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The miscibility and morphology of hexamine cross-linked novolac/poly(ε-caprolactone) blends

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The miscibility and morphology of novolac/poly(ε-caprolactone) (PCL) blends before and after curing were investigated by optical microscopy, differential scanning calorimetry (d.s.c.) and *FT* i.r. It was found that PCL is miscible with uncured novolac resin, as shown by the existence of a single glass transition temperature (T_g) in each blend. *FT* i.r. studies revealed that hydrogen bonding interaction in novolac/PCL blend occurs between the hydroxyl groups of novolac and the carbonyl groups of PCL, which is responsible for the miscibility of the novolac/PCL blends. However, remarkable changes occurred after the novolac/PCL blends were cured with hexamine (HMTA), which can be considered to be due to the dramatic changes in chemical and physical nature of novolac resin during the cross-linking. Phase separation in the initially miscible novolac/PCL blends occurred after curing with 15 wt% HMTA (relative to novolac content). The phase structures of the cured blends show composition dependence. The cured novolac/PCL blends with novolac content up to 70 wt% were observed to be partially miscible, whereas the 90/10 cured novolac/PCL blend was found to be miscible. The curing reduces the intermolecular hydrogen-bonding significantly, but there still exists a considerable amount of residual intermolecular hydrogen bond in the cured blends with its strength much lower than that in the uncured blends. The morphology of the novolac/PCL blends was remarkably affected by curing. The curing results in the disappearing of the T_g behaviour of novolac, owing to less mobility of the novolac chain segments. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(ε-caprolactone); novolac resin; polymer blends)

INTRODUCTION

The study of miscibility for polymer blends where one component is crystallizable and another is highly cross-linked has received relatively little attention[1-7]. From the point of view of thermodynamics, an increase in molecular weight for either component of a miscible blend would decrease the cloud point temperature. Therefore, the occurrence of even partial miscibility in such polymer blends containing one component with an infinite molecular weight (i.e. highly cross-linked) is uncommon and requires further comment. The complex interrelationship between morphology and composition is not yet clarified and is the subject of a research programme in this laboratory. In the previous papers[3,4] we reported the results of our study on epoxy resin (ER)/poly(ethylene oxide) (PEO) blends and, in particular, on the role of cross-linking in influencing the miscibility of ER with PEO and the phase structure of the resulting blends. It has been found that phase separation occurs as cross-linking proceeds in such blends.

Phenol-formaldehyde resins are a major class of thermosetting polymers which are widely employed as moulding compounds, laminates, adhesives, and shell moulds for metals and electrical insulations due to their low manufacturing cost, dimensional stability, age

resistance, and high tensile strength[8,9]. Therefore, blending novolacs with other polymers is of great industrial interest. It has been found that novolac resins exhibit miscibility with a number of polar polymers containing carbonyl or carbonate groups[10-14]. In such blends, intermolecular hydrogen bonding acts as a dominant driving force for miscibility. However, as most novolac resins are used in cured forms, studies of cross-linked novolac blends is also of practical importance. Curing results in chain extension, branching, cross-linking, and significant changes in chemical and physical properties of the chain, which may cause phase separation in an initially miscible novolac blend if polymer chains have sufficient mobility during the curing. On the other hand, a semi-interpenetrating network (semi-IPN) may form and the system may still be miscible or partially miscible if the curing temperature is relatively low and polymer chains are less mobile. This means that curing has an important influence on the miscibility of novolac resin blends. Although some literature have reported the effect of cross-linking on the novolac blends and its analogue blends[7,15,16], further investigations are necessary in order to fully understand the effects of cross-linking on the miscibility and morphology of novolac blends, as well as the nature of the effects.

Poly(ε-caprolactone) (PCL) is a semicrystalline polymer and it was found to be miscible with many other

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polymers for its high potentiality to form hydrogen bonds with these polymers. The blends of novolac and PCL are expected to be miscible because intermolecular hydrogen bonds can be formed between the carbonyl groups of PCL and the hydroxyl groups of novolac. In this paper, we report the results of our studies in the miscibility and morphology of uncured novolac/PCL blends as well as highly hexamine crosslinked novolac/PCL blends with attention focused on the role of crosslinking in influencing the miscibility and phase behaviour of novolac resin with PCL and the morphology of the resulting blends.

EXPERIMENTAL

Materials and preparation of samples

The poly(ϵ-caprolactone) (PCL, Placcel H-7) was purchased from Daicel Chemical Ind., Ltd., Japan; it had a number-average molecular weight M_n of 70 000–100 000. The novolac was obtained from Hefei Perfumery Factory, Hefei, China; it had a number-average molecular weight M_n of 565 determined by vapour phase osmometry. The novolac was used without further purification. Hexamine (hexamethylenetetramine, HMTA) was chemically pure and was used as a cross-linking agent.

All the blend samples were prepared by solution casting using methylene chloride/ethanol (90/10 by volume) as a common solvent for both polymers. The solvent was almost completely evaporated at ambient temperature, then the samples were dried at 50°C in a vacuum oven for 72 h to remove the residual solvent. Novolac/PCL blends were cured with 15 wt% HMTA relative to the content of novolac in the blends, i.e. with HMTA/novolac = 0.15. The curing was performed successively at 100°C for 2 h, at 150°C for 2 h, and finally at 190°C for 2 h.

Differential scanning calorimetry

The calorimetric measurements were made on a Perkin–Elmer DSC-7 differential scanning calorimeter. The instrument was calibrated with an indium standard. The measurements were conducted under a nitrogen atmosphere. All samples were first heated to 130°C and then quenched to −70°C. A heating rate of 20°C min^{-1} was used in all cases. The glass transition temperature (T_g) and the crystallization temperature (T_c) were taken as the midpoint of the transition and the minimum of the exothermic peak, respectively, whereas the melting-point temperature (T_m) was taken as the maximum of the endothermic transition.

