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Miscibility and cure kinetics of nylon/epoxy resin reactive blends

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The miscibility, phase behavior and cure kinetics of the reactive blends of an alcohol-soluble nylon with an epoxy resin, i.e. diglycidyl ether of bisphenol A (DGEBA), were studied by differential scanning calorimetry (d.s.c.) and Fourier transform infra-red spectroscopy (*FT*i.r.). Differential scanning calorimetry (d.s.c.) studies showed that all the uncured nylon/DGEBA blends were crystallizable and exhibited two glass transition temperatures (T_gs). The lower T_g is independent of composition and is due to the glass transition of DGEBA phase. The higher T_g varies with composition and is attributable to the glass transition of the nylon-rich phase. Nylon is partially miscible with DGEBA, and the extent of miscibility is dependent on the blend composition. Nylon and DGEBA in all the uncured blends can react with each other above 200°C. The curing reaction of nylon with DGEBA is dependent on the blend composition. The nucleophilic attack on oxirane ring by amide nitrogen of nylon is dominant curing reaction in low DGEBA compositions, and another type of curing reaction with relatively large activation energy and frequency factor also occurred which becomes dominant when the DGEBA content reaches 63 wt% or more. *FT*i.r. studies revealed there does exist two types of reactions during curing of nylon with DGEBA. All the cured nylon/DGEBA blends show a composition-independent T_g, which is the glass transition of cured nylon-DGEBA network. All other blends are uncrystallizable after curing except for the 90/10 and 80/20 nylon/DGEBA blends. The curing greatly destroyed the crystallinity of the blends. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: nylon/DGEBA; miscibility; phase behaviour)

INTRODUCTION

Epoxy resins are a major generic class of polymeric materials, and are widely used as matrices for composite materials and as structural adhesives. For example, blends of nylon polymers with epoxy resin, known as 'nylon–epoxy' adhesives, are usually used as a structural adhesive in aerospace industries[1–6]. In these adhesives, nylon and epoxy resin can react with each other. As binder polymer of epoxy resins, nylon polymer enjoys some advantages, such as high peel strength, high adhesive force and outstanding low-temperature properties. However, studies of these blends has received little attention[7–14] and has mainly focused on their mechanical properties. Gorton[7] studied the interaction of nylon with epoxy resins in adhesive blends, and found that the epoxy resin crosslinks the nylon through the reaction of oxirane group with amide nitrogen in nylon chain. He also considered the effects of crosslinking variations on the high performance of nylon–epoxy adhesives. Sprauer and Harrison[5] suggested that the high performance of nylon–epoxy adhesives depends upon the multiphase structure of the blends for the limited miscibility of nylon/epoxy resin and upon the stress-induced crystallization during elongation. Delollis and Montoya[8] and Butt and Cotter[9] examined the effects of humid environments on the adhesion of the nylonepoxy adhesives and aluminum substrates. Wang and Chen[10] studied the phase structure of cured nylon–epoxy adhesives, and tensile and shear properties of the cured adhesives. They found that the cured blends are of multiphase structure, and that adhesion and crosslinking effects due to incorporation of epoxy resin play more important role than the crystallinity and stress-induced crystallization during stretching. From these studies, it is clear that phase structure of the cured blend plays an important role on the high performance of nylon–epoxy adhesives. However, the phase structure of the cured blend is affected by many factors, such as the phase structure of the uncured blend and the curing procedure, and these are seldom studied. Additionally, it is usual to involve another small molecule as curing agent like dicyanadiamide in the formulation of nylon–epoxy adhesives[5,7,10]. This makes the system more complicated, and conceals other factors which affect the phase structure of the cured nylon/epoxy resin blend. Therefore, further comment is required for nylon–epoxy systems.

On the other hand, nylon is highly crystalline and has strongly self-associated hydrogen bonding characteristics[5,6,15], and it only has a limited miscibility with epoxy resin. Thus, it is expected that the uncured nylon/epoxy resin blend has multiphase structural characteristics. The multiphase structure of the blend has significant influence on the curing behavior of the system, and nylon or epoxy molecules have to diffuse from one phase to another during curing in order to react with each other. In this paper, we present the results of our studies on blends of an alcohol-soluble nylon with an epoxy resin, i.e. diglycidyl ether of bisphenol A (DGEBA). Special attention was paid to the miscibility and phase behavior of the blend before and after curing, as well as the cure kinetics and the influence of phase structure and curing on each other.

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EXPERIMENTAL

Materials and preparation of blends

The alcohol-soluble nylon with an intrinsic viscosity $[\eta] = 0.98\ \mathrm{dl\ g^{-1}}$ measured in 93% H_2SO_4 at 25°C was used in this study. It was commercially obtained from Shanghai Plastics Eighteenth Factory, Shanghai, P.R. China, and it was copolymerized by 50 wt% caprolactam and 50 wt% hexamethylenediammonium adipate salt (66 salt). The bisphenol A type epoxy resin E-51 with epoxide equivalent weight 185–210, i.e. diglycidyl ether of bisphenol A (DGEBA), was obtained from Wuxi Resin Factory, Wuxi, P.R. China.

