

Miscibility and morphology of thermosetting polymer blends of novolac resin with poly(ethylene oxide)

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 (Revised 24 March 1997)

Polymer blends of novolac resin and poly(ethylene oxide) (PEO) were prepared by solution casting from *N,N*-dimethylformamide (DMF). The miscibility and morphology of the blends before and after curing were investigated by optical microscopy differential scanning calorimetry (d.s.c.) and Fourier transform infrared (FTi.r.) spectroscopy. It was found that PEO is miscible with uncured novolac over the entire composition range, as shown by the existence of a single composition-dependence glass transition temperature (T_g). FTi.r. studies revealed that hydrogen bonding interactions exist between the hydroxyl groups of novolac and the ether oxygens of PEO. The relative amount and the average strength of the hydrogen bonds in the blends were higher than those in the pure novolac resin. The curing with 15 wt% hexamine (HMTA) (relative to novolac content) resulted in the disappearance of a detectable T_g in both the neat novolac and the novolac-rich blends, due to the reduced mobility of the novolac chain segments. An analysis of the reduction in T_m and crystallization rate with increasing novolac content revealed that the HMTA-cured blends remained completely miscible. After curing with HMTA, considerable hydrogen bonding interaction between the components still existed, which is the driving force for the miscibility of the HMTA-cured blends. The relative amount and the average strength of hydrogen bonds in the cured blends were lower than those in the uncured blends. © 1997 Elsevier Science Ltd.

(Keywords: novolac resin; poly(ethylene oxide); thermosetting polymer blends)

INTRODUCTION

Polymer blends are becoming increasingly important in the polymer industry due to the strong economic incentives arising from their use^{1–3}, and there is a large amount of papers on the subject of polymer blends published every year. However, the study of the miscibility for polymer blends where one component is crystallizable and another is highly cross-linked has received relatively little attention, and only limited work had been published before 1984^{4,5}. From a consideration of thermodynamics, an increase in the molecular weight for either of the components of miscible blend should reduce the entropy of mixing. As a result, phase separation induced by cross-linking is expected for the systems with a positive (endothermic) enthalpy of mixing. Indeed, since 1989 we have reported a series of such thermosetting polymer blends and have found that phase separation occurs as the cross-linking process proceeds^{6–15}. Subsequently, these results were further revealed by other authors^{16–21}. However, the miscibility and hydrogen bonding interactions between the components were also observed even for some highly cross-linked blends^{10–12,18–21}. The hydrogen bonding interaction was considered to be the driving force for the miscibility, and it is responsible for the exothermic heat of mixing that is the thermodynamic basis of the miscibility in these thermosetting polymer blends. The complex interrelationship between phase behaviour and cross-linking has not yet been clarified and is the subject of a research programme in our laboratory. In particular, as one of the components of thermosetting

polymer blend is semicrystalline, some important information about crystallization can be obtained because it is expected that cross-linking will influence the crystallization of the blend. Therefore, this study will help us to understand polymer crystallization more deeply.

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^{22,23}. Blending novolacs with other polymers is of great interests to the industry. In fact, it has been found that novolac resins exhibit miscibility with a number of polar polymers containing carbonyl or carbonate groups^{12,13,19,24–30}. In such blends, intermolecular hydrogen bonding acts as dominant driving force for miscibility. However, as most novolac resins are used in cured forms, studies of cross-linked novolac blends are also of practical importance. Although some literature has reported the effect of cross-linking on the novolac blends and its analogous blends^{12,13,19,31,32}, further investigations are required in order to fully understand the effects of cross-linking on the miscibility and morphology of novolac blends, as well as the nature of these effects.

Poly(ethylene oxide) (PEO) is a semi-crystalline polymer and it has been found to be miscible with many other polymers^{1–3}. The studies of PEO with other thermosetting resins such as epoxy resins^{6,7,20,21} and unsaturated polyesters¹⁸ have been reported by us and other authors. Here, we have selected a system comprising PEO with a highly cross-linked novolac resin. It has been reported that the ether oxygens of PEO can form hydrogen bond with the

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hydroxyl groups of other polymers. Therefore, PEO is expected to be miscible with novolac resin, due both to the effects of entropy and enthalpy. The entropy contribution is ascribed to the low molecular weight of novolac and the enthalpy contribution comes from the potential to form hydrogen bonds between the components. However, curing may lead to the disappearance of the entropy contribution, and may also prevent the formation of hydrogen bonds and thus reduce the enthalpy contribution. Hence, the miscibility of the cured novolac/PEO blend is uncertain and it will be affected by many factors. In this paper, we will examine the miscibility and morphology of uncured novolac/PEO blends, as well as the highly cross-linked novolac/PEO blends. Special attention will be focused on the role of crosslinking in influencing the miscibility and phase behaviour of novolac resin with PEO.

