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Hydrogen bonding in the novolac type phenolic resin blended with phenoxy resin

Hew-Der Wu and Chen-Chi M. Ma*
Institute of Chemical Engineering, National Tsing Hua University, Hsin-Chu, Taiwan, R.O.C. 30034

and Peter P. Chu
Department of Chemistry, National Central University, Chung-Li, Taiwan, R.O.C. 32054
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The hydrogen bond formation between novolac type phenolic resin (phenolic) and polyhydroxyl ether of bisphenol A (Phenoxy resin) were verified by infra-red (i.r.), gel permeation chromatography (g.p.c.) and nuclear magnetic resonance (n.m.r.). The i.r. spectrum of the 'free' hydroxyl group of the blend shows a maximum absorption area with 25 wt% phenoxy which coincides with the lowest point of the glass transition temperature (T_g) is observed. In the phenolic-rich region, almost all the hydroxyls of the phenoxy interact with the phenolic resin. The carbonyl group of benzoylated phenoxy (Bz-phenoxy) confirms further the association of hydrogen bonding with hydroxyls of phenolic resin. It was found that phenolic resin interpenetrates with the phenoxy and Bz-phenoxy and causes significant decreasing of T_g. © 1997 Elsevier Science Ltd.

(Keywords: phenolic; phenoxy; blend)

INTRODUCTION

Phenol/formaldehyde (phenolic) resins have important commercial applications[1], such as moulding compounds, coatings, adhesive and electrical insulation parts, because of their low manufacturing cost, dimensional stability, fire resistance, and high tensile strength[1–3]. However, the inherent poor impact strength limits its applications. In previous studies, it was found that the properties of phenolic resin may be improved by blending the resin with other polymers[4–7].

Intermolecular interactions are considered to play a key role in polymer compatibility. Phenolic resin contains a high density of hydroxyl groups which will interact with other polymers significantly. Hydrogen-bonds could act as physical crosslink in phenolic resin, and result in a higher glass transition temperature (T_g). The novolac type phenolic resin shows a higher T_g than other material with similar molecular weight, due to its high hydrogen bond density content. When phenolic resin is blended with phenoxy, T_g decreases significantly. A special interaction may occur in the blend system. In this study, the association of hydroxyl groups between novolac type phenolic resin and phenoxy resin was investigated.

In order to obtain the extent of mixing from the analysis of isolated normal modes, an infra-red (i.r.) probe size was used, since this is at the scale of a few angstroms[8]. Infrared spectrum is also sensitive to perturbation arising from specific intermolecular hydrogen-bonding interactions. In this study, this aforementioned technique is utilized to investigate the hydrogen bond of the phenoxy/phenolic (novolac type) blend—the lower hydroxyl group density content and mobile polymer (phenoxy) blended with higher hydroxyl group density content and rigid polymer (phenolic) resin.

The hydrogen bond of 2-propanol in phenoxy is difficult to investigate by i.r. When phenoxy resin was benzoylated (Bz-phenoxy), its secondary C=O group can interact with the hydroxyl group of the phenolic resin, similar to the action of 2-propanol on phenoxy, the hydrogen bonds can be detected easily. Bz-phenoxy was widely used instead of phenoxy to determine the miscibility[9,10]. The solubility parameters of phenolic resin, phenoxy, and Bz-phenoxy, obtained from PCAM[11], are 12.07, 9.81, and 10.28, respectively. If intermolecular hydrogen bonding did not exist, the phenoxy and Bz-phenoxy would be immiscible with phenolic resin because of the different solubility parameters between phenolic resin and phenoxy, Bz-phenoxy, respectively.

The carbonyl stretching vibration has been proved to be an excellent probe to detect the molecular mixing for a number of polymer blends[9–15]. In the phenolic-rich regions, the *inter*molecular hydrogen bond between the hydroxyl of phenolic resin and carbonyl of benzoylated phenoxy (Bz-phenoxy) is similar to the hydrogen bond between phenoxy and phenolic. This information should lead to a better understanding of the relationship between hydrogen bonding and T_g. The repeated phenoxy unit hinders the self-associated hydroxyl group of phenolic in the phenolic-rich region, and decreases the T_g of phenoxy phenolic blend.

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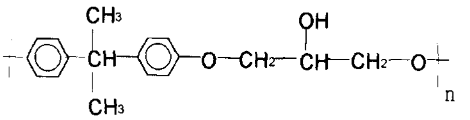
* To whom correspondence should be addressed

EXPERIMENTAL

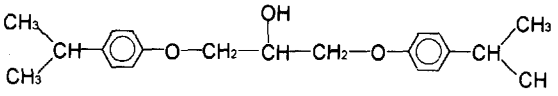
Samples

The novolac type phenolic resin (phenolic) was synthesized with sulfuric acid via a condensation reaction. The novolac type phenolic resin sample contains 0.15 wt% free phenol. The chemical structure consists of phenol ring bridge-linked randomly by methylene groups with 24% *ortho–ortho*, 57% *ortho–para*, and 19% *para–para* methylene bridges investigated by solution ^{13}C nuclear magnetic resonance (n.m.r.), and with average molecular weights $M_n = 500$ and $M_w = 1200$. The novolac type phenolic resin does not contain reactive methylol group results in crosslinking on heating. A typical novolac type phenolic resin might be considered as a complex mixture of polynuclear phenol linked by *ortho-* and *para*-methylene groups[1]. Usually, the commercial novolac phenolic chains are essentially linear (although some branching has been detected by n.m.r. in this study).

The polyhyroxyl ether of bisphenol A (Phenoxy resin, PKHH) was obtained from the Union Carbide Co., USA, $M_n = 23000$, $M_w = 48000$. The repeated phenoxy unit is described as follows:



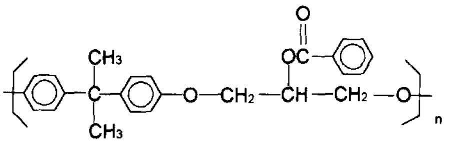
The synthesis of phenoxy resin analogue (1,3-*bis*-(4-(2-propyl) phenoxy)-2-propanol (IPPHP)), is described as follows. NaOH (40 wt% water solution) was added to isopropyl phenol (1/1 molar ratio, and the mixture was stirred at 50°C for 20 min. Epichlorohydrin (three times as many moles of epichlorohydrin than isopropyl phenol) was added and stirred at 50°C for 20 min and then refluxed for 3 h[9].



The mixture was washed with ethyl ether three times, and the organic phase was washed successively with 10% aqueous NaOH and water. The solvent was evaporated and the product was recrystallized from hexane. The sample was characterized by i.r., and ^{1}H and ^{13}C n.m.r.

