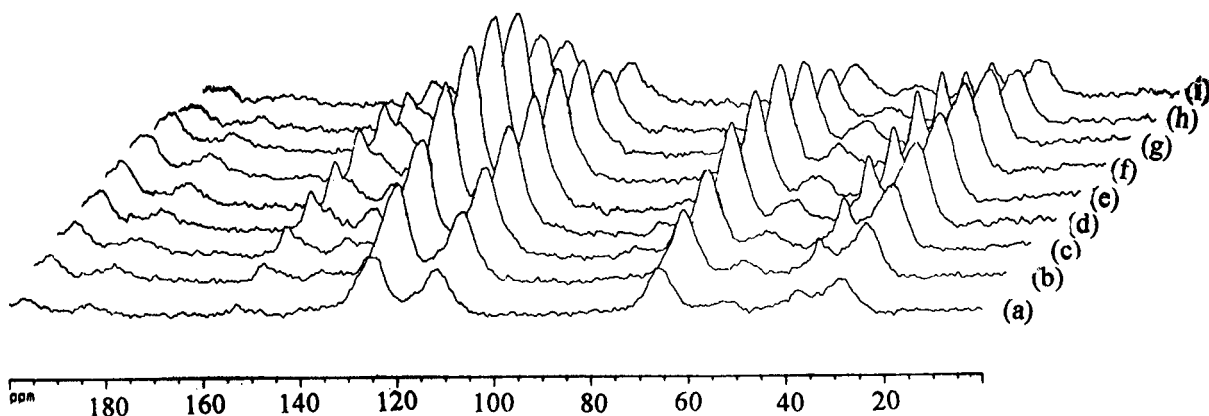


Fig. 5. The NMR spectra of the phenolic/phenoxy = 60/40 blend under various contact time ( $\tau_c$ ) (a) 0.1 ms, (b) 0.3 ms, (c) 0.5 ms, (d) 1 ms, (f) 1.5 ms, (g) 2.25 ms, (h) 5 ms, and (i) 9 ms

mobility is expected. This behavior can be monitored by the reduction of cross-polarization efficiency (i.e. revealed by the increase of  $T_{\text{CH}}$  contact time) and the shortening of  $T_{1\rho}^{\text{H}}$  relaxation time.

#### $T_{\text{CH}}$ contact times

The CP rate ( $1/T_{\text{CH}}$ ) under spin-locking conditions is determined by the effective strength of the dipolar interaction (controlled by both molecular motion and the C-H distance) and the  $^1\text{H}$  and  $^{13}\text{C}$  relaxation behaviors. A typical magnetization variation of  $^{13}\text{C}$  intensities versus the contact time is shown in Fig. 5 for  $\text{C}_3$  carbon in various phenolic/phenoxy blend compositions. Fig. 6 shows the logarithmic  $\text{C}_3$  signal intensities versus contact time for various phenolic/phenoxy blend compositions. By considering the protons as an infinite magnetization reservoir, the  $^{13}\text{C}$  variation can be described as<sup>22</sup>:

$$M(\tau_c) = \frac{M_0}{\lambda} [1 - \exp(-\lambda\tau_c/T_{\text{CH}})] \exp(-\tau_c/T_{1\rho}^{\text{H}})$$

$$\lambda = 1 + T_{\text{CH}}/T_{1\rho}^{\text{C}} - T_{\text{CH}}/T_{1\rho}^{\text{H}} \quad (2)$$

where  $M_0$  is the equilibrium magnetization,  $T_{1\rho}^{\text{C}}$ , and  $T_{1\rho}^{\text{H}}$  are the spin lattice relaxation constants for carbon and proton, respectively. The contact time  $T_{\text{CH}}$  can be modeled with experimental data by assuming  $T_{1\rho}^{\text{C}} \gg T_{1\rho}^{\text{H}}$ . Tab. 2 summarizes the  $T_{\text{CH}}$  relaxation times derived for various uncured various phenolic/phenoxy composition blends at 300 K. The quaternary carbons, i.e.  $\text{C}_3$ ,  $\text{C}_5$  and  $\text{C}_6$ , show a longer  $T_{\text{CH}}$  than other carbons since the hydrogen is a long distance away from these carbons. In all cases, the  $T_{\text{CH}}$  values do not change monotonically. As seen in Tab. 2, the  $\text{C}_3$  carbon increases first with initial addition of phenoxy followed by a sharp decrease with a continuing increase of phenoxy. Similarly, a slight initial increase is observed, for carbons  $\text{C}_5$ ,  $\text{C}_6$ , and  $\text{C}_7$  (phenoxy), followed by a decrease on more incorporation of