EXPERIMENTAL

Materials and preparation of samples

The poly(ethylene oxide) (PEO) had a quoted number-average molecular weight $MN = 18\,000\text{--}20\,000$ and was obtained from Shanghai Reagent Inc., Shanghai, China. The novolac resin with a number-average molecular weight $MN = 565$ determined by vapour phase osmometry was obtained from Hefei Perfumery Factory, Hefei, China. The novolac was used without further purification, Hexamine (hexamethylenetetramine, HMTA) was chemically pure and was used as a cross-linking agent.

Films of uncured novolac/PEO blends were prepared by solution casting from *N,N*-dimethylformamide (DMF) at 50°C . To remove the residual solvent, the blends were further dried in a vacuum oven at 50°C for at least 2 weeks. Novolac/PEO blends formed in DMF were cured with 15 wt% HMTA relative to the content of novolac in the mixtures, i.e. with $\text{HMTA/novolac} = 0.15$. The curing was performed successively at 100°C for 2 h, at 160°C for 2 h, and finally at 190°C for 2 h.

Differential scanning calorimetry (d.s.c.)

The thermal properties measurements were carried on a Perkin-Elmer d.s.c.-7 differential scanning calorimeter. The measurements were conducted under a nitrogen atmosphere with a nitrogen flow rate of about 30 ml min^{-1} and the instrument was calibrated with an Indium standard. All samples were first scanned from -70 to 120°C and then rapidly quenched to -70°C and heated again (rescan). A heating rate of 20 K 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 (FTi.r.) spectroscopy

A Nicolet 750 Fourier-transform infrared (FTi.r.) spectrometer was used to study hydrogen bonding interactions. Thin films of the uncured novolac/PEO blends were cast onto a KBr window from a 2% (w/v) solution of DMF. After evaporation of most of the solvent, the films were kept in a vacuum oven at 50°C for 2 weeks to remove the residual solvent. To prepare the samples of the cured blends for FTi.r. study, the thin films obtained containing curing agent HMTA were further cured successively at 100°C for 2 h, at 160°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.

Morphological observations

The overall morphology of the pure PEO, the novolac/PEO blends, as well as the cured novolac/PEO blends was investigated by optical microscopy using a Jiangnan XIPR-2 optical microscope equipped with cross-polarizers. The samples between two glass covers were crystallized from the melt before observation.

RESULTS AND DISCUSSION

Uncured novolac/PEO blends

The uncured novolac/PEO blends prepared by solution casting with a PEO content more than 50 wt% were opaque at room temperature. However, all the novolac/PEO blends became clear when the blends were heated just above the melting point of PEO, which suggests the system is miscible in the molten state. It is likely that the opacity of the PEO-rich blends is due to the crystallinity of PEO in these blends. The d.s.c. thermograms of the first scan are shown in Figure 1, and several observations can be made. First, the novolac/PEO blends with PEO content of 50 wt% or more are crystalline and this is consistent with the transparency observation. Second, the melting point temperature (T_m) of PEO essentially decreases with increase of novolac content and there are no crystallization exotherms of PEO over the entire composition range. Thirdly, there are two melting endotherms for the blends containing PEO at compositions of 60–80 wt%. Finally, no glass transition can be detected for the pure PEO and the 10/90 novolac/PEO blend and this can be considered to be due to the high crystallinity of these compositions.

Because the thermal behaviour of novolac/PEO blends is expected to be greatly influenced by the thermal history of the blends, a second scan is required in order to judge the miscibility of the blends by d.s.c. The d.s.c. thermograms of

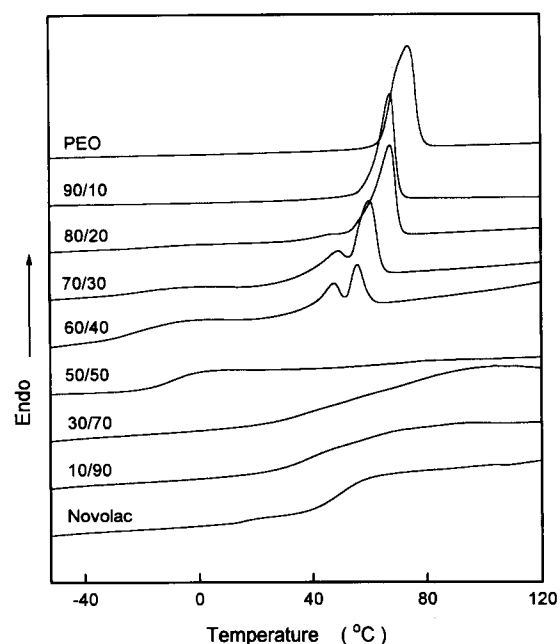


Figure 1 The d.s.c. thermograms of the uncured novolac/PEO blends (first scan)