Benzoylated-phenoxy resin[9]

Phenoxy resin was dissolved in anhydrous pyridine (1/20) and benzoyl chloride (with three times as many moles as the repeated unit of phenoxy) was then added. After the addition of benzoyl chloride, the mixture was refluxed for 2 h until the reaction was complete. The mixture was then poured into a 0.5 wt% Na_2CO_3 aqueous solution to remove the residual benzoyl chloride and to separate the benzoylated polymer. The dried polymer was dissolved in THF, precipitated in hexane twice, then dried in a vacuum oven at 50°C for 2 days. A fully benzoylated phenoxy resin was obtained. The structure is as follows:



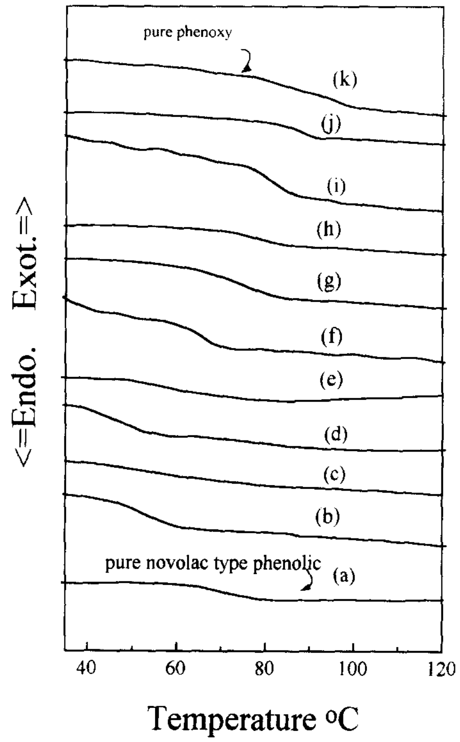


Figure 1 D.s.c. curves of phenoxy/phenolic blends with various compositions (wt%): (a) 0/100; (b) 5/95; (c) 10/90; (d) 15/85; (e) 20/80; (f) 25/75; (g) 30/70; (h) 40/60; (i) 60/40; (j) 80/20; (k) 100/0

The polymer was characterized by i.r., ^{1}H and ^{13}C n.m.r., differential scanning calorimetry (d.s.c.) and gel permeation chromatography (g.p.c.). The Bz-phenoxy T_g is 75°C, M_n is 34 000 and M_w is 69 000.

Characterization

Differential scanning calorimetry. The T_gs of the polymer blend films were determined by d.s.c. (DuPont, DSC Model 2900). The scan rate was 20°C min^{-1} within a temperature range of 10–130°C. The measurement was made with 3–4 mg samples on a d.s.c. sample plate after the specimens were quickly cooled to room temperature following the first scan. This procedure was adopted to ensure a complete mixing of the polymer blends, and to remove the residual solvent and water in the specimen completely. 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 was within ±1°C.

Infra-red spectroscopy. The phenoxy/phenolic and Bz-phenoxy/phenolic blends were prepared by the solution-casting method. These two materials were mixed in tetrahydrofuran (THF, 1% (w/v)) at room temperature according to the designed compositions. The mixed solution was stirred for 6–8 h, and the solution was allowed to evaporate slowly at room temperature for 1 day. The blending films were then dried at 50°C for 2 days and annealed at 140°C for 2 h under vacuum. I.r. studies were carried out on a Perkin-Elmer i.r. spectrometer with the conventional NaCl disc method. The samples were scanned at a resolution of 2 cm^{-1} at various temperatures. A maximum temperature of 190°C was used in this case, as it was determined independently that a significant chemical reaction may occur at 200°C or higher. I.r. spectra recorded at elevated temperature were obtained by using a heating cell mounted

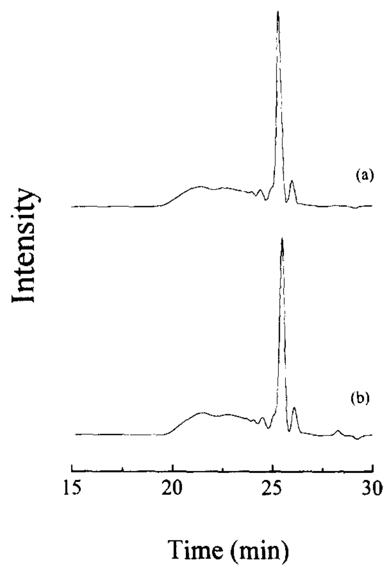


Figure 2 G.p.c. curves of 50/50 (wt%) IPPHP/phenolic blends: (a) unheated; (b) heated at 140°C for 2 h

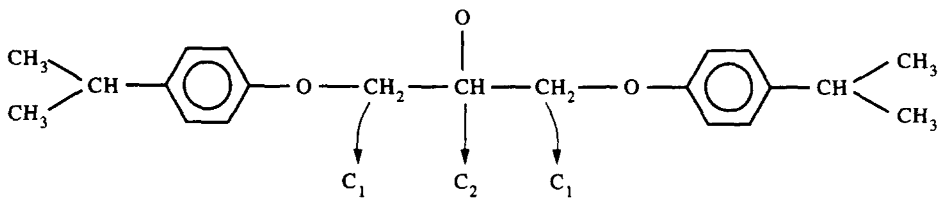
inside the sample compartment of the spectrometer. Temperature was controlled within ±0.1°C.

Solution ^{13}C nuclear magnetic resonance and gel permeation chromatography. Solution ^{13}C n.m.r. of the phenoxy/phenolic blend was measured by using a Bruker AM 400 spectrometer operating at 100 MHz for ^{13}C. Deuterated acetone was used as lock solvent and tetramethylsilane as the internal standard. G.p.c. of the phenolic/phenoxy blends was measured with a Waters styragel HR series of g.p.c. columns. THF was used as the mobile phase, and the flow rate was 1 ml min^{-1}. The two measurements provide information which confirms that chemical reaction does not take place between the blended components under the blending conditions at 140°C for 2 h.

RESULTS AND DISCUSSION

D.s.c. analysis

The T_gs of pure phenoxy and pure phenolic measured by d.s.c. were 95 ± 1°C and 70 ± 1°C, respectively. The phenoxy resin is amorphous and flexible, while the phenolic resin is an amorphous and relatively rigid material.