Fourier transform infrared spectroscopy

A Nicolet 170SX Fourier-transform infrared spectrometer was used to study hydrogen bonding interaction. Thin films of the blends were cast onto a KBr window from a 2% (w/v) solution of methylene chloride/ethanol mixture (90/10 by volume). After evaporation of most of the solvent, the films were kept in a vacuum oven at 50°C for 72 h to remove the residual solvent. To prepare the samples of the cured blends for *FT*i.r. study, the thin films so obtained, but containing curing agent HMTA, were further cured successively at 100°C for 2 h, at 150°C for 2 h, and finally at 190°C for 2 h. Both the uncured and cured samples obtained were stored in a desiccator to avoid moisture absorption. All spectra were recorded at

room temperature and a minimum of 32 scans at a resolution of 4 cm^{-1} were signal averaged. The films used in this study were sufficiently thin to obey the Beer–Lambert law[17].

Morphological observation

The overall morphology of pure PCL, the novolac/PCL blends, and the various cured novolac/PCL blends was investigated by optical microscopy using a Jiangnan XPR-2 optical microscope.

RESULTS AND DISCUSSION

Uncured novolac/PCL blends

All the uncured novolac/PCL blends were transparent just above the melting point of PCL. *Figure 1* shows the optical micrographs of the uncured novolac/PCL blends. The birefringent spherulite structure of the pure PCL was observed. The spherulites have been truncated by impingement and displayed a 'Maltese cross' in the optical microscope with polars. For the blends, similar birefringent spherulites with a 'Maltese cross' were also observed. Moreover, there exists a very markedly ringed texture within the spherulitic superstructure, as shown in the figure. Such a 'ringed' or 'banded' texture arises from a regular periodic twisting of crystalline lamellae as they grow in the radial direction[18]. Additionally, it can be seen from *Figure 1* that the texture of the spherulites becomes increasingly open, coarser, and more irregular with increasing amounts of novolac. This phenomenon was also observed in other miscible PCL blends such as PCL/poly(styrene-*co*-acrylonitrile)[19], PCL/poly(vinyl chloride)[20–22], PCL/chlorinated polyethylene[23], PCL/poly(hydroxyether of bisphenol A)[24], and PCL/poly-(styrene-*co*-maleic anhydride)[25] blends. In these blend systems, the ring spacing (periodicity) of the PCL spherulites tends to be a function of blend composition. Furthermore, as shown in *Figure 1* the spherulites observed in the novolac/PCL blends are completely volume-filling and no interspherulitic segregation of novolac could be seen. Consequently, amorphous novolac molecules had to be segregated interlamellarly or interfibrillarly during the crystallization process of PCL.

The d.s.c. thermograms (second heat) are shown in *Figure 2*, and the results are summarized in *Figure 3* and *Table 1*. *Figure 2* clearly reveals a single glass transition temperature, which varied with overall blend composition as indicated by the full squares in *Figure 3*. *Figure 3* also shows the calculated weight-average values for T_g (broken line). It is noted that the experimental T_g data exhibit marked deviations from simple additivity. Nevertheless, the appearance of a single glass transition temperature varying with blend composition strongly suggests that the blend presents a homogeneous single amorphous phase, i.e. the two components are miscible in the amorphous phase. The miscibility of the novolac/PCL blends can be considered to be due mainly to the non-negligible entropy contribution as the molecular weight of novolac is rather low.

Figure 3 also shows the T_c and T_m of the quenched samples as functions of blend composition. For the pure PCL and 10/90 novolac/PCL blend, no crystallization exotherm was observed since crystallization was sufficiently rapid to occur completely during the quenching.
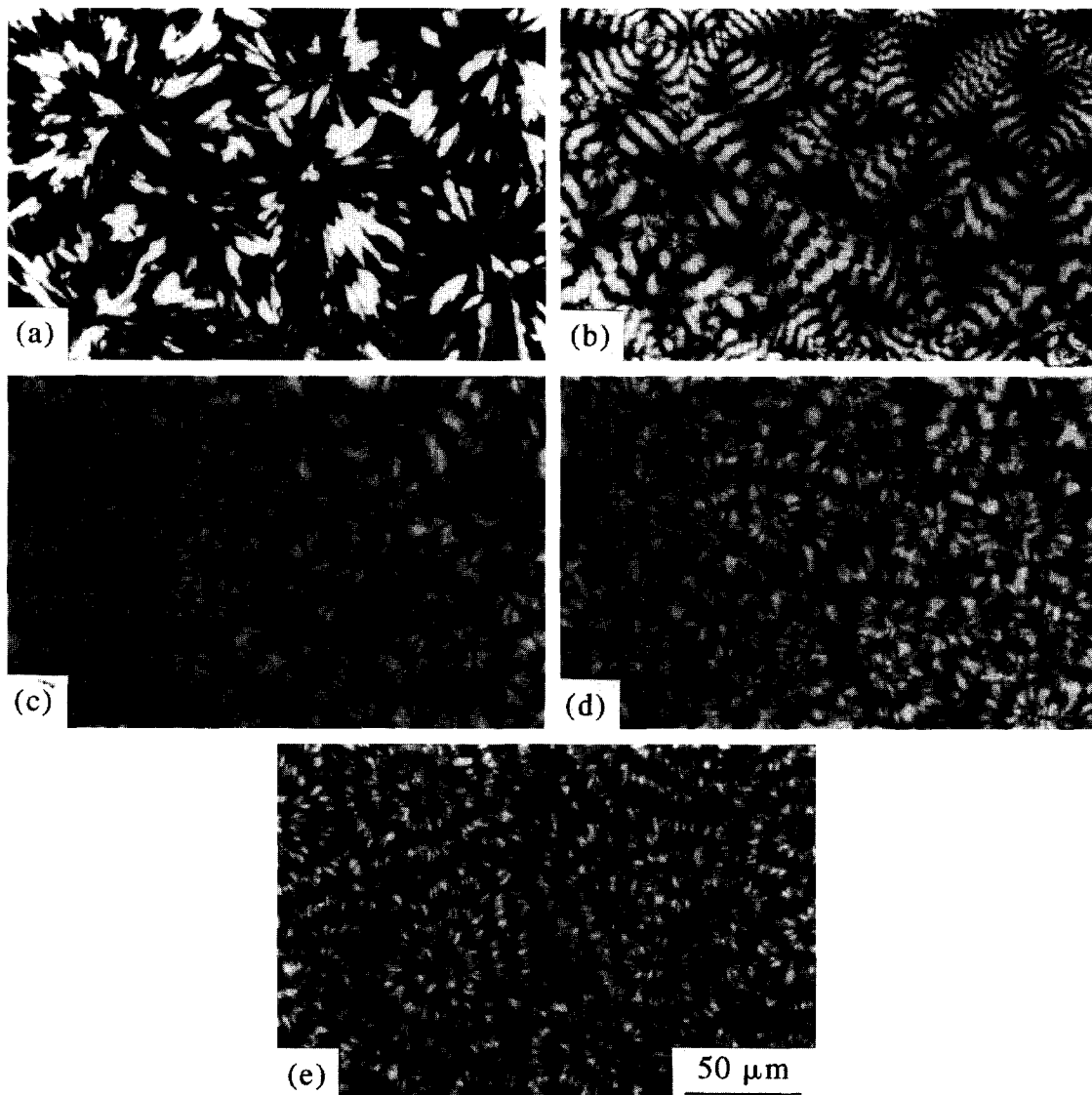
Figure 1 Optical micrographs of the novolac/PCL blends. Novolac/PCL: (a) 0/100, (b) 10/90, (c) 20/80. (d) 30/70, and (e) 40/60