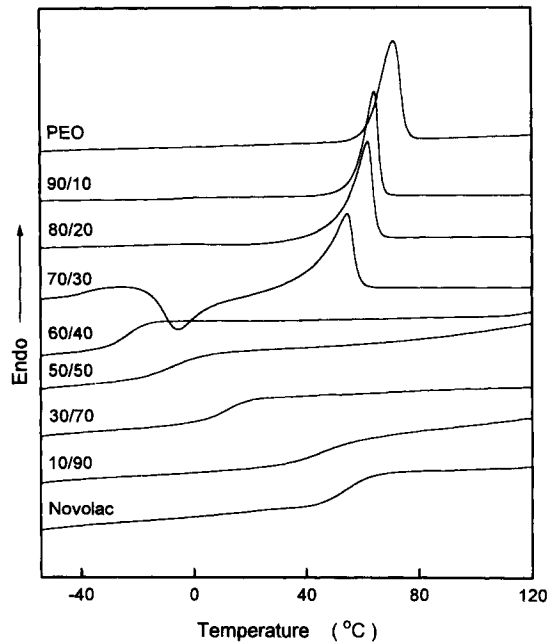


Figure 2 The d.s.c. thermograms of the uncured novolac/PEO blends (rescan)

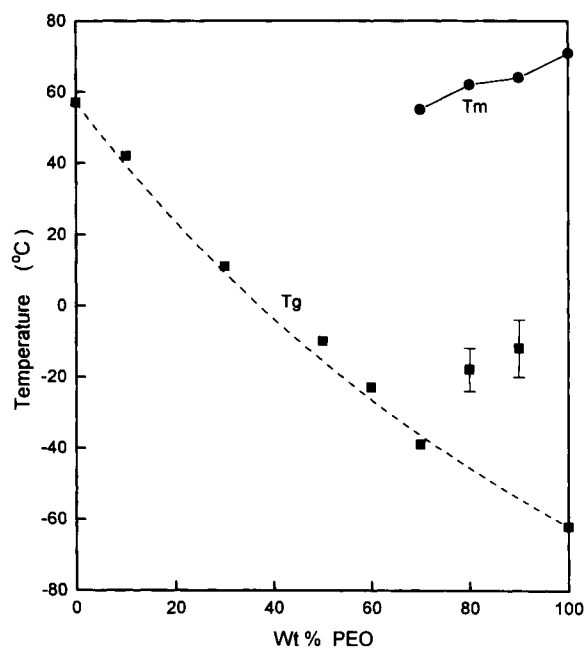


Figure 3 Composition dependence of T_g (■) and T_m (●) for novolac/PEO blends. (— —) Fox equation prediction. The T_g value for the pure PEO is taken from the previous work⁷

the second scans are shown in Figure 2, and the results are summarized in Figure 3 and Table 1. As indicated by the full squares in Figure 3, all the novolac/PEO blends exhibit only one glass transition temperature (T_g), which varied with overall blend composition. The appearance of a single T_g strongly suggests that the blend presents a homogeneous single amorphous phase, i.e. the two components are miscible in the amorphous phase.

Several theoretical and empirical equations have been used to describe the T_g -composition dependence of miscible blends. One of these, the Fox equation³³, is written as

$$\frac{1}{T_g^{\text{blend}}} = \frac{W_{\text{novolac}}}{T_g^{\text{novolac}}} + \frac{W_{\text{PEO}}}{T_g^{\text{PEO}}} \quad (1)$$

Table 1 Thermal properties of uncured novolac/PEO blends (rescan)

PEO/ novolac	T_g (°C)	T_m (°C)	ΔH_f (J g ⁻¹ blend)	T_c (°C)	ΔH_c (J g ⁻¹ blend)	X_c blend (%)
100/0	-62 ^a	71	175.7			86
90/10	-12	64	135.8			66
80/20	-18	62	107.4			52
70/30	-39	55	63.3	-6	-56.2	4
60/40	-23					
50/50	-10					
30/70						
10/90	42					
0/100	57					

^aThis value was taken from the previous work⁷

where T_g^{blend} is the glass transition temperature of the blend, T_g^{novolac} and T_g^{PEO} are those of the plain novolac and PEO, respectively, and W_{novolac} and W_{PEO} are the corresponding weight fractions.

It can be seen from Figure 3 that the Fox equation fits the experimental T_g data of the blends quite well except for the 10/90 and 20/80 novolac/PEO blends. The deviation of experimental obtained T_g data from the Fox equation at high PEO content is ascribed to the crystallization of PEO in the blends during quenching. This is not only because the crystallization of PEO in the blends can change the composition of the amorphous phase, but also because the crystal of PEO can act as a physical cross-linking point which may hinder the molecular mobility of amorphous components³⁴. Both of these two factors can result in an increase in the T_g of the blends.