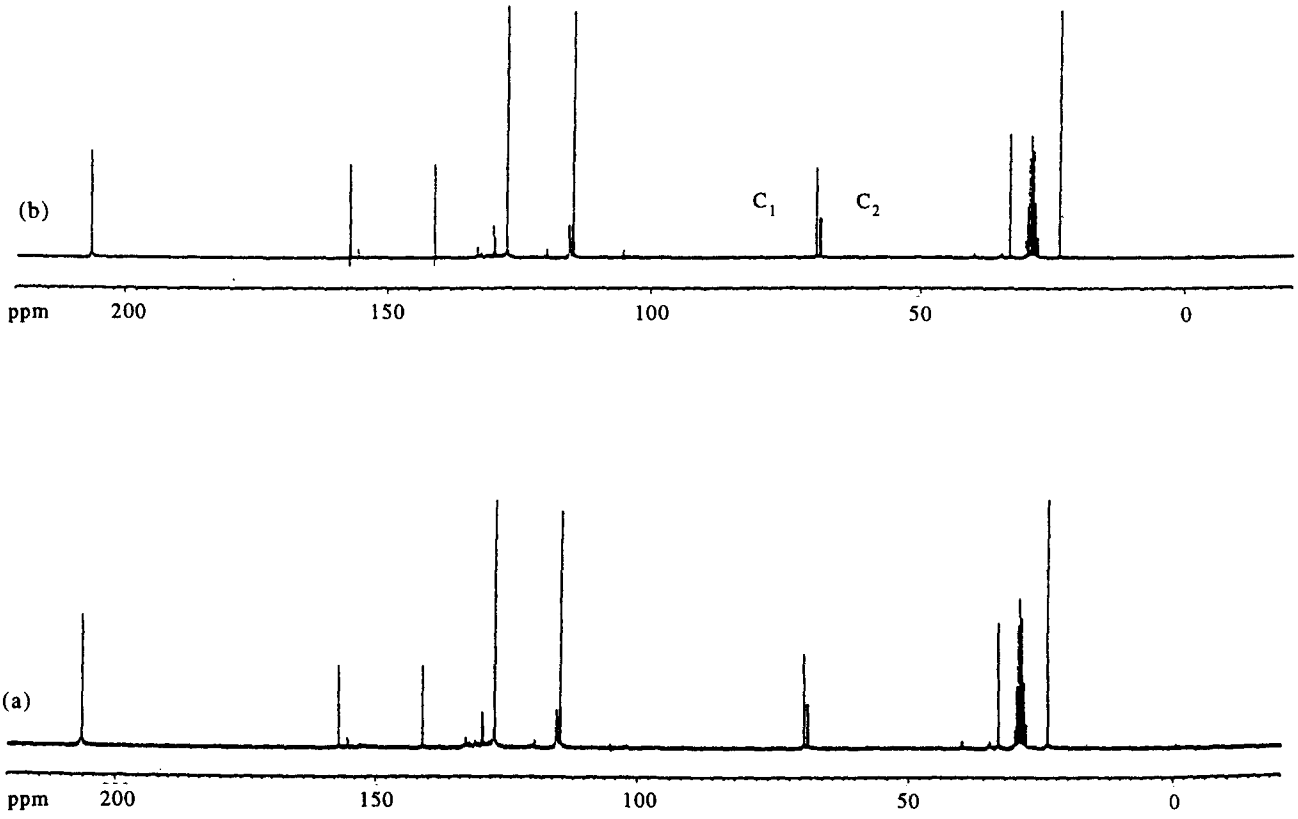


Figure 3 Solution ^{13}C n.m.r. spectra of the 50/50 (wt%) IPPHP/phenolic blends: (a) before, and (b) after heating at 140°C for 2 h

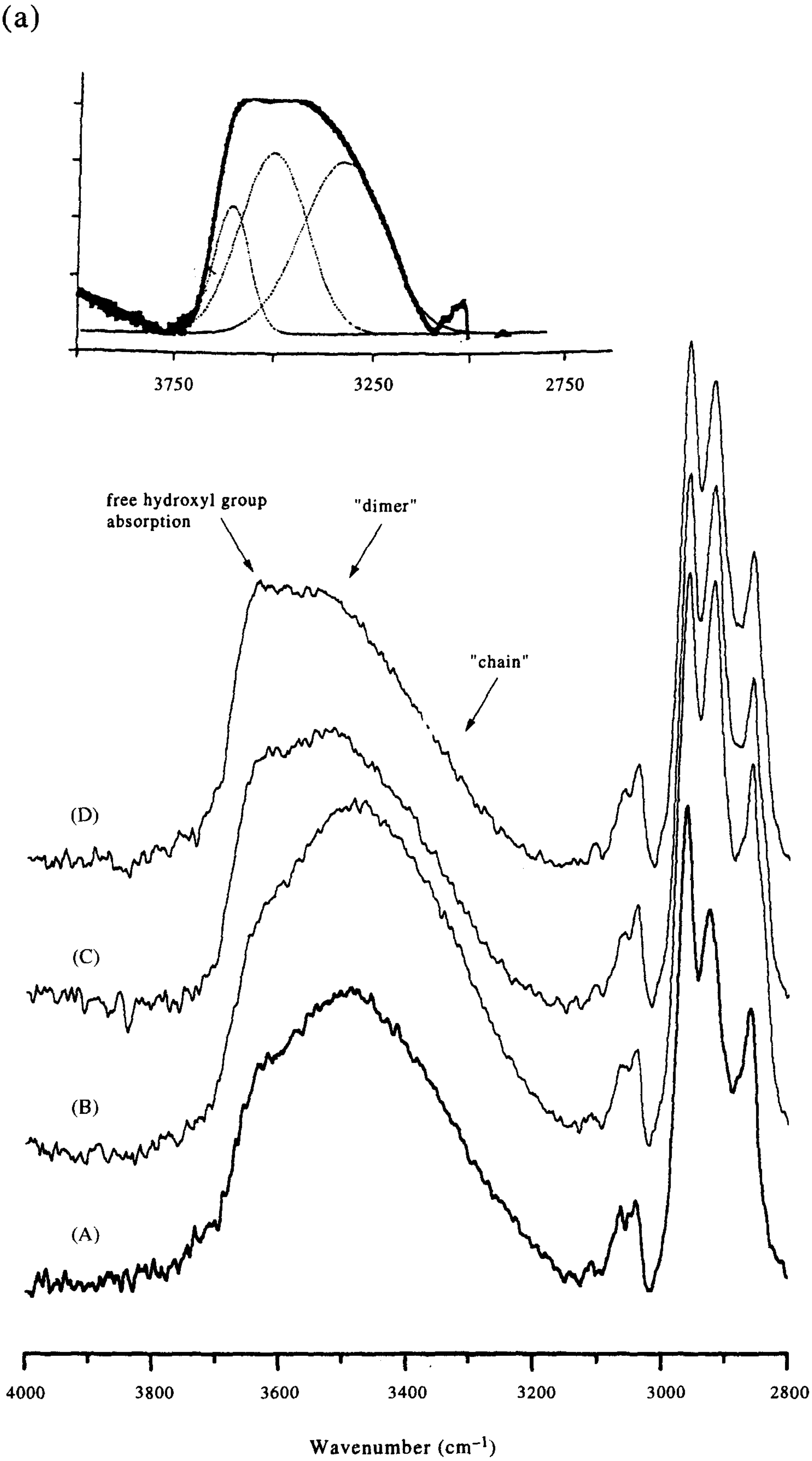


Figure 4 (a) I.r. spectra of the hydroxyl stretching range of the pure phenoxy at various temperatures: (A) 50°C; (B) 100°C; (C) 120°C; (D) 160°C. (b) I.r. spectra of the hydroxyl stretching range of the pure phenolic at various temperatures: (A) 50°C; (B) 100°C; (C) 120°C; (D) 160°C

Figure 1 shows the d.s.c. thermograms after the second run for pure phenoxy and pure phenolic as well as blends with different compositions. All thermograms exhibit a single but broad T_g which does not corroborate systematically with the blending compositions, and even 30°C lower than the prediction in 20/80 (w/w) phenoxy/phenolic blend. There is a high special interaction in the blend system. The phenolic resin contains a high density hydroxyl group that causes the strong *intra*-hydrogen bonding, and shows a higher T_g than other similar molecular weight polymers. The lowering of the T_g due to the self-association of phenolic was removed when blended with the phenoxy in the phenolic-rich region. Similar thermal behaviour was observed for the Bz-phenoxy/phenolic blends. The special behaviour of the T_g indicates not only that the phenoxy and phenolic are miscible, but that a special interaction between these two polymers may be substantiated[14,15]. These results motivate the investigation of the interactions between phenoxy and phenolic specific repeated units.