However, for the blends with novolac content from 20 wt% to 40 wt%, T_c increases with the increase of novolac content. This phenomenon indicates that crystallization of PCL in the blend becomes progressively difficult with increase of novolac content. Furthermore, blends with novolac content of 50 wt% and higher did not show any crystallization exotherm. The crystallinity of PCL was calculated from

$$X_c = (\Delta H_f - \Delta H_c)/\Delta H_f^\circ \qquad (1)$$

where X_c is percent crystallinity, ΔH_f and ΔH_c are the heats of fusion and crystallization of PCL, respectively, and $\Delta H_f^\circ = 136 \, J \, g^{-1}$ [26] is the heat of fusion of 100% crystalline PCL. The results so obtained for the uncured novolac/PCL blends are presented in *Table 1*. These results support the idea that novolac is completely miscible with PCL over the entire composition range in the melt. The decrease in the crystallinity of PCL with increase of novolac content is attributed both to the higher T_g of novolac than ⌐t of PCL and to the hydrogen bonding interactions between these two components.

Because of this crystallinity, the weight fraction of PCL in the amorphous phase, W', does not equal the overall weight fraction of PCL in the blend, W. These quantities are related by[28]

$$W' = (W - X_c)/(1 - X_c) \qquad (2)$$

The open squares in *Figure 3* represent a replot of T_g vs. the amorphous fraction of PCL, which also show marked deviations from simple additivity, the T_g–composition relation is rather complicated. A similar phenomenon has been observed by other investigators[7,11] for uncured novolac/poly(methyl methacrylate) (PMMA) blends. It can be considered as a result of the combination of the contribution of mixed entropy and that of hydrogen bond[11] which can be formed in this system as will be proven by *FT* i.r. study below.

It can also be seen from *Figure 3* that the T_m of PCL in the blends decrease with increase of novolac content. The T_m depression is a common phenomenon for the miscible blends containing one crystallizable component. In the present case, it can be attributed to both enthalpic and entropic effects in the novolac/PCL blends owing to the small molecular weight of novolac[29]. However, the
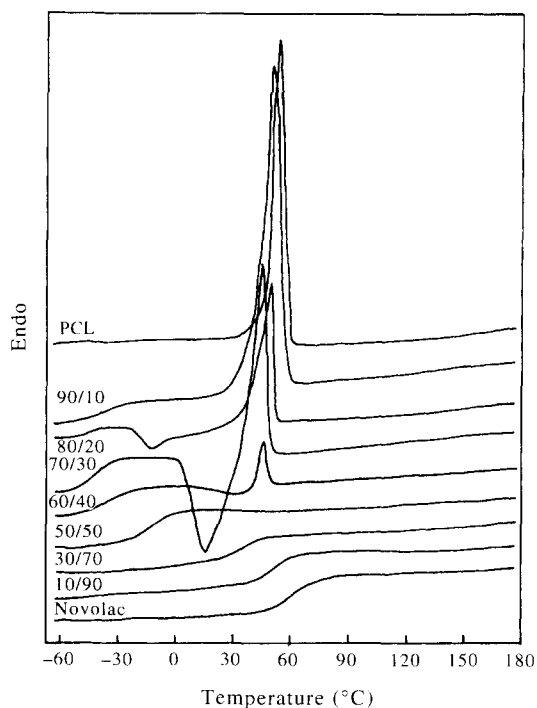
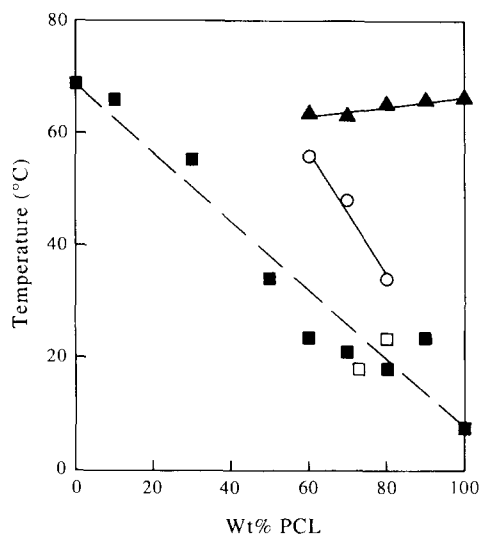**Figure 2** The d.s.c. thermograms of the uncured novolac/PCL blends