All the blends were prepared by solution casting from ethanol. The solution was allowed to evaporate most of the solvent at room temperature. To remove the residual solvent, the blend films obtained were further dried under vacuum for one week.

Differential scanning calorimetry

The calorimetric measurements were performed on a Perkin-Elmer DSC-7 differential scanning calorimeter (d.s.c.) in dry nitrogen atmosphere. The instrument was calibrated with indium and zinc standards for lower and high temperature regions, respectively. All samples were first heated to 180°C to remove any crystallinity, followed by quenching to − 60°C. A heating rate of $20°\mathrm{C\ min^{-1}}$ was used to obtain the glass transition temperature (T_g), melting temperature (T_m), and crystallization temperature (T_c). The T_g was taken as the midpoint of the heat capacity change, whereas the T_m and T_c were taken as the maximum of the endothermic peak and the minimum of the exothermic peak, respectively. The curing processes were also carried out on a differential scanning calorimeter at various heating rates: 5, 10, 15, $20°\mathrm{C\ min^{-1}}$.

Fourier transform infra-red spectroscopy

A Nicolet 750 Fourier-transform infra-red (*FT*i.r.) spectrometer was used to study the curing reaction of nylon with DGEBA. Thin films of the blends were cast onto a KBr window from a 2% (w/v) solution of hot ethanol. After evaporation of most of the solvent, the films were kept in a vacuum oven at room temperature 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 were further cured at 250°C for 0.5 h under N_2 protection. Both the uncured and the 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 $4\ \mathrm{cm^{-1}}$ were signal averaged.

RESULTS AND DISCUSSION

Miscibility of uncured nylon/DGEBA blends

D.s.c. was employed to study the miscibility and phase behaviour of the nylon/DGEBA blends before and after curing. *Figure 1* presents the d.s.c. thermograms of uncured nylon/DGEBA blends, and the results are summarized in *Figures 2–4*. *Figure 2* is a plot of T_gs of the uncured nylon/DGEBA blends against the composition. It can be seen that all blends clearly showed two separated T_gs, indicating their multi-phase structure. The lower T_g is attributable to the glass transition of DGEBA phase, i.e. $T_{g(\mathrm{DGEBA})}$, and it is independent of composition in the entire composition range. The higher T_g is attributable to the glass transition of nylon-rich phase, i.e. $T_{g(\mathrm{nylon})}$, and it varies with the composition: $T_{g(\mathrm{nylon})}$ of the blends is lower than that of the pure nylon component (42°C) and keeps almost invariant at about 37°C up to 40 wt% DGEBA. Then $T_{g(\mathrm{nylon})}$ decreases gradually with increasing content of DGEBA. When the content of DGEBA reaches 60 wt% or more, $T_{g(\mathrm{nylon})}$ remains basically constant at about 27°C. These results can be explained as follows: nylon is partially miscible with DGEBA in all blends, and the extent of the miscibility is dependent on the composition. The extent of the miscibility of the low-DGEBA compositions is lower than that of the