As seen in Figure 2 no crystallization exotherm is observed for pure PEO and the blends with a novolac content up to 20 wt% since crystallization was sufficiently rapid to occur completely during the quenching process. However, the 70/30 novolac/PEO blend shows a crystallization exotherm. Furthermore, the blends with novolac content of 40 wt% or more did not show any crystallization exotherm. This result implies that crystallization of PEO in the blend becomes progressively more difficult with increasing novolac content, supporting the idea that novolac is miscible with PEO over the entire composition range in the melt.

The T_m data of the quenched samples as a function of composition are also depicted in Figure 3. It can also be seen from Figure 3 that the T_m of PEO in the blend substantially decreases with an increase of novolac content. The T_m depression is a common phenomenon for the miscible blends containing one crystallizable component^{35,36}. In the case when molecular weights of both components are sufficiently large, only the enthalpy contribution to melting point depression is significant. However, in the novolac/PEO system, it can be attributed to both enthalpy and entropy effects due to the low molecular weight of the novolac.

By measuring the area under the melting and crystallization peaks of the d.s.c. thermograms, it should be possible to evaluate the heats of fusion and crystallization, and hence the crystallinity of the blend. The crystallinity of the blend, X_c , was calculated from

$$X_c = \frac{\Delta H_f - \Delta H_c}{\Delta H_f^0} \quad (2)$$

where X_c is percentage crystallinity, ΔH_f and ΔH_c are the heats of fusion and crystallization of PEO, respectively, and $\Delta H_f^0 = 205 \text{ J g}^{-1}$ is the heat of fusion of 100% crystalline

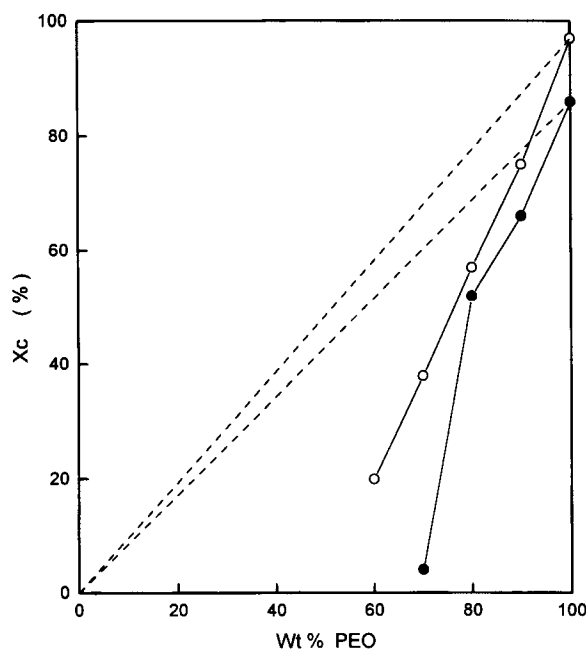


Figure 4 Crystallinity of the blends obtained from *Figure 1* (○) and *Figure 2* (●) as functions of the weight percentage of PEO. (— — —) Weight-average prediction

PEO³⁷. The results so obtained for the uncured novolac/PEO blends are presented in *Table 1* and are plotted in *Figure 4* against blend composition. *Figure 4* also shows the crystallinity of the novolac/PEO blends obtained from the d.s.c. thermograms of the first scan for comparison. The X_c values of the blends obtained from both the first and the second scans of d.s.c. thermograms are lower than those of the corresponding weight-average prediction and decrease rapidly with increasing novolac content. The decrease in crystallinity of PEO with increasing novolac content is attributed both to the higher T_g of novolac than that of PEO and to the hydrogen bonding interactions between the two components, as will be shown later. From *Figure 4*, it can also be seen that the crystallinity of the as-cast samples (the first scan) is larger than that of the corresponding quenched samples (the second scan): this is understandable if one considers the different thermal histories of the as-cast samples and the quenched samples. These results confirm that novolac/PEO blends are completely miscible in the melt.

The crystalline morphology of the pure PEO and the novolac/PEO blends was studied by optical microscopy. Optical micrographs with crossed polars for the blends are shown in *Figure 5*. The spherulites of PEO display a 'Maltese cross' birefringence pattern and have regular shape with defined borders. In *Figure 5*, it appears that the novolac/PEO blend samples are always completely volume-filled with PEO spherulites, and there is no evidence that the non-crystallizable novolac segregates in large domains in interspherulitic contact zones under the resolving power of the technique used. Comparing with the pure PEO, spherulites of the blends show a less regular texture. This is probably due to that the uncrystallized materials such as novolac and amorphous PEO becoming engulfed in the interlamellar region as the crystallization of PEO proceeds, and hence disturbing the radial orientation and coarsening of the crystalline lamellae. The above observations for the novolac/PEO blends suggest that PEO is miscible with