Wt% PCL

Figure 3 Thermal transition behaviour of uncured novolac/PCL blends. Full squares denote the plot of T_g vs. overall blend composition, open squares the plot of T_g vs. overall calculated amorphous composition. (- - -) Calculated weight-average values of T_g of the components. They also show the dependence of T_c (O), and T_m (▲) of the quenched novolac/PCL blends on the wt% of PCL

morphological factors could also have an influence on T_m of the PCL. It is noted that the samples were quenched in the d.s.c. before the second heating and therefore had different crystallization temperature, which influenced semi-crystalline morphology and hence T_m. This is the reason why the 60/40 blend has a higher T_m than the 70/30 blend.

*FT*i.r. studies revealed that hydrogen bonding in novolac/PCL blends occurs between the hydroxyl groups of novolac and the carbonyl groups of PCL. There are two areas of interest in the infrared spectra of the blend, one in the hydroxyl stretching region from 3600 to 3000 cm^{-1} and the other in the carbonyl stretching region from 1800 to 1650 cm^{-1}.

Figure 4 shows the *FT*i.r. spectra of the novolac/PCL blends in the stretching region of the novolac hydroxyl groups ranging from 2790 to 3710 cm^{-1}. The spectrum in this region of pure novolac may be considered to be composed to two components: a broad band centred at 3321 cm^{-1} which is attributed to the self-associated hydroxyl, i.e. hydrogen bonded hydroxyl groups, and a relatively narrow band at 3538 cm^{-1} which is assigned to non-associated, free hydroxyl groups. Upon blending with PCL, the non-associated hydroxyl band at 3538 cm^{-1} apparently remains constant for all composition in the blend, but the associated hydroxyl band at 3321 cm^{-1} shifts to higher frequency as a function of increasing PCL concentration, indicating that there is hydrogen bonding interaction between the hydroxyl groups of novolac and the carbonyl groups of PCL. The frequency difference between the free hydroxyl absorption and those of the hydrogen bonding species ($\Delta\nu$) is a measure of the average strength of the intermolecular interactions[30]. The above results indicate that the average strength of the hydrogen bond between the hydroxyl groups of novolac and the carbonyl groups of PCL in the blends ($\Delta\nu = 154$ cm^{-1} for the 50/50 novolac/PCL blend) is much lower than that between the hydroxyl groups in pure novolac resin ($\Delta\nu = 217$ cm^{-1}). Similar results have been observed by other investigators. Coleman *et al.* found the average strength of the hydrogen bond between the PCL carbonyl groups and the PVPh hydroxyl group ($\Delta\nu = 105$ cm^{-1}) is less than that occurring between hydroxyl groups in pure PVPh ($\Delta\nu = 165$ cm^{-1}) in the PVPh–PCL system[31], and the average strength of the hydrogen bond between the PCL carbonyl group and the phenoxy hydroxyl group ($\Delta\nu = 90$ cm^{-1}) is less than that occurring between hydroxyl groups in pure phenoxy ($\Delta\nu = 170$ cm^{-1}) in the phenoxy–PCL system[32].

Figure 5 shows the *FT*i.r. spectra of novolac/PCL blends in the region from 1605 to 1821 cm^{-1}, corresponding to

Table 1 Thermal properties of uncured novolac/PCL blends

PCL/novolac	T_m ($^{\circ}$C)	ΔH_f (J g^{-1} blend)	ΔH_f (J g^{-1} PCL)	T_c ($^{\circ}$C)	ΔH_c (J g^{-1} blend)	ΔH_c (J g^{-1} PCL)	X_c blend (%)	X_c (PCL) (%)	T_g ($^{\circ}$C)
100/0	53	80.4	80.4				59	59	-65^a
90/10	51	69.2	76.9				51	57	-33
80/20	50	50.8	63.5	-12	-17.1	-21.4	25	31	-44
70/30	46	27.3	39.0	16	-25.5	-36.4	1	2	-38
60/40	47	0.8	1.3	32	-0.8	-1.3	0	0	-33
50/50									-12
30/70									30
10/90									51
0/100									57

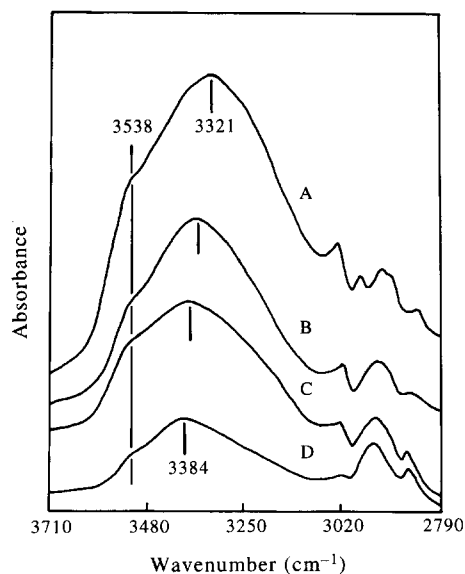^{a} This value was taken from the previous work[27]