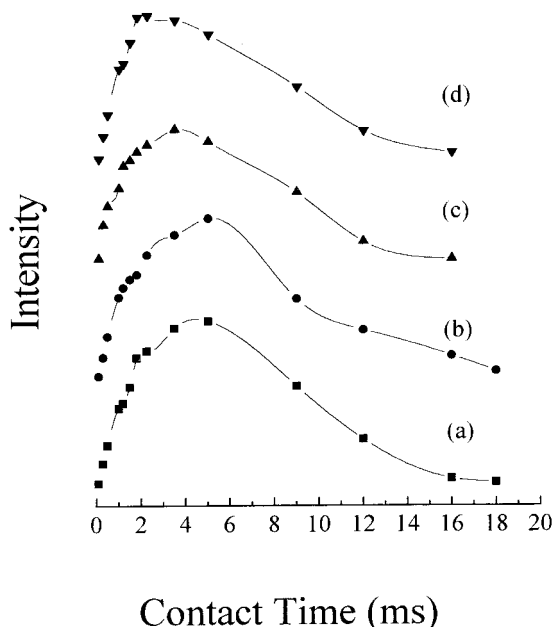


Fig. 6. Logarithmic  $^{13}\text{C}$  signal intensities of  $\text{C}_3$  versus contact time for various phenolic/phenoxy composition blends. (a) 100/0,  $\blacksquare$ ; (b) 80/20,  $\bullet$ ; (c) 60/40,  $\blacktriangle$ ; and (d) 40/60,  $\blacktriangledown$  phenolic/phenoxy blend

phenolic. The initial rise of  $T_{\text{CH}}$  in both phenolic and/or the phenoxy-rich region suggests that the polymer network is more loosely packed, requiring longer contact times for the cross-polarization to take effect. The OHs are more effectively paired to form a tighter H-bonding network in the mid-region. This indicates sufficient dipolar interaction leading to a more efficient CP process, as reflected in the reduction of the  $T_{\text{CH}}$  in the mid-region. The conclusion that the blend is highly miscible is consistent with the observations in the chemical shifts. The initial addition of phenoxy (and/or phenolic) results in more free OHs, presumably due to the long repeat units of phenoxy.

Tab. 2.  $T_{CH}$  relaxation times (in ms) of phenoxy and uncured phenolic, phenolic/phenoxy blends at 300°K

	C <sub>3</sub> 150 ppm	C <sub>5</sub> 153 ppm	C <sub>6</sub> 140 ppm	C <sub>7</sub> 66 ppm
Pure phenolic	3.86			
Phenolic/phenoxy = 80/20	4.04	1.69		0.38
Phenolic/phenoxy = 60/40	2.6	2.21	1.54	0.62
Phenolic/phenoxy = 40/60	1.79	2.43	3.07	0.70
Phenolic/phenoxy = 20/80		3.63	3.51	0.73
Pure phenoxy		3.34	3.28	0.68

### $T_{1\rho}^H$ relaxation times

Proton  $T_{1\rho}$  via a resolved carbon resonance provides similar information on the molecular motion of the complicated class of polymer blends. Fig. 7 shows the logarithmic plots of the C<sub>7</sub> (phenoxy) <sup>13</sup>C signal intensities versus the spin-lock time for phenoxy and uncured various phenolic/phenoxy blend compositions. The carbon signal can be formulated by a simple exponential decay equation<sup>23</sup>. The  $T_{1\rho}^H$  values derived from such a relation for all compositions are estimated to be accurate within  $\pm 0.2$  ms which are summarized in Tab. 3. With the miscibility appearing in the molecular level, a single relaxation time can be approximated by interpolation using the following additive relation:

$$T_{1\rho}(H)_{\text{Blend}} = \left[ \frac{M(H)_{\text{Phenolic}}}{T_{1\rho}(H)_{\text{Phenolic}}} + \frac{M(H)_{\text{Phenoxy}}}{T_{1\rho}(H)_{\text{Phenoxy}}} \right]^{-1} \quad (3)$$