G.p.c. and solution ^{13}C n.m.r. analysis

Two preliminary measurements, ^{13}C solution n.m.r. and g.p.c., were carried out to investigate whether chemical reaction occurred or not between phenoxy and phenolic resins. The 1,3bis-(4-(2-propyl) phenoxy)-2-propanol (IPPHP) was used as a chemical analogous phenoxy. In *Figure 2*, a sharp elution peak at 25.3 min is assigned to IPPHP. For 50/50 IPPHP/phenolic blends, the intensity of elution peak has not changed after heating at 140°C for 2 h. In *Figure 3*, the n.m.r. spectra of IPPHP/phenolic, the C–OH carbon resonance of IPPHP is assigned to a chemical shift of 68.7 ppm. This chemical shift still exists after heating for 2 h at 140°C for the IPPHP/phenolic blend. It may be concluded that no chemical reaction occurred between

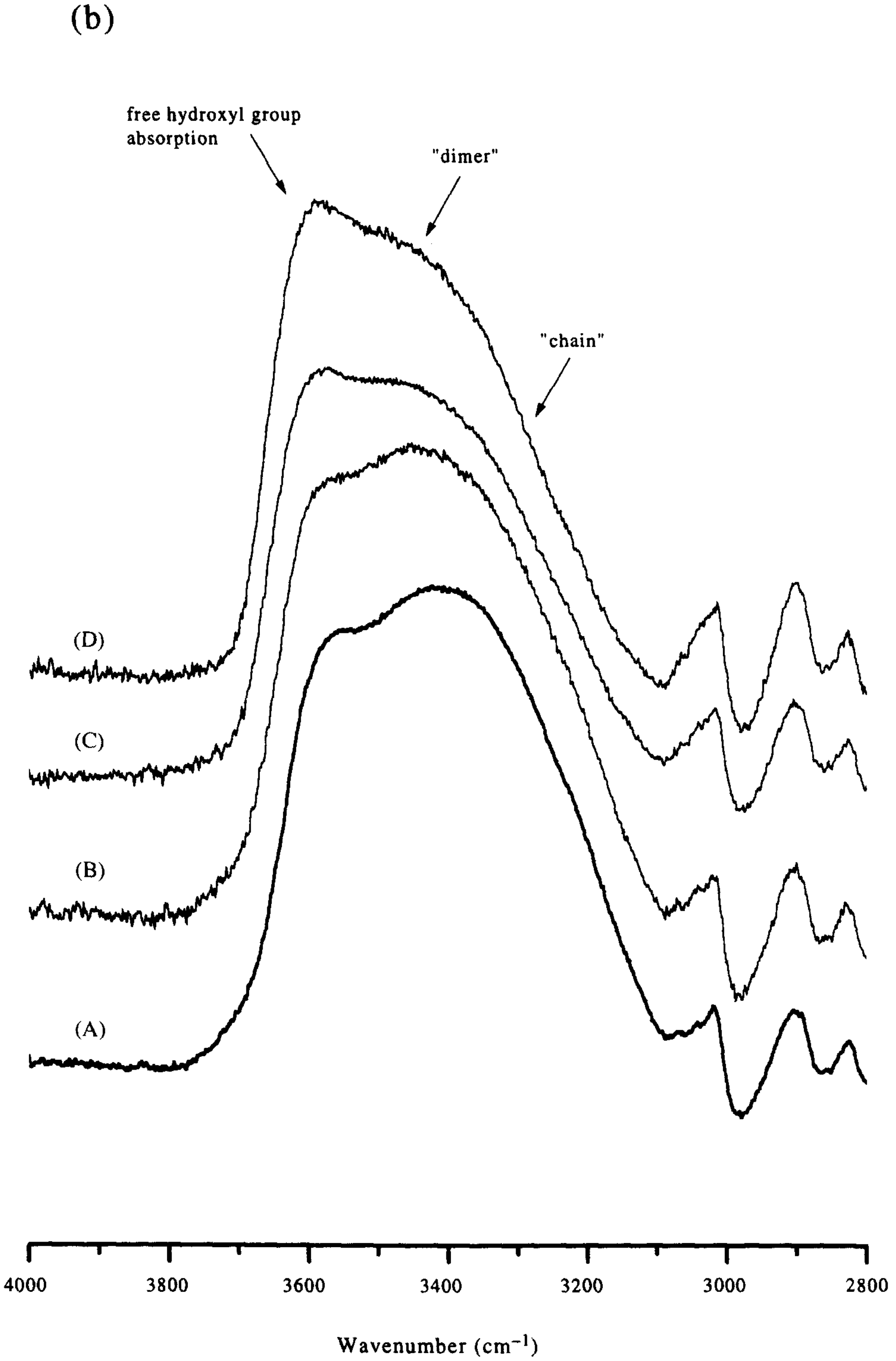


Figure 4 (Continued)

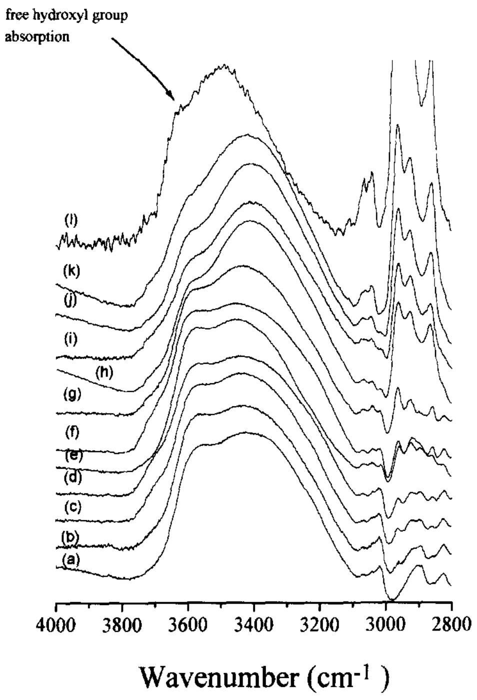


Figure 5 I.r. spectra of the hydroxyl stretching range with various compositions of phenoxy/phenolic blends at 100°C: (a) 0/100; (b) 5/95; (c) 10/90; (d) 15/75; (e) 20/80; (f) 25/75; (g) 30/70; (h) 40/60; (i) 50/50; (j) 60/40; (k) 80/20; (l) 100/0