Figure 4 *FT* i.r. spectra in the 2790–3710 cm⁻¹ region of the uncured novolac/PCL blends. Novolac/PCL: (A) 100/0, (B) 90/10, (C) 70/30 and (D) 50/50
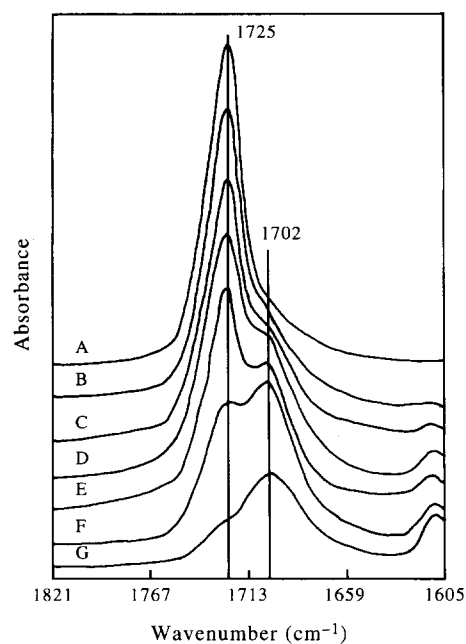

Figure 6 The d.s.c. thermograms of the novolac/PCL blends cured with 15 wt% HMTA

Figure 5 *FT* i.r. spectra in the 1605–1821 cm⁻¹ region of the novolac/ PCL blends. Novolac/PCL: (A) 0/100, (B) 10/90, (C) 20/80, (D) 30/70, (E) 40/60, (F) 50/50, and (G) 70/30

HMTA-cured novolac/PCL blends

Except for that of 90/10 novolac/PCL composition, all the novolac/PCL blends cured with 15 wt% HMTA (relative to novolac content, i.e. HMTA/novolac = 0.15 in the blends) were translucent at room temperature and did not become clear above the T_m of PCL. The previously mentioned uncured novolac/PCL blends exhibited opacity or were hazy at low temperature owing to PCL crystallinity, but all became fully transparent above T_m. This phenomenon indicates that phase separation occurred during curing in these cured blends. However, the 90/10 cured novolac/PCL blend was clear, which suggests the homogeneity of the blend. These observations imply that the cured novolac/PCL blends are partially miscible and the phase structures of the cured blends show composition dependence.

Figure 6 shows the d.s.c. thermograms of the novolac/ PCL blends cured with 15 wt% HMTA, and the thermal properties obtained from the thermograms are listed in *Table 2*. In this figure, there is not an apparent glass transition temperature but a very broad range of second-grade phase transitions, ca. 120–200°C, which is consistent with the observation by Zhang and Solomon[7] in the novolac/PMMA blends cured with 20 wt% HMTA. This is a common phenomenon for highly cross-linked novolac blends. For the curing process of novolacs with a high amount of cross-linking agent, curing could occur at most phenolic rings. Thus, the crosslink density could be high enough to restrict segmental motions of novolac chains and to result in the disappearing of T_g behaviour for cured novolac resin. On the other hand, the T_g of PCL is very low, it is also not observed under the present experimental conditions. These results show that it cannot be ascertained by the use of conventional T_g judgement, whether or not the cured blends are miscible. However, it has been shown for blends with crystallizable components, that both a decrease in the crystallinity and in the crystallization rate are indicative of miscibility phenomena in the amorphous state[29]. In the present case, it can be seen from *Figure 6* that no crystallization exotherm occurred for all of the cured blends, implying

the stretching vibration of the carbonyl groups of PCL. It can be seen from the figure that the carbonyl stretching vibration band of pure PCL is at 1725 cm⁻¹. However, upon blending with novolac, a second band is developed at 1702 cm⁻¹, corresponding to the hydrogen-bonded carbonyl groups, and its intensity, relative to that of the free carbonyl groups band, increases with increasing novolac concentration. This is also indicative of hydrogen bonding interaction between the hydroxyl groups of novolac and the carbonyl groups of PCL.

All the above *FT* i.r. results further confirm that the novolac/PCL blends are completely miscible.
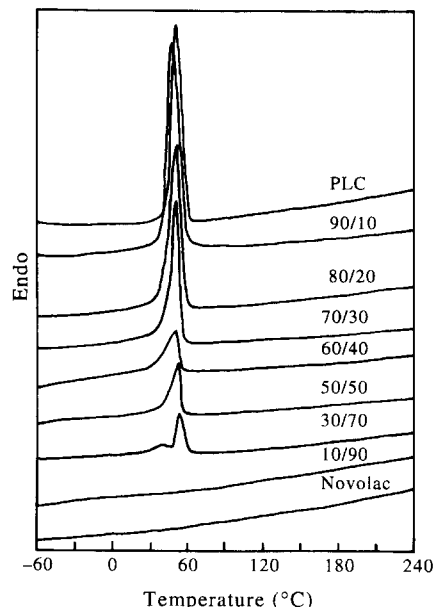
Table 2 Thermal properties of the novolac/PCL blends cured with HMTA/novolac = 0.15

PCL/novolac	T_m (°C)	ΔH_f (J g^{-1} blend)	ΔH_f (J g^{-1} PCL)	X_c (PCL) (%)	X_c (blend) (%)
100/0	53	80.4	80.4	59	−65[a]
90/10	52	70.8	78.7	58	52
80/20	53	51.5	64.4	47	38
70/30	53	43.1	61.6	45	32
60/40	49	27.2	45.3	33	20
50/50	51	24.3	48.6	36	18
30/70	54	8.6	28.7	21	6
10/90					
0/100					

[a] This value was taken from the previous work[27]
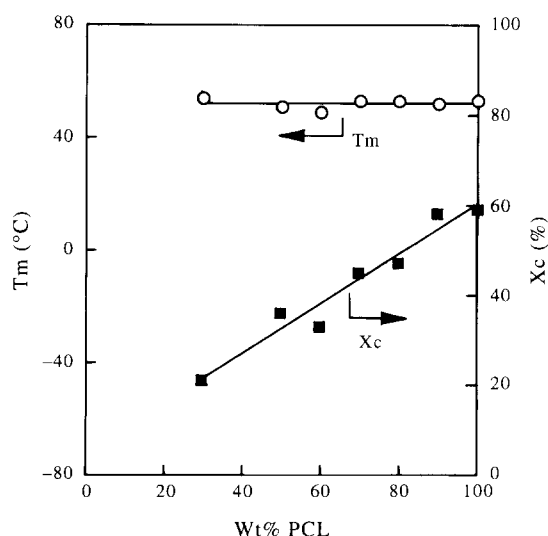