where  $M(H)_{\text{Phenolic}}$  and  $M(H)_{\text{Phenoxy}}$  are mole fractions of proton in the parent polymers and  $T_{1\rho}(H)_{\text{Phenolic}}$  (6.86 ms) and  $T_{1\rho}(H)_{\text{Phenoxy}}$  (4.24 ms) are the relaxation times for uncured phenolic and phenoxy, respectively. The weighted values by Eq. (3) are summarized in the last column in Tab. 3 for comparison. Knowing that the relaxation occurred in the region on the right-hand side of the V-shape correlation of the  $\ln(T_{1\rho}^H)$  versus correlation  $(1/T)$  plot<sup>24</sup>, the shorter  $T_{1\rho}^H$  implies a shorter  $\tau$  value and indicates a higher molecular motion. Notice that the  $T_{1\rho}^H$ 's of the carbons originated from phenolic and phenoxy are of the same value in the intermediate region and is greater than that calculated from Eq. (3). This result gives strong evidence that the blends are miscible in the molecular scale<sup>25</sup> and exhibit a stiffer framework than those blends without the specific interaction. It is worth noting that  $T_{1\rho}^H$  values of C<sub>5</sub> and C<sub>7</sub> of the 20/80 and 80/20 (phenolic/phenoxy) blends are substantially lower than those calculated values. The values are also lower than those from the neat polymers. One can conclude that when one of the polymers is the major component, the presence of H-bonding reorganization and the presence of more free OHs leads to less H-bonding and the component polymer matrix is more flexible than that of the corresponding parent components.

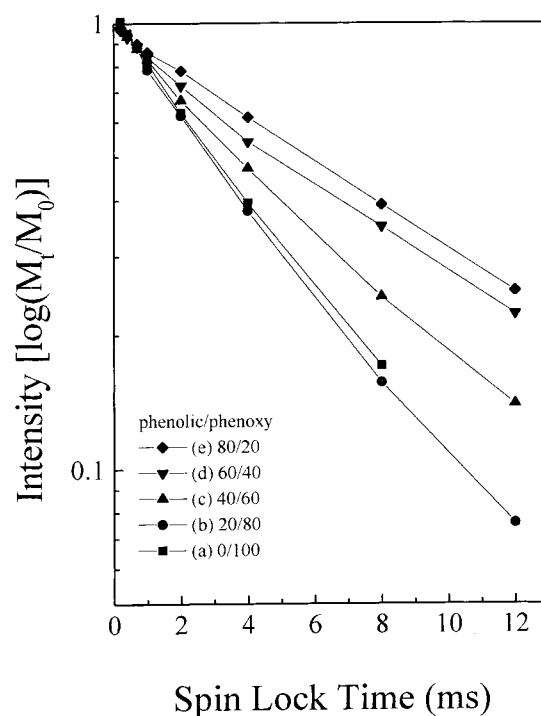


Fig. 7. Logarithmic <sup>13</sup>C signal intensities of C<sub>7</sub> versus the spin-lock time ( $T_{1\rho}^H$ ) for phenoxy and phenolic/phenoxy blends. (a) 0/100, ■; (b) 20/80, ●; (c) 40/60, ▲; (d) 80/20, ▼ phenolic/phenoxy blend

Tab. 3.  $T_{1\rho}^H$  relaxation times of phenoxy, and uncured phenolic, phenolic/phenoxy blends at 300 K

	C <sub>3</sub> 150 ppm	C <sub>5</sub> 153 ppm	C <sub>7</sub> 66 ppm	Calc. from Eq. (3)
Pure phenolic	6.86			6.86
Phenolic/phenoxy = 80/20	4.22			6.11
Phenolic/phenoxy = 60/40	6.52	6.62	6.50	5.49
Phenolic/phenoxy = 40/60	5.72	5.70	4.75	5.07
Phenolic/phenoxy = 20/80		3.72	3.69	4.59
Pure phenoxy		4.12	4.24	4.24

The intimate miscibility is consistent with the picture of a tightly-bound H-bonded matrix, whilst the higher mobility in the phenolic-rich region is consistent with the picture that the longer repeating unit in phenoxy expands the matrix, creating more free OHs and leads to a looser framework. The presence of more free OH groups in the phenolic-rich and phenoxy-rich regions, leads to micro-domain heterogeneity and a more flexible framework. The substantial improvement in the unnotched Izod impact strength is likely to be associated with the extended framework of the blend, which effectively absorbs excess energy upon impact<sup>10</sup>.

## Conclusions

In the present study of a complete miscible phenolic/phenoxy blend system, an unusual volume expansion and  $T_g$

reduction are observed. This observation is inconsistent with the expected strong intermolecular H-bonding formation in a conventional mixture. This unusual observation can be attributed to the formation of the intermolecular H-bonding between phenolic and phenoxy, leading to more "free" OHs present in the phenolic-rich region.