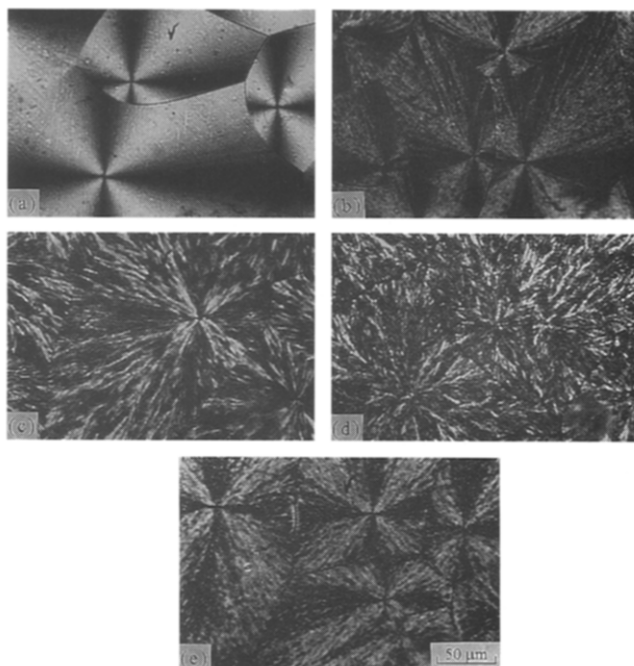


Figure 5 Optical micrographs of the novolac/PEO blends. Novolac/PEO: (a) 0/100; (b) 10/90; (c) 20/80; (d) 30/70; (e) 40/60

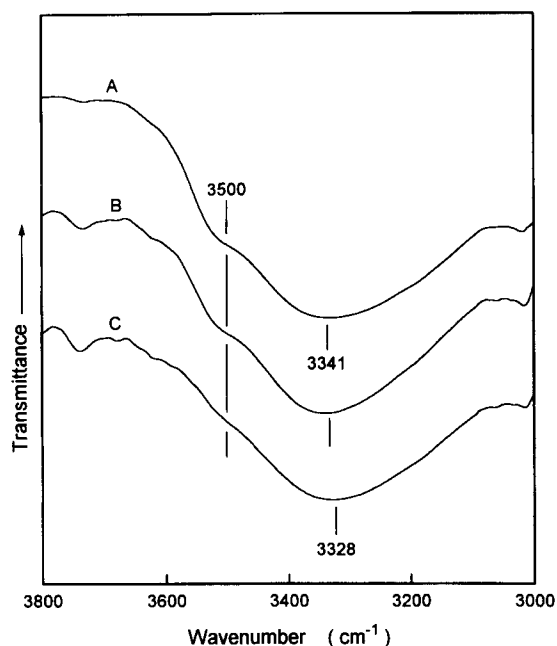


Figure 6 FTi.r. spectra in the 3000–3800 cm^{-1} region of the novolac/PEO blends. Novolac/PEO: (a) 100/0; (b) 90/10; (c) 70/30

novolac in the molten state, and the novolac is incorporated in the interlamellar regions of PEO spherulites during the crystallization process.

FTi.r. studies can provide important information about intermolecular interactions in the novolac/PEO system. *Figure 6* shows the FTi.r. spectra of novolac/PEO blends in the stretching region of the novolac hydroxyl groups ranging from 3000 to 3800 cm^{-1} . For the pure novolac, two absorptions were observed: one is a broad band centred at 3341 cm^{-1} which is attributable to the self-associated hydroxyl groups, and the other is a shoulder band at about

3500 cm^{-1} which is assigned to the non-associated, free hydroxyl groups. After incorporating PEO, the free hydroxyl band at 3500 cm^{-1} remains constant for all compositions, whereas the associated hydroxyl band at 3341 cm^{-1} shifts slightly to lower frequency as a function of increasing PEO concentration. Furthermore, it can be seen from Figure 6 that the relative strength of non-associated hydroxyl band to associated hydroxyl band decreases with increase of PEO content, which means that the number of non-associated hydroxyl groups becomes increasingly less and that of associated hydroxyl groups becomes steadily greater with increasing PEO content. All these observations indicate that hydrogen bonding interactions exist between the hydroxyl groups of novolac and the ether oxygens of PEO. 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 intermolecular interactions³⁸. Therefore, the results shown in Figure 6 indicate that the average strength of hydrogen bond between the hydroxyl groups of novolac and the ether oxygens of PEO ($\Delta\nu = 172 \text{ cm}^{-1}$ for 70/30 novolac/PEO composition) is higher than that between the self-associated hydroxyl groups in the pure novolac resin ($\Delta\nu = 159 \text{ cm}^{-1}$). Similar results have been reported by Coleman and coworkers in the other systems^{3,39,40}. All the above results further support the idea that PEO is completely miscible with uncured novolac resin.

From the results of d.s.c., optical microscopy and FTIR spectroscopy, it can reasonably be concluded that PEO is completely miscible with uncured novolac over the entire composition range in the amorphous state. The miscibility of the uncured novolac/PEO blends can be considered to be due both to the enthalpy contribution and the existence of hydrogen bonding between the components and to the significant entropic contribution as the molecular weight of novolac is rather low.