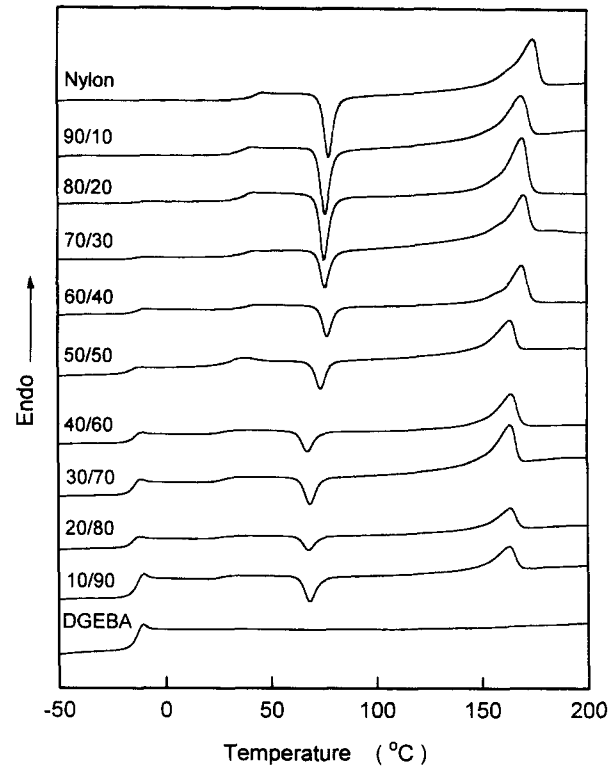


Figure 1 D.s.c. thermograms of uncured nylon/DGEBA blends

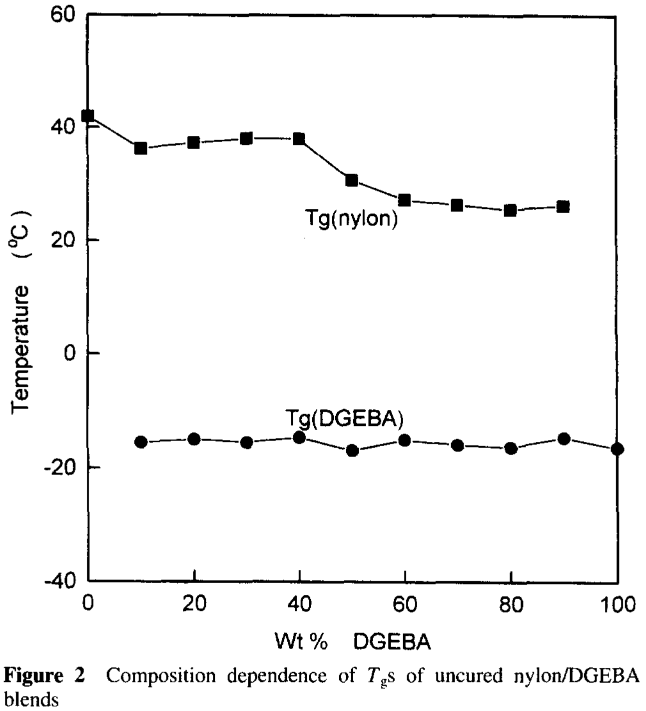


Figure 2 Composition dependence of T_gs of uncured nylon/DGEBA blends

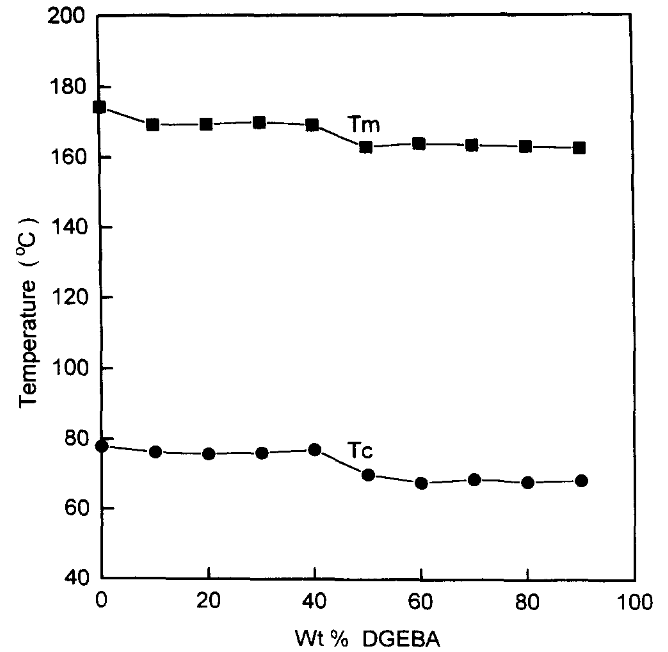


Figure 3 Composition dependence of T_m (■) and T_c (●) of uncured nylon/DGEBA blends

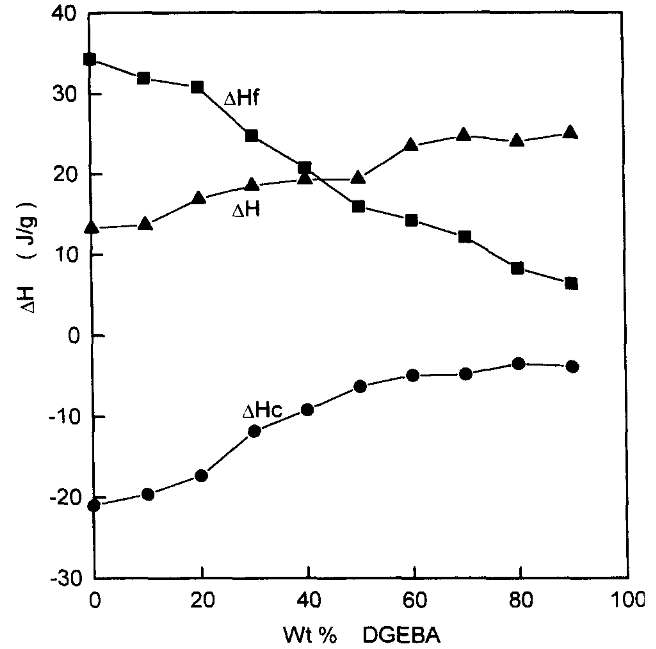


Figure 4 Composition dependence of ΔH_f (■), ΔH_c (●) and ΔH (▲) of uncured nylon/DGEBA blends

high-DGEBA compositions. For the compositions from 40 wt% to 60 wt% DGEBA, the miscibility of nylon with DGEBA increases with increasing content of DGEBA. The partially miscible nylon/DGEBA blends consist of two amorphous phases, one is an essentially pure DGEBA phase, the other is a nylon-rich phase which consists mainly of a nylon component with a small amount of DGEBA incorporated. For the blends with DGEBA content up to 40 wt%, some DGEBA is incorporated in nylon to form a nylon-rich phase, and this leads to the decrease of T_g of the blends. When the content of DGEBA in the blends is more than 40 wt%, the weight fraction of DGEBA in nylon-rich phase becomes larger and larger, and consequently the T_g of the blends decreases gradually. When the overall content of DGEBA in the blends reaches 60 wt% or more, the content of DGEBA in nylon-rich phase does not change with composition, thus the T_g of the blends remains constant.