The solid state NMR parameters (i.e. chemical shift, efficiency of cross-polarization, and  $T_{1\rho}^{\text{H}}$  relaxation time) confirm the presence of more free OH groups when one of the polymers is the minor component. The entropic factor from longer repeated units of the phenoxy explains the substantial glass temperature reduction and volume expansion, which leads to a swollen framework and an increase in molecular mobility (as shown by the  $T_{\text{CH}}$  and  $T_{1\rho}^{\text{H}}$  values for this highly miscible blend). In the mid-range composition, more effective pairing of H-bonding results in more intermolecular H-bonding and drives the miscibility as well as a stiffer framework.

The present results raise the issue that the structure of a modifier can play an important role in the properties of the polymer blend. The structural factor of a polymer can introduce an additional entropy factor in considering the thermodynamics of the polymer blend, as well as the effects on the mechanical properties.

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- 1) Y. Zaks, L. Jeelen, D. Raucher, E. M. Pearce, *J. Appl. Polym. Sci.* 1982, **27**, p. 913
- 2) A. Knop, L. A. Pilot, "*Phenolic Resin*", Springer, Berlin 1985
- 3) P. Ernest, *Plast. Eng.* Nov. (1988) p. 39
- 4) G. R. Bishop, P. A. Sheard, *Comp. Struct.* **21**, 85 (1992)

- 5) C.-C. M. MA, W. C. Shih, US Patent 4873 128, 1989
- 6) T. P. Yang, T. K. Kwei, E. M. Pearce, *J. Appl. Polym. Sci.* **41**, p. 1327 (1991)
- 7) A. Matsumoto, K. Hasegawa, A. Fukuda, K. Otsuki, *J. Appl. Polym. Sci.* **43**, 365 (1991); (a) A. Matsumoto, K. Hasegawa, A. Fukuda, K. Otsuki, *J. Appl. Polym. Sci.* **44**, 205 (1992); (b) A. Matsumoto, K. Hasegawa, A. Fukuda, K. Otsuki, *J. Appl. Polym. Sci.* **44**, 1547 (1992)
- 8) H. D. Wu, C.-C. M. Ma, M. S. Li, Y. D. Wu, *Angew. Makromol. Chem.* **235**, 35 (1996)
- 9) X. Zhang, D. H. Solomon, *Macromolecules* **27**, 4919 (1994)
- 10) H. D. Wu, C.-C. M. Ma, J. M. Lin, *J. Appl. Polym. Sci.* **63**, 911 (1997)
- 11) H. D. Wu, C.-C. M. Ma, P. P. Chu, *Polymer* **39**, 3, 703 (1998)
- 12) E. Espi, M. Alberdi, J. J. Iruin, *Macromolecules* **26**, 4586 (1993)
- 13) C. Uriarte, J. I. Eguiazabal, M. Llanos, J. I. Iribarren, J. J. Iruin, *Macromolecules* **20**, 3038 (1997)
- 14) C. Uriarte, J. J. Iruin, M. J. Fernandez-Berridi, J. M. Elorza, *Polymer* **30**, 1155 (1989)
- 15) M. Iriarte, E. Espi, A. Etxeberria, M. Valero, M. J. Fernandez-Berridi, J. J. Iruin, *Macromolecules* **24**, 5546 (1991)
- 16) R. N. Ibbett, "*NMR Spectroscopy of Polymer*", Blackie Academic & Professional, an imprint of Chapman & Hall, Glasgow, U.K., 1993
- 17) R. A. Komoroski, "*High Resolution NMR Spectroscopy of Synthetic Polymers in Bulk*", VCH Publishers, Inc. Deerfield Beach, Florida, 1986
- 18) H. W. Spiess, K. Schmidt-Rohr, "*Multidimensional Solid State NMR and Polymers*", Academic Press inc., San Diego, CA 1994
- 19) P. C. Painter, J. F. Graf, P. C. Painter, *Macromolecules* **24**, 5630 (1991)
- 20) I. C. Sanchez, R. H. Lacombe, *J. Phys. Chem.* **80**, 2352 (1976)
- 21) R. H. Lacombe, I. C. Sanchez, *J. Phys. Chem.* **80**, 2568 (1976)
- 22) R. A. Komoroski, "*High Resolution NMR Spectroscopy of Synthetic Polymers in Bulk*", VCH, Weinheim 1986, Ch. 2
- 23) T. T. P. Cheung, B. C. Gerstein, *J. Appl. Phys.* **52**, 5517 (1981)
- 24) T. M. Connor, *NMR: Basic Princ. Prog.* **4**, 247 (1971)
- 25) J. F. Parmer, L. C. Dickinson, J. C. W. Chien, R. S. Porter, *Macromolecules* **22**, **3**, 1078 (1988)