HMTA-cured novolac/PEO blends

All the novolac/PEO blends cured with 15 wt% HMTA (relative to the content of novolac) were transparent just above the melting point of PEO. Optical micrographs with crossed polars for the HMTA-cured novolac/PEO blends are displayed in Figure 7. It is noticeable that the crystalline morphology of PEO in the HMTA-cured novolac/PEO blends show essentially no differences from those of the uncured blends. The PEO spherulites are always completely

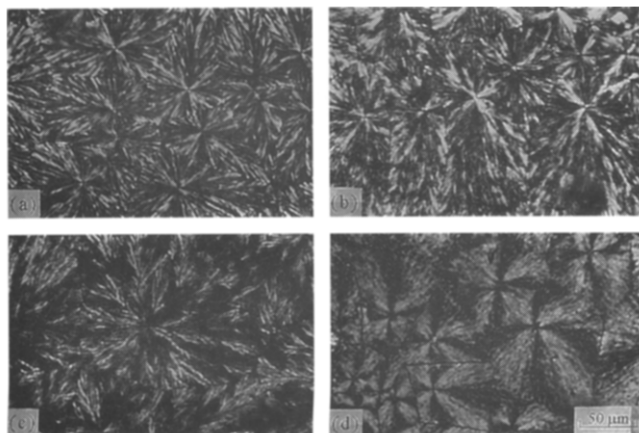


Figure 7 Optical micrographs of the novolac/PEO blends cured with 15 wt% HMTA. Novolac/PEO: (a) 10/90; (b) 20/80; (c) 30/70; (d) 40/60

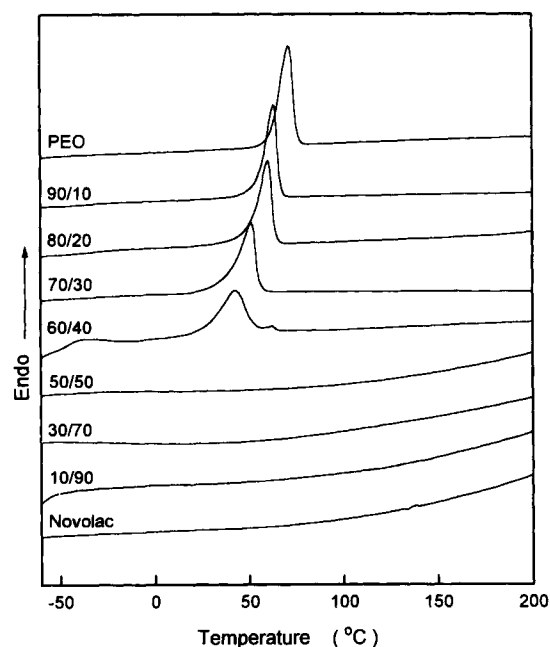


Figure 8 The d.s.c. thermograms of the novolac/PEO blends cured with 15 wt% HMTA

Table 2 Thermal properties of HMTA-cured novolac/PEO blends

PEO/ novolac	T_m (°C)	ΔH_f (J g^{-1} blend)	T_c (°C)	ΔH_c (J g^{-1} blend)	X_c blend (%)
100/0	71	175.7			86
90/10	63	135.5			66
80/20	60	102.8			50
70/30	51	52.3			26
60/40	43	15.7	-15	-1.6	7

volume-filled. The optical micrographs of the cured blends display a significant 'Maltese cross' except the 30/70 cured novolac/PEO blend which exhibits some characteristic of dendritic texture. It is also noted that, with increasing novolac content, PEO spherulites become increasingly open, coarser and more irregular. All these observations suggest that the cured blends are still miscible.

The d.s.c. thermograms of the novolac/PEO blends cured with 15 wt% HMTA are shown in Figure 8. The thermal properties obtained from Figure 8 are summarized in Table 2 and Figure 9. It is interesting to see that there are no apparent glass transition temperatures, but a very broad range of second-grade phase transitions for both the neat novolac resin and the novolac-rich blends after cure with HMTA. This is consistent with our previous observation in the systems of the HMTA-cured novolac/poly(*N*-vinyl-2-pyrrolidone) (PVP)¹² and the HMTA-cured novolac/poly(ϵ -caprolactone) (PCL)¹³, as well as with that reported by Zhang and Solomon¹⁹ in the novolac/poly(methyl methacrylate) blends cured with 20 wt% HMTA. The disappearance of glass transitions is a common phenomenon for highly cross-linked novolac blends. For the curing process of novolacs with a high amount of curing agent, cross-linking could occur at most phenolic rings. Thus, the cross-link density could be high enough to restrict segmental motions of novolac chains and to result in the disappearance of T_g behaviour for cured novolac resin. On the other hand, the T_g of the PEO-rich compositions is affected by the crystallization of PEO and therefore it is not discernible.