Figure 7 Crystallinity and melting point of PCL in the blends as functions of PCL content for the novolac/PCL blends cured with 15 wt% HMTA

that crystallization was so rapid and had been completed during the quenching. It seems that the crystallization rate did not have a substantial decrease in the cured blends compared to the miscible uncured blends. *Figure 7* displays crystallinity of PCL as a function of PCL content in the novolac/PCL blends cured with 15 wt% HMTA. It should be noticed that the cured blends have much higher crystallinity than the uncured blends. The d.s.c. thermograms of the uncured blends with novolac content of 50 wt% and higher do not show any crystallinity (*Figure 2*), but the cured blend remains crystallizable with cured novolac content up to 70 wt% (*Figure 6*). These results suggest that phase separation could occur in these blends after curing. However, it can be seen from *Figure 6* that the 90/10 cured novolac/PCL blend was amorphous, indicating its homogeneous nature, i.e. this blend was miscible. *Figure 7* also gives the melting point of PCL, T_m, as a function of PCL content in the HMTA-cured novolac/PCL blends. It can be seen from the figure that the T_m of PCL in the blends remains constant within experimental errors. It is quite evident that PCL is only partially miscible with the highly cured novolac resin.

Optical micrographs for the novolac/PCL blends cured with 15 wt% HMTA are shown in *Figure 8*. It is interesting to see that the crystalline morphology of PCL in 10/90 cured novolac/PCL blend displays a dendritic,

branch-like texture (*Figure 8a*) and this is because the total velocity of crystallization of PCL is anisotropic. The texture of branch-like crystal becomes increasingly coarser and more irregular with increase of novolac content and it takes on a ringed spherulitic texture when the amount of novolac reached about 30 wt% in the blend (*Figure 8c*). Finally, spherulites of 40/60 novolac/PCL blend show a less regular texture; this may be referred to the fact that the novolac domains gradually become bigger and bigger, dispersing in the crystal of PCL. These results imply that phase separation occurred in the novolac/PCL blends during the curing. Comparing with the spherulite texture of uncured novolac/PCL blends shown in *Figure 1*, it is clear that curing has a very apparent effect on the morphology of the novolac/PCL blends.

Figure 9 shows the *FT* i.r. spectra of novolac/PCL blends cured with 15 wt% HMTA in the region of 2790–3710 cm^{-1}. The band at 3498 cm^{-1} is attributed to the free hydroxyl groups stretching vibration and the band at 3383 cm^{-1} corresponds to the self-associated hydroxyl groups of cured novolac. The position of the free hydroxyl band at 3498 cm^{-1} remains constant while the hydrogen bonded hydroxyl band at 3383 cm^{-1} slightly shifts to high frequency with the increase of PCL content. That is to say that there is still a considerable amount of intermolecular hydrogen bond in the novolac/PCL blends cured with 15 wt% HMTA although it is very small compared to uncured novolac/PCL blends. This phenomenon is more clear as we examine the *FT* i.r. spectra of novolac/PCL blends in the region of 1605 to 1821 cm^{-1} shown in *Figure 10*. However, comparing with the spectra of uncured novolac/PCL blends in *Figure 4*, the following results can be obtained. First, the average strength of the hydrogen bond in pure HMTA-cured novolac ($\Delta\nu = 115$ cm^{-1}) is much lower than that in pure uncured novolac ($\Delta\nu = 217$ cm^{-1}). Second, the average strength of the hydrogen bond between the hydroxyl groups of novolac and the carbonyl groups of PCL in the cured blends ($\Delta\nu = 95$ cm^{-1} for the 50/50 HMTA-cured novolac/PCL blend) is also much lower than that in the uncured blends ($\Delta\nu = 154$ cm^{-1} for the 50/50 uncured novolac/PCL blend). Third, as can be seen from the relative intensities of the absorption bands, the ratio of free hydroxyl groups to the self-associated hydroxyl groups in cured novolac/PCL blends is almost constant and is much higher than that in uncured blends. This phenomenon can be explained as following: novolac was cured with a high amount of cross-linking agent and the high cross-linking density makes the segmental motion of novolac chains very difficult. Therefore, it is
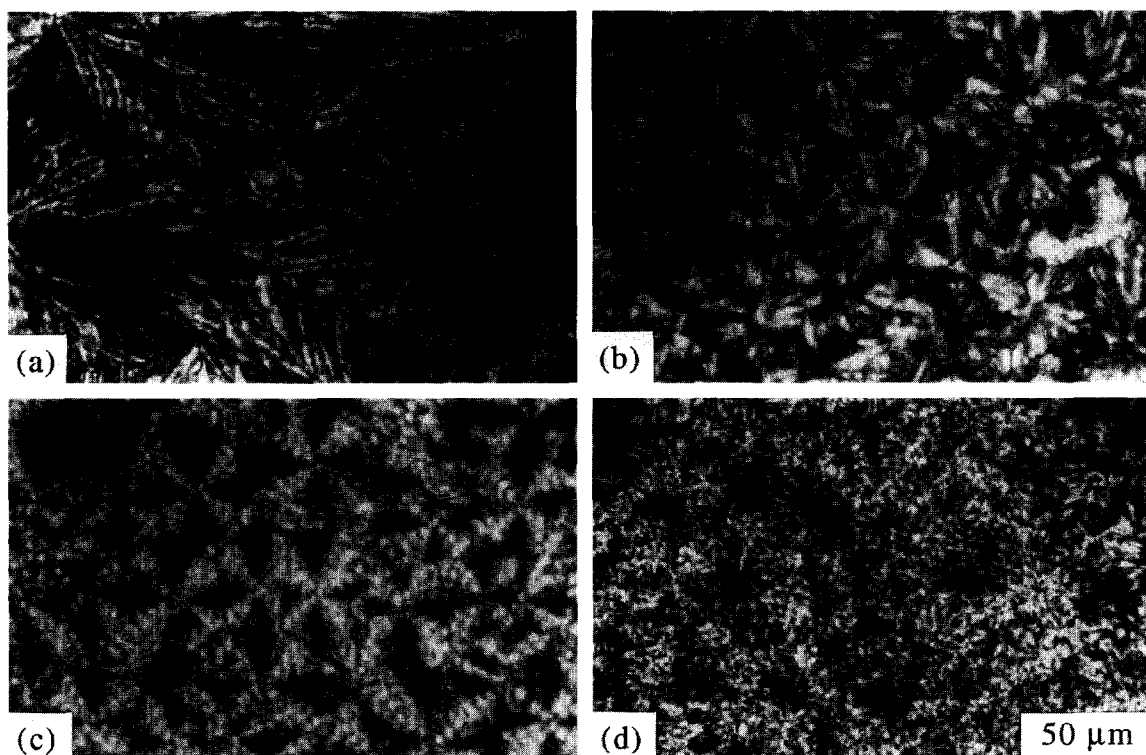
Figure 8 Optical micrographs of the novolac/PCL blends cured with 15 wt% HMTA. Novolac/PCL: (a) 10/90, (b) 20/80, (c) 30/70, and (d) 40/60
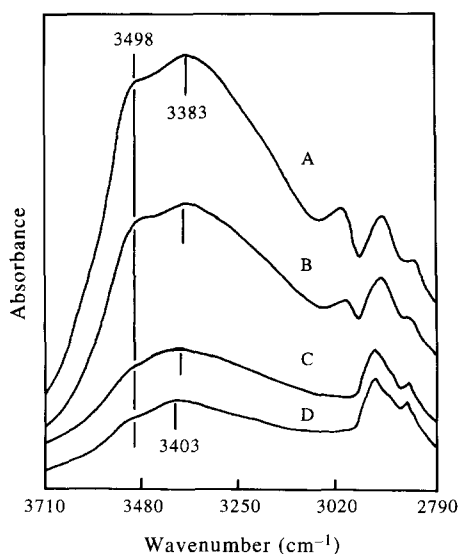