Figure 3 shows the plots of T_m and T_c against composition. It can be seen that both T_m and T_c exhibited variation in trend *versus* the composition similar to that of the $T_{g(\text{nylon})}$ in the blends: Both T_m and T_c of the blends are lower than those of the pure nylon, their values remaining constant when the content of DGEBA is not more than 40 wt%; they then slightly decrease with the increase of DGEBA content. When the DGEBA content is higher than 60 wt%, T_m and T_c are almost independent of the composition. The decrease in the T_m of the blends is due to the partial miscibility of nylon with DGEBA. The fact that the T_ms of the high-DGEBA-content blends are lower than those of the low-DGEBA-content blends is because of the high extent of the miscibility of these composition blends. The decrease in the T_c suggests that the crystallization is more rapid in the blends. The incorporation of DGEBA into the nylon phase reduces the T_g of the system and enhances the chain mobility, therefore the T_c of the blends decreases. This means that the incorporation of DGEBA is favourable to the crystallization of nylon. The advantage of the crystallization of nylon after incorporating of DGEBA can also be seen from the variation of ΔH with the composition in *Figure 4*. *Figure 4* shows the variation of ΔH_f, ΔH_c and ΔH against the composition. The ΔH was calculated according to equation (1):

$$\Delta H = (\Delta H_f + \Delta H_c)/W_{\text{nylon}} \qquad (1)$$

where W_{nylon} is the weight fraction of nylon in the blend, and ΔH_f and ΔH_c are the heats of fusion and crystallization of nylon in the blends. ΔH can be considered as a measure of the crystallinity of nylon in the blend after the blend was quenched from molten state (180°C), and the larger ΔH is, the higher the crystallinity of nylon in the blend is. *Figure 4* shows that ΔH of nylon in the blend which contains 60–90 wt% DGEBA is higher than that of other blends, and the ΔHs of all blends are higher than that of pure nylon. These mean that, in the blends, nylon is easier to crystallize.

Cure kinetics of the nylon/DGEBA blends

D.s.c. is a valuable technique for determining the curing rate constant and the resulting kinetic parameters[16–18]. *Figure 5* presents the typical dynamic traces for the curing reaction of the nylon/DGEBA blends at 10°C min^{-1}. It can be seen that the curing reaction essentially does not occur below 200°C under experimental conditions, and d.s.c. traces of curing at other heat rate display the same results. Above 200°C, the d.s.c. trace exhibits an exothermic peak. The peak exotherm temperature (T_p) increases with the increase of DGEBA content in the blends. Especially, T_p increases greatly when the content of DGEBA is beyond 60 wt%, i.e. for the 37/63 (which is the equimolar ratio composition of epoxide group and amide hydrogen) and 20/80 nylon/DGEBA blends (*Figure 5*). This suggests that the curing reaction is dependent on the composition.

From the peak exotherm temperature and the heating rate (ϕ), we can obtain the kinetic parameters of cure reaction, such as activation energy (E_a) and the frequency factor (A_0). According to work by Ozawa[19,20], Prime[21] and Peyser and Bascon[22], the relationship of E_a, ϕ and T_p

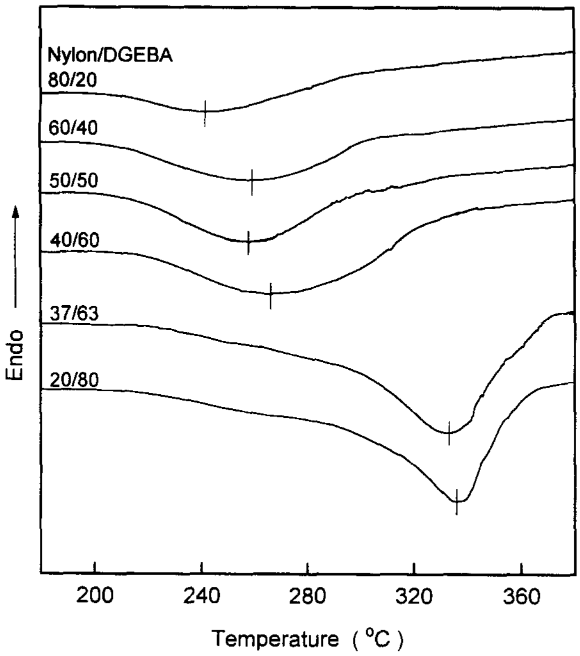


Figure 5 Dynamic curves at 10°C min^{-1} for the curing of nylon/DGEBA blends

Table 1 Values of activation energy and frequency factor for nylon/DGEBA blends

Nylon/DGEBA	E_a (kJ mol^{-1})	A_0 (min^{-1})
80/20	68.1	2.7×10^6
60/40	71.8	3.4×10^6
50/50	77.0	2.3×10^7
40/60	80.4	3.3×10^7
37/63	100.1	1.9×10^8
20/80	119.1	1.6×10^{10}

can be described as:

$$E \approx (-R/1.052)\cdot(\Delta \ln\phi/\Delta(1/T_p)) \tag{2}$$

where R is the gas constant. By plotting $1/T_p$ *versus* $\ln\phi$ at different heating rates (5, 10, 15 and 20°C min^{-1}) (*Figure 6*, solid circles) and using equation (2), the values of E_a for nylon/DGEBA blends were obtained and are listed in *Table 1*. Kissinger[23] derived a expression for the frequency factor for *n*th-order reactions:

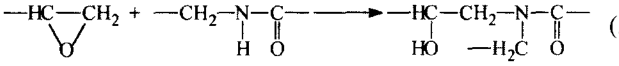
$$A_0 \approx (\phi E_a\cdot\exp(E_a/R\cdot T_p))/(R\cdot T_p^2) \tag{3}$$

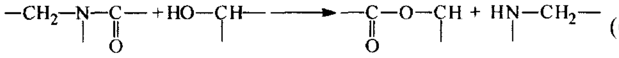
Rearrangement of equation (3) results in:

$$\ln\phi = \ln(A_0R/E_a) + 2\ln T_p - E_a/RT_p \tag{4}$$

Using the resulting E_a from equation (2), plotting ($2\ln T_p - E_a/RT_p$) *versus* $\ln\phi$ (*Figure 6*, solid squares), the values of the pre-exponential factor of nylon/DGEBA blends can be obtained and are also listed in *Table 1*. The data of E_a and A_0 in *Table 1* illustrate that both E_a and A_0 increase only slightly with the increase of DGEBA content up to 60 wt%, and that they increase sharply beyond that composition. These results are consistent with the variation of T_p against composition, and suggest that the curing reaction of nylon with DGEBA is dependent on the blend composition.

As shown in the literature[17,24], the maximum extent of cure is governed by network rigidity and the curing reaction of epoxy resin is diffusion controlled, and this is the case especially in the nylon/DGEBA multiphase system. As we have discussed, the nylon/DGEBA blends have two amorphous phases. After fusing of nylon above 180°C, it can be reasonably deduced that nylon/DGEBA blends have two phases: nylon-rich phase and DGEBA phase. The curing reaction occurs in the nylon-rich phase, which has both nylon and DGEBA, or on the phase boundary. The DGEBA molecules in the DGEBA phase should, at first, diffuse into nylon-rich phase in order to react with nylon, and the diffusion is significantly influenced by the composition of the blends. The more there is DGEBA in the blends, the more DGEBA has to diffuse into the nylon-rich phase. On the other hand, the curing reaction causes the linkage of nylon macromolecule with DGEBA molecule to form network and the crosslink density of the network increases with increasing content of DGEBA in the blends. Therefore the diffusion becomes more and more difficult with the increase of DGEBA content. Thus E_a and A_0 increase with increasing content of DGEBA. As we will show below, there are two types of curing reactions occurred during the curing of nylon with DGEBA. The first type of reaction (equation (5)) is nucleophilic attack on the oxirane ring by the amide nitrogen of nylon, and is expected to be the dominant reaction for DGEBA content up to 60 wt%. In this case, the amide nitrogen is in stoichiometric excess. However, with increasing DGEBA content, the second type of reaction (equation (6)) becomes more and more important, especially when the epoxide group excesses, i.e. more than 63 wt% DGEBA. The second type of reaction occurs at elevated high temperatures and has relatively large activation energy and frequency factor, and therefore the T_p, the overall activation energy, and the frequency factor of the whole curing reaction become larger and larger with increasing content of DGEBA in the blends and increase greatly beyond 40/60 nylon/DGEBA composition.


(5)



$$-CH_2-\underset{|}{N}-\underset{\underset{O}{\|}}{C}- + HO-\underset{|}{C}H- \longrightarrow -\underset{\underset{O}{\|}}{C}-O-\underset{|}{C}H + H\underset{|}{N}-CH_2- \tag{6}$$

Fourier transform infra-red spectroscopy

Curing reaction of nylon with DGEBA can result in significant changes of the chemical structure of molecule and these changes may be reflected in the i.r. spectrum of the blend. *FT*i.r. spectra of the nylon/DGEBA blends before and after curing are shown in *Figures 7–9*. *Figure 7* shows the *FT*i.r. spectra of the 80/20 nylon/DGEBA blend before and after cured at 250°C for 0.5 h. For the uncured blend, it exhibits a sharp absorptive peak at 3304 cm^{-1}, and a shoulder peak at about 3480 cm^{-1}. The absorptive peak in this range is due mainly to the stretching vibration of the N- – H group (3304 cm^{-1}), and the stretching vibration of the O–H group (3480 cm^{-1}) in DGEBA also locates in this range. After curing, the absorptive peaks in this range broadened, and the contribution of the stretching vibration of N–H group decreased while the contribution of the stretching vibration of O–H group increased. These mean that the number of N–H groups decreases while the number of O–H groups increase after curing. From the *FT*i.r. spectrum of the cured blend, however, it can be seen that there still exists N–H groups in the blend. Comparing the spectrum of the blend before and after curing, it can also be seen that the characteristic absorption of the oxirane ring at