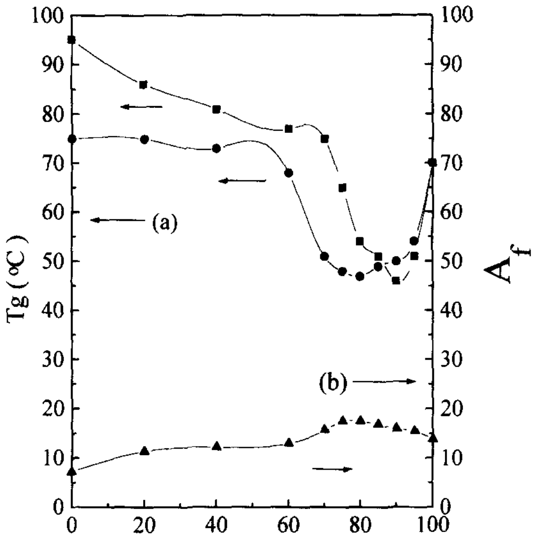


Figure 6 (a) T_g vs phenolic content of phenoxy/phenolic (■) and Bz-phenoxy/phenolic (●) blend composite. (b) A_f vs phenolic content of phenoxy/phenolic blend composite (▲)

or within the polymer blend system, from those measurements.

Infra-red spectrum

I.r. measurements provide further information regarding the additional interaction existed among the polymer blend systems. An intuitive explanation for the variation of T_g with different compositions is that the hydrogen bond configuration influences the property of the blends significantly. In order to verify our hypothesis, i.r. spectroscopic measurements were carried out in the hydroxyl group of the polymer blends. The absorption region is between 3800 and 3100 cm^{-1}. As shown in *Figures 4a, 4b, 5* and *7*, the free hydroxyl group absorption appears at the region 3650–3580 cm^{-1}, while the hydrogen-bonded hydroxyl group shows a broad absorption band at the region 3550–3300 cm^{-1}. The presence of such i.r. absorption components support the idea that hydrogen bonds exist in the polymer blends[16]. An iterative least-square computer program was used to obtain the best fit of the recorded spectrum in this region. A linear baseline was drawn from 3800 to 3100 cm^{-1} to facilitate the curve-fitting procedure. It was confirmed that there are three Gaussian peaks in the hydroxyl stretching region, instead of just two major spectral components observed visually. This hydrogen-bonded hydroxyl band could be further resolved into a 'dimer' hydrogen-bonded hydroxyl peak at 3430–3550 cm^{-1} and the 'multimer' hydrogen-bonded hydroxyl peak around 3250–3380 cm^{-1}[17].

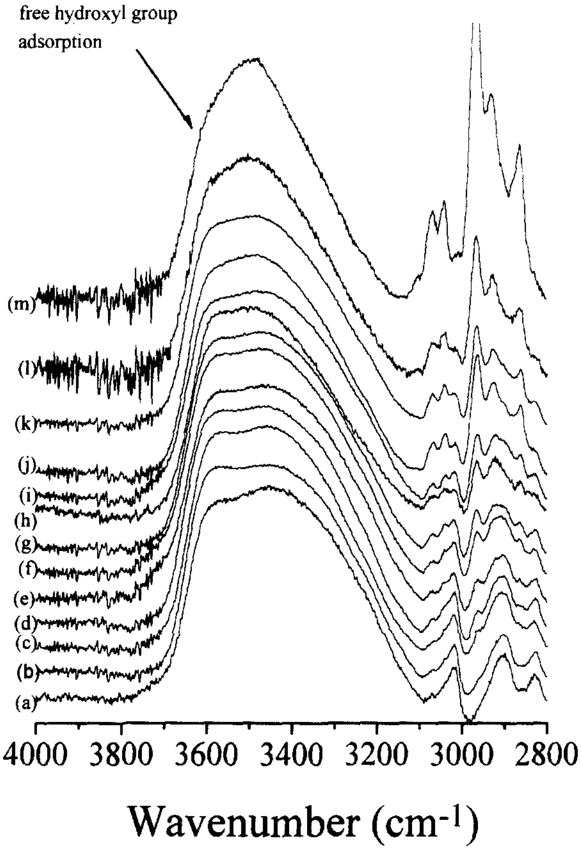


Figure 7 I.r. spectra of the hydroxyl stretching ragne with various compositions of Bz-phenoxy/phenolic blends at 100°C: (a) 0/100; (b) 5/95; (c) 10/90; (d) 15/75; (e) 20/80; (f) 25/75; (g) 30/70; (h) 40/60; (i) 50/50; (j) 60/40; (k) 70/30; (l) 80/20; (m) 100/0

Both the parent components of various temperatures as well as the blends of various compositions are analysed following the procedure.

Figure 4a shows the i.r. spectra of phenoxy at different temperatures in the region 3800–3100 cm^{-1} which correspond to the O–H stretching. At 50°C, one peak of the pure phenoxy spectra is centred at 3636 cm^{-1}, which is contributed by the free hydroxyl groups. The other broad band is observed centred between 3527 cm^{-1} and 3365 cm^{-1}, which is attributed to a wide distribution of 'dimer' and 'multimer' hydrogen-bonded hydroxyl stretching frequencies, respectively. In *Figure 4b*, the peak of the pure novolac type phenolic resin is observed at 3591 cm^{-1}, that is contributed by the free hydroxyl

Table 1 Curve-fitting data from i.r. spectra of phenoxy, phenolic, and their blends

Composition (phenoxy/phenolic)	Temperature (°C)	'Free' hydroxyl ν (cm^{-1})	($W_{1/2}$ cm^{-1})	A_f (%)
100/0	50	3636	61	4.6
	100	3638.2	78.7	7.13
	150	3644.6	73.2	11.3
	190	3646.7	67.6	11.8
0/100	50	3591.6	106.1	12.5
	100	3602.4	105.2	13.8
	150	3615.6	95.7	14.6
	190	3618.5	94	16.2
100/0	100	3638.2	78.7	7.13
80/20	100	3619.7	98.3	11.4
60/40	100	3610.8	97.5	12.2
50/50	100	3608.5	97.5	13.4
40/60	100	3603.9	94.8	13
30/70	100	3605	98.1	15.7
25/75	100	3596	49.7	17.5
20/80	100	3604.7	98.4	17.5
15/85	100	3604.2	102.8	16.9
10/90	100	3600.8	103.4	16
5/95	100	3599.8	103.6	15.5
0/100	100	3602.4	105.2	13.8

group, a very broad band is observed centred at 3447 cm^{-1} which attributed to a wide distribution of 'dimer' and 'multimer' hydrogen-bonded hydroxyl stretching frequencies, respectively. The change of the i.r. spectra shown in both *Figures 4a* and *4b* agree with the decreasing association of hydrogen-bonded hydroxyl at higher temperature that had been documented[18,19]. This particular behaviour is also consistent with the observation of the breaking of the hydrogen bonds of the phenoxy and phenolic resin as temperature increases[9]. The redistribution of intensity of absorption would be useful to the study of hydrogen-bond formation between phenoxy/phenolic blends of various compositions. The comparison between *Figures 4a* and *4b* suggests that the proportion of free hydroxyl (non hydrogen-bonded) groups in phenoxy resin is less than that of phenolic resin.