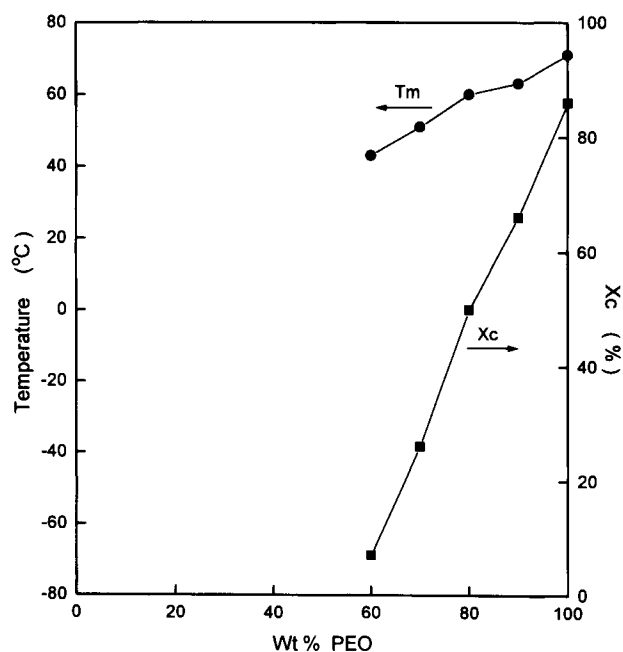


Figure 9 Composition dependence of X_c (■) and T_m (●) for the novolac/PEO blends cured with 15 wt% HMTA

These results show that the miscibility of the cured blends cannot be ascertained by the use of conventional T_g judgement. However, it has been shown for systems with a crystallizable component that both a decrease in the crystallinity and in the crystallization rate are indicative of miscibility phenomena in the amorphous state³⁶.

As shown in *Figure 8* no crystallization exotherm is observed for pure PEO and the HMTA-cured blends with a novolac content up to 30 wt%, implying that crystallization was sufficiently rapid to occur completely during quenching. However, the 60/40 HMTA-cured novolac/PEO blend shows a very broad range of crystallization exotherm. Furthermore, the cured blends with a novolac content of 50 wt% or more did not show any crystallization exotherm. This result demonstrates that crystallization of PEO in the cured blend becomes progressively more difficult with increasing novolac content, implying that the HMTA-cured novolac/PEO blends were still completely miscible in the melt.

It can also be seen from *Figure 8* that there exists a melting peak for the blends containing 70 wt% PEO or more which decreases with increasing novolac content, whereas no melting transition appears for the compositions containing 50 wt% PEO or less. Furthermore, the HMTA-cured novolac/PEO blend containing 60 wt% PEO exhibits an interesting melting behaviour: a very small melting peak is observed at the high temperature side of the major melting peak. This small melting peak at 62°C is presumably due to the crystallization during the heating and its melting. The T_m value of the 40/60 cured novolac/PEO blend was obtained from the major melting peak at the low temperature side. *Figure 9* shows the T_m values of the cured blends as a function of composition. It can be seen from *Figure 9* that the T_m of PEO in the cured blend substantially decreases with novolac content. The crystallinity of the cured blend, X_c , was calculated from equation (2). The results thus obtained are listed in *Table 2* and are also plotted in *Figure 9* against blend composition. From *Figure 9*, it can be seen that the crystallinity of PEO in the cured blends decreases rapidly with increasing novolac concentration, which

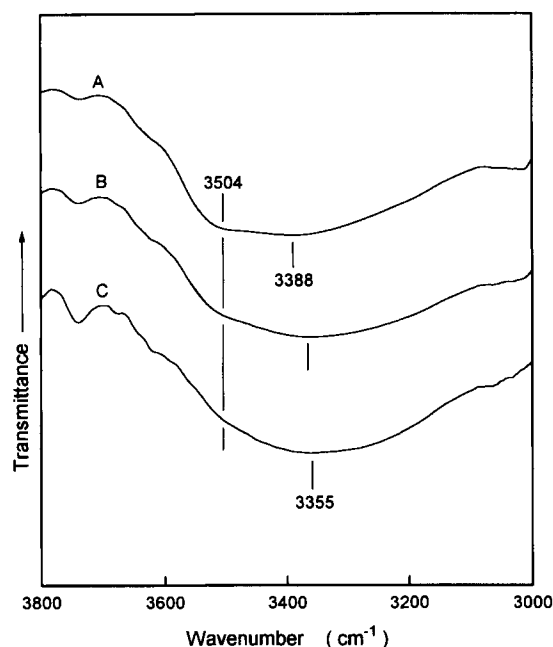


Figure 10 FTIR spectra in the 3000–3800 cm^{-1} region of the novolac/PEO blends cured with 15 wt% HMTA. Novolac/PEO: (a) 100/0; (b) 90/10; (c) 70/30

indicates that the crystallization rate of PEO decreases progressively. The T_m depression and the decrease in the crystallization rate further suggest that the cured novolac/PEO blends remained miscible over the entire composition range in the molten state.