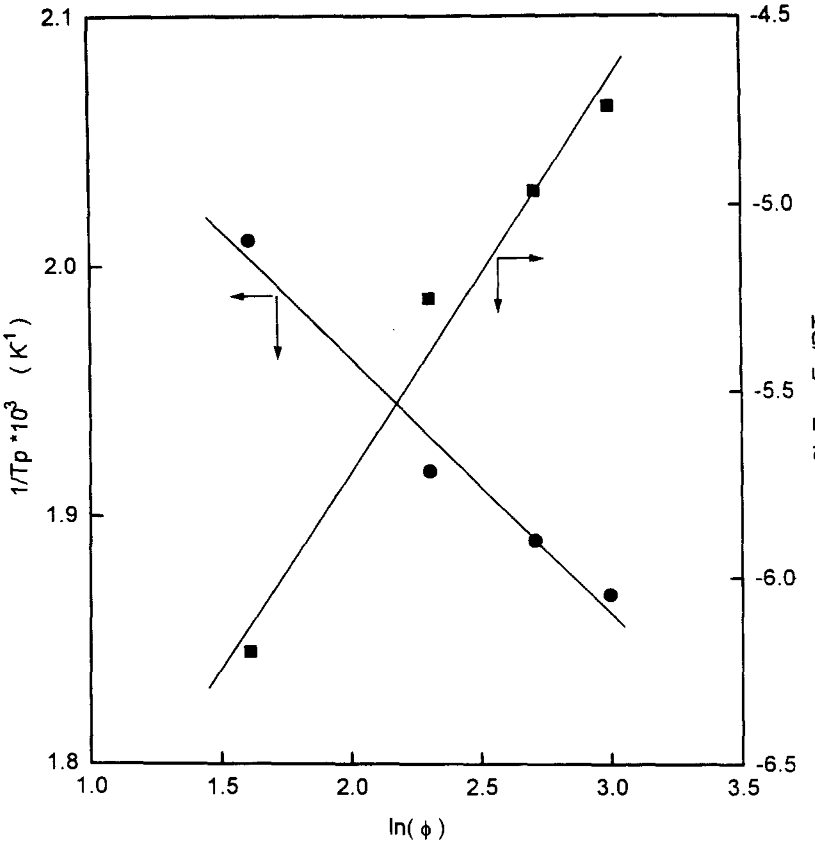


Figure 6 Determination of the activation energy (●) and frequency factor (■) by dynamic method for the curing of the 50/50 nylon/DGEBA blend

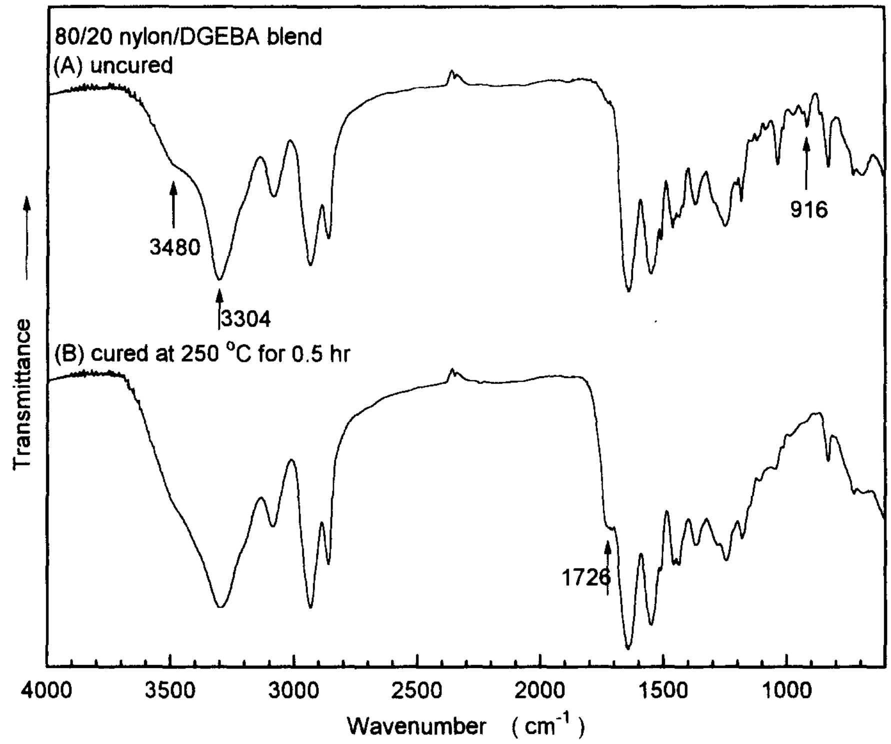


Figure 7 *FT*i.r. spectra of the 80/20 nylon/DGEBA blend (A) before and (B) after curing at 250°C for 0.5 h