Figure 5 shows the i.r. spectra of the hydroxyl stretching range at a temperature (100°C) higher than the T_g of various phenoxy/phenolic compositions. The ratio of the area of the free hydroxyl absorption to the total area of hydroxyl group absorption, A_f, is used here as an index to infer the extent of 'free' hydroxyl groups existing in various blends. The frequency ν, the width at half-height $\omega_{1/2}$, and the intensity A_f of the 'free' hydroxyl bands are presented in *Table 1* and *Figure 6*. Starting from pure phenolic resin, the fraction of 'free' hydroxyl increases initially with increasing phenoxy content, up to 25 wt%, followed by a decrease up to 100 wt% phenoxy. It is contrary to what one would expect, that the lowest dissociation of hydrogen bonds of the blends system was found[20,21]. The pure phenoxy showed the lowest A_f value, while the 25/75 phenoxy/phenolic blends showed the highest A_f value. *Figure 6* shows that this trend of A_f vs composition is similar to that of T_g vs composition. The highest A_f value implies that there is less interaction of hydrogen bonding between phenoxy and phenolic in the phenolic-rich region. The band of the hydroxyl is contributed almost from the phenolic in the phenolic-rich region. It is obvious that the self-association of hydrogen-bonded phenolic is decreasing by phenoxy chain in the phenolic-rich region. That will be discussed in the n.m.r. study in the next report.

The variation of the two types (the interactions of phenoxy–phenolic and phenolic–phenolic are considered, and the phenoxy–phenoxy interaction is neglected in the phenolic-rich region) of associated hydroxyl group component is mainly caused by the blend composition. It is considered that the phenoxy chain may hinder the self-association of the hydroxyl within the phenolic resin, while provide more opportunity for intermolecular hydrogen bonding. However, the total amount of hydrogen bonding is decreased in blend system due to the lower density of hydroxyl groups of phenoxy resin, compared with phenolic resin.

The details regarding the change of curve pattern and the shift of maximum for the bands corresponding to the 'dimer' and the 'multimer' associated hydroxyl will be discussed in a further study. It should be emphasized that the i.r. band of the alkyl group from the polymer can overlap with the band of the hydroxyl group. This creates a potential error during peak-fitting, and therefore the free hydroxyl quantity can only be considered approximately and not absolutely.

In this case, the actual hydrogen-bond associations between phenoxy and phenolic remain somewhat ambiguous. In the following section, in order to illustrate these relations more clearly, the carbonyl group of benzoylated phenoxy resin will be used, instead of the hydroxyl of the phenoxy.

The association of phenolic with Bz-phenoxy

In this study, the Bz-phenoxy resin was used as a blend component in order to detect the apparent hydrogen-bonded fraction. The Bz-phenoxy does not exhibit *intra*molecular hydrogen bonding. The i.r. band of C=O stretching is far removed from other absorption. The use of Bz-phenoxy is very promising in delivering a much clearer picture regarding the hydrogen bonding association. Again, the fraction of hydrogen-bonded carbonyl group was measured as a function of temperature, as well as for various phenoxy/phenolic blend compositions through the C=O stretching region. It was a straightforward task to distinguish and quantify those carbonyl groups where the hydrogen bond appeared in the hydroxyl groups of phenolic. *Figure 8* shows the i.r. spectra of carbonyl stretching region of various Bz-phenoxy/phenolic blend compositions at 50°C. The carbonyl stretching vibration of pure Bz-phenoxy in the blend (self-association) occurs at 1723 cm^{-1}. Upon blending of Bz-phenoxy with phenolic, an additional band at 1699 cm^{-1} is observed which is increased in relative intensity as a function of phenolic content. Upon mixing with phenolic resin, the overlapping peaks broaden gradually. The stretching vibration of hydrogen-bonded carbonyl groups is readily attributed to the hydroxyl group of the phenolic. By using an appropriate base line, the band envelope may be readily decomposed into two Gaussian peaks. The fraction of the hydrogen-bonded carbonyl can be calculated from the following equation[11]