Figure 10 shows the FTIR spectra of novolac/PEO blends cured with 15 wt% HMTA in the region of 3000–3800 cm^{-1} . For the neat HMTA-cured novolac resin, the band at 3504 cm^{-1} is attributed to the free hydroxyl stretching vibration and the band at 3388 cm^{-1} corresponds to the self-associated hydroxyl groups. For the cured blends, the following results were observed: the free hydroxyl band at 3504 cm^{-1} apparently remains constant while the associated hydroxyl band at 3388 cm^{-1} shifts slightly to a lower frequency with increasing PEO content. Similar to the uncured blends, the relative amount of the free hydroxyl groups to the associated hydroxyl groups decreases with an increase of PEO content. Therefore, it is clear that there still exists a remarkable hydrogen bonding interaction between the hydroxyl groups of the cured novolac and the ether oxygens of PEO in the HMTA-cured novolac/PEO blends. Comparing the FTIR spectra of the cured blends with those of the uncured blends shown in *Figure 6* can provide more important information about curing. First, the average strength of the hydrogen bond in the neat HMTA-cured novolac ($\Delta\nu = 116 \text{ cm}^{-1}$) is lower than that in the neat uncured novolac ($\Delta\nu = 159 \text{ cm}^{-1}$). Secondly, the average strength of the hydrogen bond between the hydroxyl groups of novolac and the ether oxygens of PEO in the cured blends ($\Delta\nu = 149 \text{ cm}^{-1}$ for the 70/30 cured novolac/PEO blend) is also somewhat lower than that in the corresponding uncured blends ($\Delta\nu = 172 \text{ cm}^{-1}$ for the 70/30 uncured novolac/PEO blend). Finally, the relative amount of the non-associated hydroxyl groups to the hydrogen-bonded hydroxyl groups is much higher than that in the uncured blends. This phenomenon can be explained as follows: novolac was cured with a large amount of cross-linking agent HMTA and the high cross-linking density makes the segmental motion of novolac chains very difficult. Therefore, it is difficult to

form a hydrogen bond even in the neat cured novolac resin. In other words, both the relative amount and the average strength of the hydrogen bond in the cured blends were lower than those in the uncured blends.

It is clear that the miscibility of the HMTA-cured novolac/PEO blends is significantly different from that of the uncured blends. As the HMTA-cured novolac/PEO blends were highly cross-linked and the cured novolac component possessed an infinite molecular weight, the entropy effect contributed little to the miscibility. Therefore, it is reasonable to conclude that the miscibility in the cured blends is mainly due to the enthalpy contribution. The hydrogen bonding interactions between the components are responsible for the favourable enthalpy of mixing and hence for the miscibility of the HMTA-cured novolac/PEO blends. The still miscibility of the cured blends was also observed in our previous study on the novolac/PVP system¹². However, a different result was obtained in our previous work on the novolac/PCL system¹³ in which we found phase separation in the HMTA-cured novolac/PCL blends. This can be presumably related to the different hydrogen bond interactions between the components. The average strength of the hydrogen bond between the hydroxyl groups of novolac and the carbonyl groups of PCL is much lower than that between the self-associated hydroxyl groups in neat novolac resin¹³, whereas the hydrogen bond between the hydroxyl groups of novolac and the proton-accepting groups of PVP¹² or the ether oxygens of PEO is stronger than that of the self-associated hydroxyl groups of novolac.

CONCLUSIONS

From the above results it can be concluded that both the uncured novolac/PEO blends and the HMTA-cured novolac/PEO blends were completely miscible over the entire composition range. The miscibility of the uncured novolac/PEO blends is due both to the enthalpy contribution and to the entropy contribution, whereas the miscibility of the cured novolac/PEO blends is due only to the enthalpy contribution. FTi.r. investigation showed there existed hydrogen bonding interaction between the hydroxyl groups of novolac and the ether oxygens of PEO in both the uncured system and the highly cured system. The relative amount and the average strength of the hydrogen bond in the cured blends were lower than those in the uncured blends, whereas the relative amount and the average strength of the hydrogen bond in both the uncured and the cured novolac/PEO blends were higher than those in the corresponding control novolac resin. After curing with 15 wt% HMTA, remarkable changes occurred. The curing resulted in disappearing of T_g behaviour of the novolac and the novolac-rich blends, owing to the less mobility of novolac chain segments.

ACKNOWLEDGEMENTS

This work was supported by the Presidential Fund of the Chinese Academy of Sciences and by the State Science and Technology Commission of China. The authors also wish to express their appreciation to the National Natural Science

Foundation of China for awarding a 'Premier Grant' for Outstanding Young Scientists (no. 59525307).

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