916 cm^{-1} disappeared completely after curing, implying the complete reaction of DGEBA during curing. The main reaction is nucleophilic attack on the oxirane ring by the amide nitrogen of nylon, which produces a hydroxyl group (equation (5)), and this reaction is a typical reaction of the curing of epoxy resin with an amine hardener[16]. In addition, a new absorptive peak at 1726 cm^{-1} appeared after curing, indicating another type of reaction occurred during the curing. The peak at 1726 cm^{-1} is the absorption of carbonyl (C = O) of the ester group. This suggests that the second type of reaction occurs through equation (6). The resulted secondary amine group can react further with the epoxide

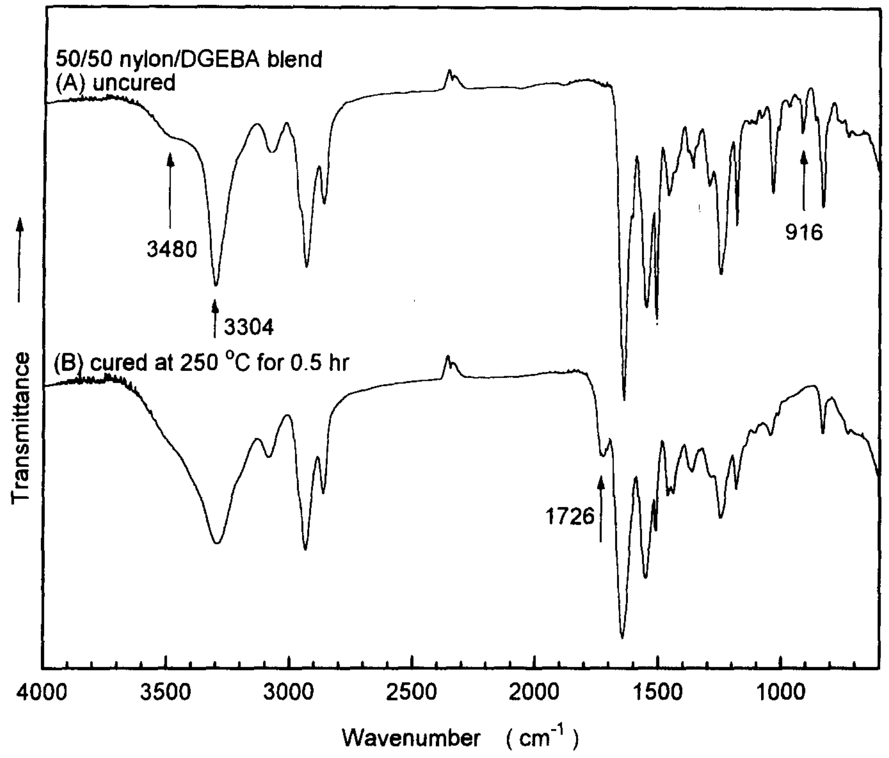


Figure 8 *FT*i.r. spectra of the 50/50 nylon/DGEBA blend (A) before and (B) after curing at 250°C for 0.5 h

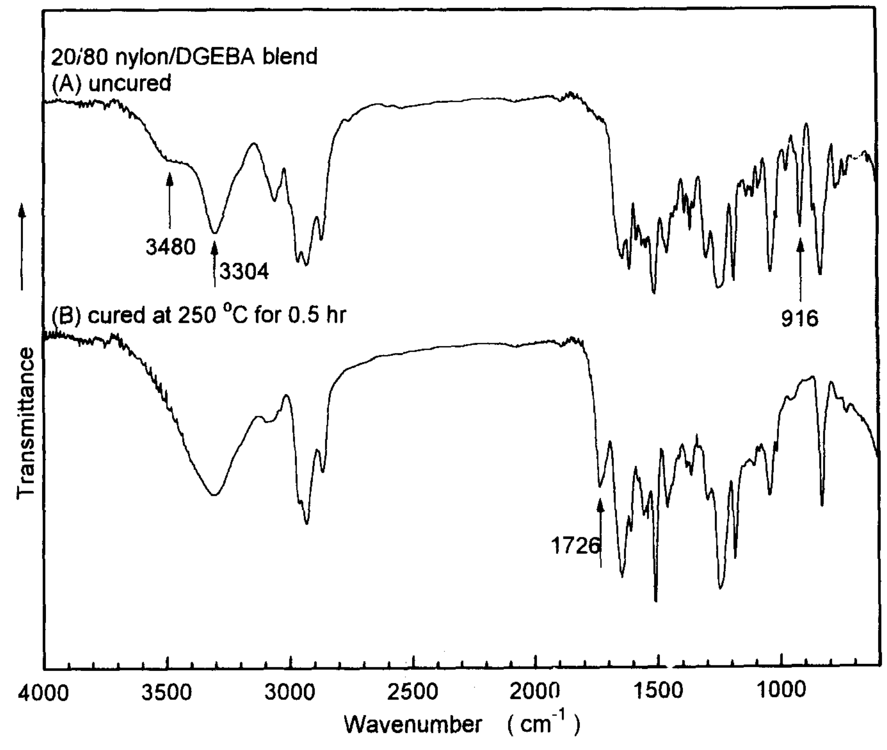


Figure 9 *FT*i.r. spectra of the 20/80 nylon/DGEBA blend (A) before and (B) after curing at 250°C for 0.5 h

group. The multiple reactions has also been reported by Prime and Sacher[25] and Lane *et al.*[26] in DGEBA/ polyamide system.