$$f_b = \frac{\frac{A_b}{1.5}}{\frac{A_b}{1.5} + A_f} \qquad (1)$$

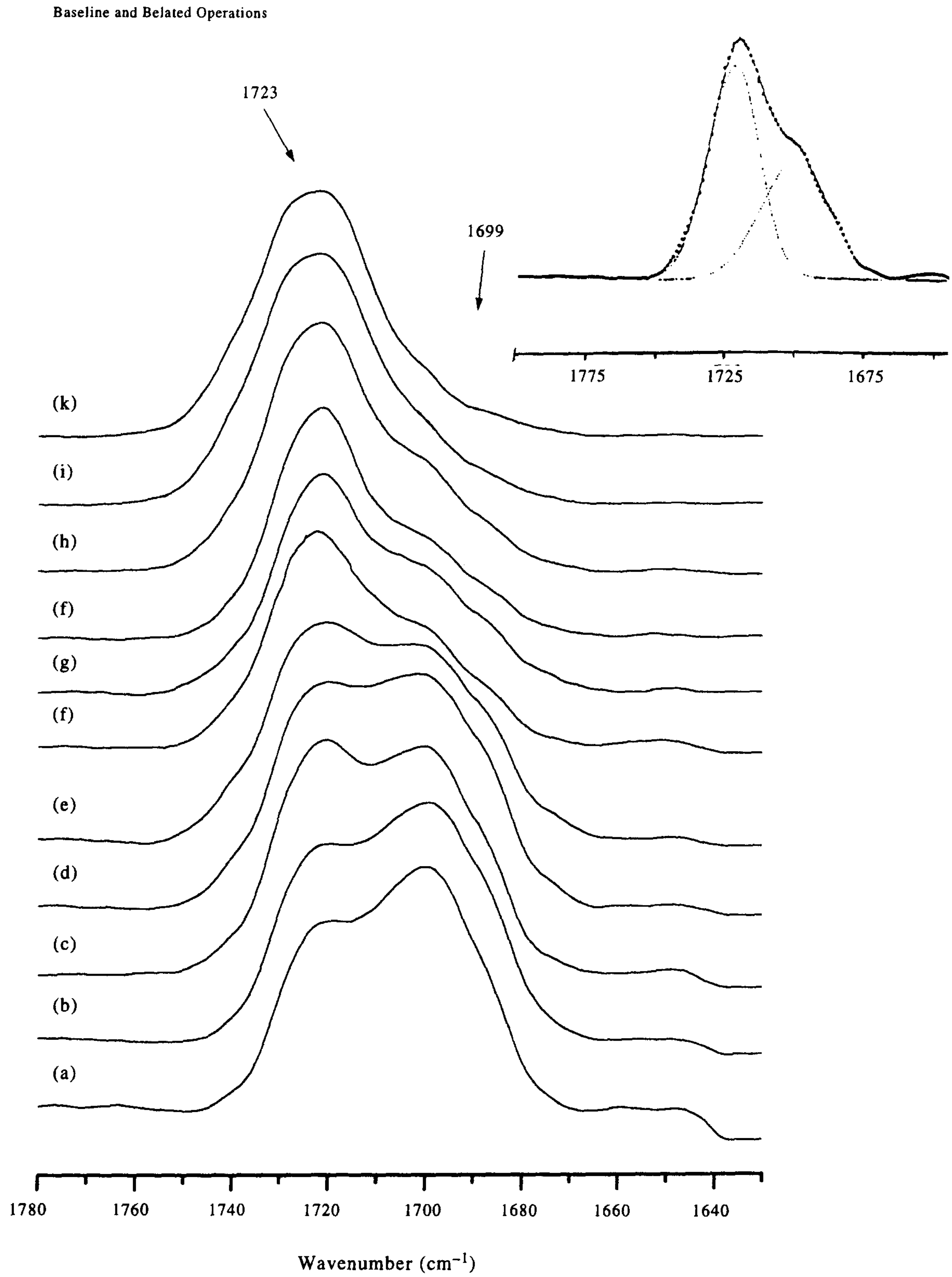


Figure 8 I.r. spectra of the carbonyl stretching range of varying composition Bz-phenoxy/phenolic blends observed at 50°C: (a) 5/95; (b) 10/90; (c) 20/80; (d) 30/70; (e) 40/60; (f) 50/50; (g) 60/40; (h) 70/30; (i) 80/20; (j) 90/10; (k) 100/0

where A_b is the area of the hydrogen-bonded carbonyl absorption, A_f is the area of the free carbonyl absorption, and the conversion coefficient 1.5 is the ratio of absorptive coefficients of two bands for the free and hydrogen-bonded carbonyl in an ester group, according to Coleman *et al.*[11] Peak-decomposition reveals that only two bands match the spectrum of the blend quite satisfactorily in the carbonyl region. As expected, the 1699 cm^{-1} band is significantly broader than that of the 1722 cm^{-1}, which reflects a reasonably wider hydrogen-bond distance distribution in the polymer blend. With values concerning the relative absorption coefficients for the two carbonyl stretching vibrations, a measurement of the fraction of interacting species could be calculated from the fractional area of the 1699 cm^{-1} band which is shown in *Table 2* and *Figure 9*. The ratio of hydrogen-bonded carbonyl appeared

Table 2 Curve-fitting results for 30/70 Bz-phenoxy/phenolic blends

	'Free' C=O			H-bonded C=O			
Temperature (°C)	ν (cm^{-1})	$W_{1/2}$ cm^{-1}	A_f (%)	ν (cm^{-1})	$W_{1/2}$ cm^{-1}	A_{HB} (%)	$f_b{}^a$
50↑	1724	22.5	39.8	1699	28.1	60.2	0.50
100↑	1724	24.3	47.9	1699	23.4	52.1	0.42
115↑	1724	24.6	48.5	1699	27.1	51.5	0.40
130↑	1724	26.8	50.9	1700	26.8	49.1	0.39
150↑	1724	25.1	52.5	1700	26.8	47.5	0.38
170↑	1724	26.7	59.3	1700	25.0	40.7	0.31
190	1724	27.2	62.4	1699	25.6	37.6	0.28
170↓	1724	26.5	60.5	1699	25.4	39.5	0.30
150↓	1724	25.0	54.9	1699	25.1	45.1	0.35
130↓	1724	25.4	52.7	1699	26.9	48.3	0.38
115↓	1724	24.1	50.8	1700	26.8	49.2	0.39
100↓	1724	24.0	49.9	1699	27.0	50.1	0.40
50↓	1724	22.2	42.0	1699	27.2	58.0	0.48

[a] Calculated from equation (1)
↑ Temperature increase
↓ Temperature decrease

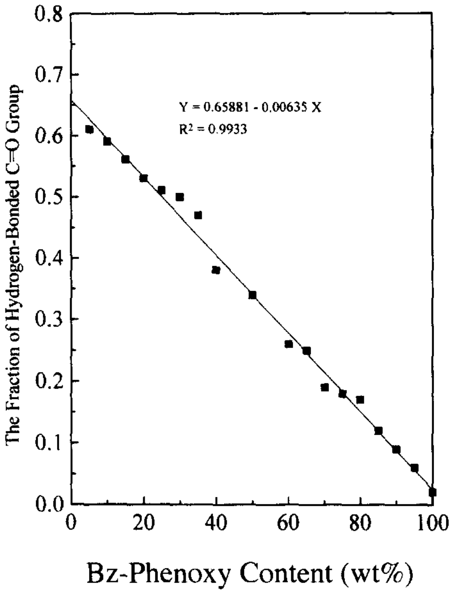


Figure 9 The correlation between the fraction of the Bz-phenoxy content and hydrogen-free C=O group of Bz-phenoxy

almost composition dependent. It is clear that Bz-phenoxy would be associated with the phenolic directly, and that no phase separation occurred. The Bz-phenoxy is compatible with the phenolic resin. In the phenolic-rich region, the self-associated hydrogen bonds of the phenoxy can be neglected. The Bz-phenoxy/phenolic blend behaviour could be analogous to the phenoxy blended with phenolic in the phenolic-rich region.

As similar to the previous experiments, the i.r. spectra have been studied for blending films at various temperatures. The results are illustrated in *Figure 10*, where the carbonyl stretching region of the 1670–1745 cm^{-1} for the 30/70 Bz-phenoxy/phenolic blend is recorded as a function of temperature. The carbonyl band could be resolved into a 'free' carbonyl peak at 1723 cm^{-1} and the 'bonded' carbonyl peak at 1699 cm^{-1}, as shown in *Figure 10*. The results are summarized in *Table 3*, and it can be seen that approximately 50% of the carbonyl groups of the Bz-phenoxy is hydrogen-bonded in the 30/70 Bz-phenoxy/phenolic blend at 50°C. The fraction of hydrogen-bonded carbonyl groups decreases as the temperature increases, and regains its original value upon cooling to 50°C. From the above observations, it is easy to confirm that the polymer mixture is in a dynamic equilibrium with the