Figure 9 *FT* i.r. spectra in the 2790–3710 cm^{-1} region of the novolac/PCL blends cured with 15 wt% HMTA. Novolac/PCL: (A) 100/0, (B) 90/10, (C) 70/30, and (D) 50/50

difficult to form a hydrogen bond even in the pure cured novolac resin. In other words, the average strength of hydrogen bond in cured samples is very low and the ratio of non-associated hydroxyl groups to the self-associated hydroxyl groups in a cured system is larger than that in an uncured system. This is consistent with the observation of the reduced miscibility and T_g behaviour disappearing in the d.s.c. study of the cured blends.

Figure 10 shows the *FT* i.r. spectra of novolac/PCL blends cured with 15 wt% HMTA in the region of 1605–1821 cm^{-1}. The absorption band of non-hydrogen-

bonded carbonyl groups stretching vibration of PCL is observed to centre at 1725 cm^{-1}. However, with increasing novolac content, a second band at 1705 cm^{-1} appears; which can be attributed to the hydrogen-bonded carbonyl groups stretching vibration of PCL. Compared with the uncured blends, one can find that the average strength of the hydrogen bond between the hydroxyl groups of novolac and the carbonyl groups of PCL in the cured blends ($\Delta\nu = 20$ cm^{-1} for the HMTA-cured novolac/PCL blend, *Figure 10*) is lower than that in the uncured blends ($\Delta\nu = 23$ cm^{-1} for the uncured novolac/PCL blend, *Figure 5*). It is also noticed that the relative intensity of the band at 1705 cm^{-1} in the cured blends (*Figure 10*) is relatively lower than that at 1702 cm^{-1} for the uncured blends (*Figure 5*), suggesting that three is a much less amount of intermolecular hydrogen bonds in the cured novolac/PCL blends than in the uncured novolac/PCL blends. Besides, it is observed that a band centered at 1649 cm^{-1} appears with the increase in novolac content and it can be assigned to the stretching vibration of the azomethine (-CH=N-) groups[33,34] of the cured novolac.

It is clear that the curing causes phase separation in the initially miscible novolac/PCL blends. PCL is only partially miscible with the highly cross-linked novolac and the phase structures of the cured blends are of composition dependence. The cross-linking reaction between novolac and HMTA resulted in the formation of cross-linked novolac network which was then separated out. The 'network effect' makes the cross-linked novolac resin more stable in the isolated state than in the form of an homogeneous blend. Similar results have been observed for the amine-cured ER/PCL blends[2], the amine-cured ER/PEO blends[3,4], and the HMTA-cured novolac/PMMA blends[7].
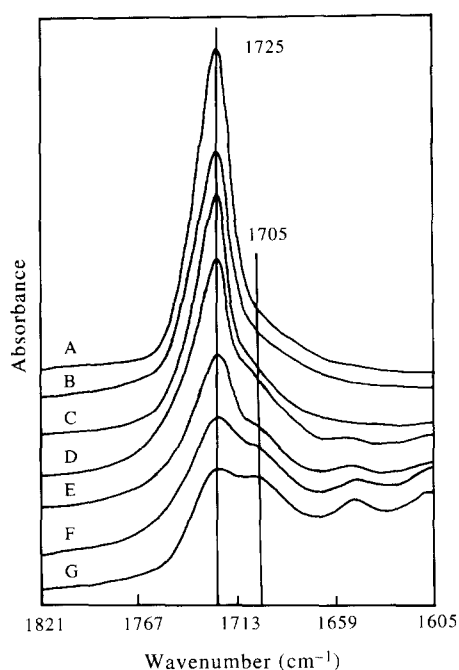
Figure 10 *FT* i.r. spectra in the 1605 to 1821 cm^{-1} region of the novolac/PCL blends cured with 15 wt% HMTA. Novolac/PCL: (A) 0/100, (B) 10/90, (C) 20/80, (D) 30/70, (E) 40/60, (F) 50/50, and (G) 70/30