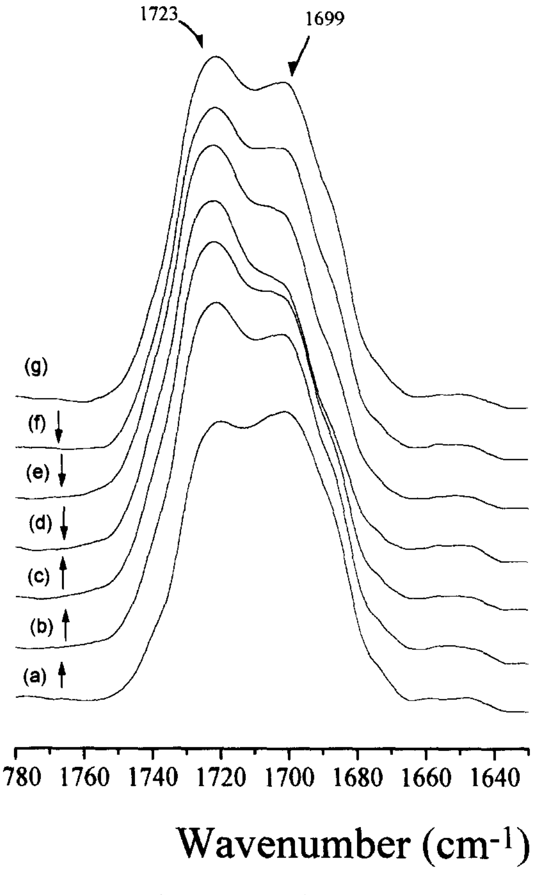


Figure 10 I.r. spectra of carbonyl stretching region for a sample of 30/70 Bz-phenoxy/phenolic blend recorded as a function of temperature: (a) 50°C; (b) 100°C; (c) 150°C; (d) 170°C; (e) 150°C; (f) 100°C; (g) 50°C (↑, temperature increase; ↓, temperature decrease)

Table 3 Curve-fitting data from i.r. spectra of Bz-phenoxy/phenolic blends

Bz-phenoxy/phenolic (wt%)	'Free' C=O			H-bonded C=O			
	ν (cm^{-1})	$W_{1/2}$ cm^{-1}	A_f (%)	ν (cm^{-1})	$W_{1/2}$ cm^{-1}	A_{HB} (%)	f_b[a]
5/95	1722.7	17.7	30.7	1700	24.9	69.3	0.60
10/90	1723.5	19.3	30.7	1699.4	28.2	69.3	0.60
15/85	1724.3	21.3	34.1	1699.2	30	66.9	0.57
20/80	1722.9	22	36.9	1698.8	26	63.1	0.53
25/75	1723.3	21.9	39.9	1699.1	26.9	60.1	0.50
30/70	1723.5	22.5	39.8	1699.2	28.1	60.2	0.50
35/65	1723.2	21.1	43.8	1700	28.2	56.2	0.46
40/60	1723.4	24.5	48.9	1698.5	24.5	51.1	0.41
50/50	1722.4	22.6	58.2	1698.9	23.4	41.8	0.32
60/40	1722	21.9	67.5	1698.9	22.6	32.5	0.24
65/35	1722.4	21.6	67.1	1699.5	21.7	32.9	0.25
70/30	1722.3	22.7	73.7	1698.8	19.9	26.3	0.19
80/20	1722.9	25.2	77.1	1698.1	21.9	22.9	0.17
85/15	1723	25.6	82.6	1696.8	22.5	17.4	0.12
90/10	1723.3	28.5	87.4	1696	24.7	12.6	0.09
95/5	1723.4	28.5	91.7	1693.8	24.8	8.3	0.06
100/0	1722.4	28.5	96.9	1688	29.5	3.1	0.02

[a] Calculated from equation (1)

hydrogen bonds forming and breaking continuously. This is consistent with an equilibrium process, the fraction of hydrogen-bonded carbonyl groups being determined by an equilibrium constant[18,22].

In *Figure 7*, the Bz-phenoxy/phenolic blends cast from THF exhibit a board absorption in the hydroxyl stretching region in the i.r. spectrum, that can be resolved into three Gaussian peaks. As the Bz-phenoxy increases, the hydroxyl-free band is also increased in the phenolic rich region, and a maximum value appeared at 30 wt% Bz-phenoxy content, as shown in *Figure 5*. Concurrently, the hydrogen-bonded hydroxyl band decreased from about 3550 to 3200 cm^{-1}. Comparing with *Figure 5*, the hydrogen bonds of the 'dimer' interaction is increased, and the 'multimer' interaction is apparently less than that of *Figure 5*. Unlike phenoxy/phenolic blends, the benzene ring of the Bz-phenoxy would hinder the interaction of carbonyl group with the multi-hydroxyl interaction of phenolic in the Bz-phenoxy/phenolic blends. There is less 'multimer' interaction between the hydroxyl group of phenolic and Bz-phenoxy. Besides the hydroxyl group, the other group of both phenoxy and Bz-phenoxy blended with the phenolic would hinder the self-associated hydrogen bonds of phenolic resin. Both the hydroxyl groups of the phenoxy and the carbonyl group of Bz-phenoxy have the same hydrogen-bonded interaction with the hydroxyl group of phenolic, in varying compositions. There is also a distinct similar result of the d.s.c. studies, which reveal a minimum single T_g for both phenoxy/phenolic and Bz-phenoxy/phenolic blend systems, as shown in *Figure 6*. In *Figure 6*, there is a clear picture that both phenoxy and Bz-phenoxy have an interaction with the hydroxyl group of phenolic in the phenolic-region blends. In the region, both phenoxy would hinder the self-associated hydroxyl of the phenolic resin. The density of physical crosslinks decreased with the decrease of hydrogen bonds, and consequently the T_g decreased.

CONCLUSIONS

The present study reveals that the phenoxy repeating units hinder the self-association of hydroxyl of phenolic, which decrease the T_g significantly in the phenolic-rich region.

The use of Bz-phenoxy provides complementary information regarding the hydrogen-bonding configuration between phenoxy and phenolic resins. Although there is no self-association in the Bz-phenoxy, it analogized to the phenoxy phase behaviour in the phenolic-rich region. Since Bz-phenoxy has strong C=O absorption and the *intra*molecular hydrogen bonding is absent, it can provide more straightforward and less complicated i.r. spectra interpretation. The association through hydrogen bonding between Bz-phenoxy and phenolic can be reasonably extrapolated to that between phenoxy and phenolic in the phenolic-rich region.

The two blends exhibit intimate mixing in the molecular scale, and the phenoxy unit interprets the phenolic resin through strong *inter*molecular hydrogen bonding. The amount of *intra*molecular hydrogen bonds of self-associated hydroxyls of phenolic is decreased, due to the rigid phenolic segment is interpenetrated by the phenoxy units. The 'physical crosslinks' in the rigid phenolic resin are disturbed significantly by the mobile phenoxy segment, and a suppression of T_g temperature. Although the total amount of hydrogen-bonds decreases, there exists a complete miscible polymer blend in the phenolic-rich region.

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