CONCLUSIONS

In summary, PCL is miscible with uncured novolac resin. *FT* i.r. studies revealed that hydrogen bonding interaction in novolac/PCL blends occurs between the hydroxyl groups of novolac and the carbonyl groups of PCL, and it is this driving force that results in the complete miscibility of the novolac/PCL blends. Remarkable changes occurred after the novolac/PCL blends were cured with 15 wt% HMTA, which can be considered to be due to the dramatic changes in chemical and physical nature of novolac resin during the crosslinking. Phase separation in the initially miscible novolac/PCL blends occurred after curing. The cured novolac/PCL blends are partially miscible and the phase structures of the cured blends are of composition dependence. The curing reduces the intermolecular hydrogen-bonding significantly, and the morphology of the novolac/PCL blends was remarkably affected by curing. The curing results in the disappearance of T_g behaviour of novolac, owing to the lower mobility of novolac chain segments.

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REFERENCES

1 Noshay, A. and Robeson, L. M. *J. Polym. Sci., Polym. Chem. Ed.* 1974, **12**, 689
2 Clark, J. N., Daly, J. H. and Garton, A. *J. Appl. Polym. Sci.* 1984, **9**, 3381
3 Guo, Q., Peng, X. and Wang, Z. *Polym. Bull.* 1989, **21**, 593
4 Guo, Q., Peng, X. and Wang, Z. *Polymer* 1991, **32**, 53
5 Luo, X., Zheng, S., Zhang, N. and Ma, D. *Polymer* 1994, **35**, 2619
6 Mucha, M. *Colloid Polym. Sci.* 1994, **272**, 1090
7 Zhang, X. and Solomon, D. H. *Macromolecules* 1994, **27**, 4919
8 Knop, A. and Scheib, W. 'Chemistry and Application of Pehnolic Resins', Heidelberg, Springer-Verlag, 1985
9 Knop, A. and Pilato, L. A. 'Phenolic Resins', Heidelberg, Springer-Verlag, 1979
10 Fahrenholtz, S. R. and Kwei, T. K. *Macromolecules* 1981, **14**, 1076
11 Kwei, T. K. *J. Polym. Sci., Polym. Lett.* 1984, **22**, 307
12 Pennacchia, J. R., Pearce, E. M., Kwei, T. K., Bulkin, B. J. and Chen, J.-P. *Macromolecules* 1986, **19**, 973
13 Yang, T. P., Pearce, E. M., Kwei, T. K. and Yang, N. L. *Macromolecules* 1989, **22**, 1813
14 Kalkar, A. K. and Roy, N. K. *Eur. Polym. J.* 1993, **29**, 1392
15 Coleman, M. M., Serman, C. J. and Painter, P. C. *Macromolecules* 1987, **20**, 226
16 Kim, H. I., Pearce, E. M. and Kwei, T. K. *Macromolecules* 1989, **22**, 3374
17 Coleman, M. M. and Painter, P. C. *J. Macromol. Sci., Rev. Macromol. Chem.* 1978, **C16**, 1975
18 Bassett, D. C. 'Principles of Polymer Morphology', Cambridge University Press, Cambridge, 1981
19 Li, W., Yan, R. and Jiang, B. *Polymer* 1992, **33**, 889
20 Khambatta, F. B., Warner, F., Russell, T. and Stein, R. S. *J. Polym. Sci., Polym. Phys. Ed.* 1976, **14**, 1391
21 Nojima, S., Watanabe, K., Zheng, Z. and Ashida, T. *Polym. J.* 1988, **20**, 823
22 Keith, H. D., Padden, F. S. and Russel, T. P. *Macromolecules* 1989, **22**, 666
23 Defieuw, G., Groeninckx, G. and Reynaers, H. *Polymer* 1989, **30**, 565
24 Defieuw, G., Groeninckx, G. and Reynaers, H. *Polymer* 1989, **30**, 2164
25 Defieuw, G., Groeninckx, G. and Reynaers, H. *Polymer* 1989, **30**, 2158
26 Crescenzi, V., Manzini, G., Calzalari, G. and Borri, C. *Eur. Polym. J.* 1972, **8**, 449
27 Guo, Q. *Macromol. Chem.* 1990, **191**, 2639
28 Fernandes, A. C., Barlow, J. W. and Paul, D. R. *J. Appl. Polym. Sci.* 1984, **29**, 1971
29 Imken, R. L., Paul, D. R. and Barlow, J. W. *Polym. Eng. Sci.* 1976, **16**, 593
30 Purcell, K. F. and Drago, R. S. *J. Am. Chem. Soc.* 1968, **89**, 2874
31 Coleman, M. M. and Moskala, E. J. *Polymer* 1983, **24**, 251
32 Moskala, E. J., Varnell, D. F. and Coleman, M. M. *Polymer* 1985, **26**, 228
33 Colthup, N. B., Daly, L. H. and Wiberley, S. E. 'Introduction to Infrared and Raman Spectroscopy', 2nd Edn, Academic, London, 1975
34 Aranguren, M. I., Borrajo, J. and Williams, R. J. J. *J. Polym. Sci., Polym. Chem. Ed.* 1982, **20**, 311