Figures 8 and 9 show the *FT*i.r. spectra of the 50/50 and 20/80 nylon/DGEBA blends, respectively. The spectra of these two blends before and after curing exhibit characteristics similar to that of the 80/20 nylon/DGEBA blend: broadening of the peaks in the range of 3150–3600 cm^{-1}, complete disappearance of the peak at 916 cm^{-1}, and appearance of a new peak at 1726 cm^{-1} after curing at 250°C for 0.5 h. The new peak at 1726 cm^{-1} becomes more and more significant with increasing content of DGEBA, implying that the second type of reaction becomes more and more predominant with the increase of DGEBA content. It can also be seen that there still exist some N–H groups in the 50/50 nylon/DGEBA blend after curing, whereas the absorption of the N–H group in the spectrum of the 20/80 nylon/DGEBA blend is not

Table 2 Thermal properties of cured nylon/DGEBA blends

Nylon/DGEBA	T_g (°C)	T_m (°C)	ΔH_f (J per g blend)	T_c (°C)	ΔH_c (J per g blend)
90/10	47	159	23.0	109	−20.9
80/20	47	155	3.12	106	−1.6
70/30	47				
60/40	47				
50/50	46				
40/60	45				
37/63	46				
30/70	46				
20/80	45				

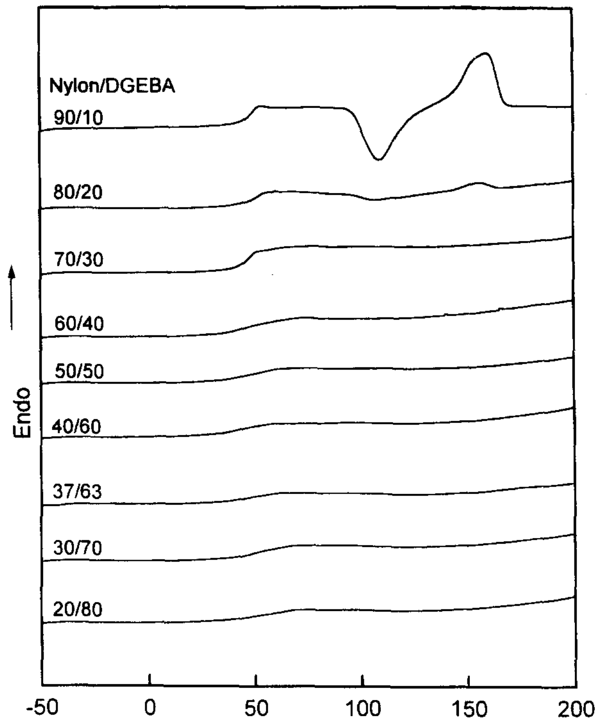


Figure 10 D.s.c. thermograms of the cured nylon/DGEBA blends

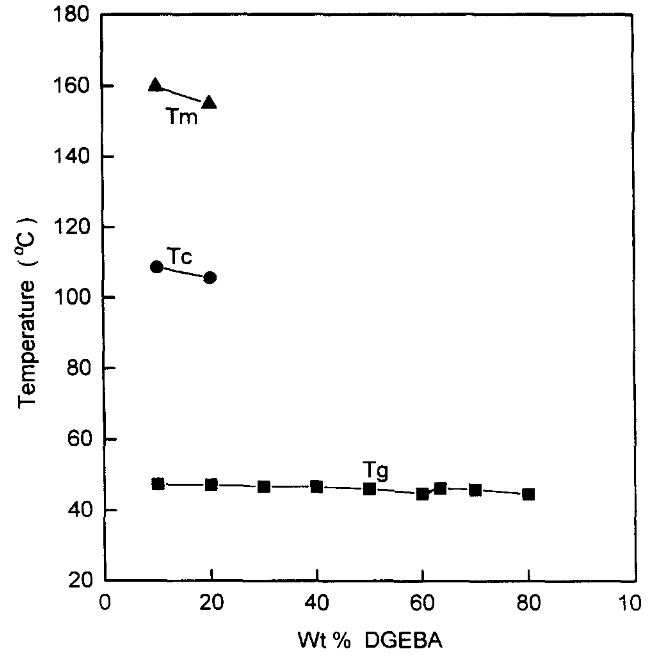


Figure 11 Thermal transitions of the cured nylon/DGEBA blends

significant. These results and the complete disappearance of the absorptive peak of the oxirane ring of the 20/80 nylon/DGEBA blend indicate that the secondary amine group produced by the second type of reaction has further reacted with the epoxide group.

Phase behaviour of cured nylon/DGEBA blends

All the nylon/DGEBA blends cured at the heating rate of 10°C $\min^{-1}$ in the d.s.c. were quenched to −60°C and then heated to 200°C at the rate of 20°C $\min^{-1}$ to determine their transition temperatures. The d.s.c. thermograms of the cured nylon/DGEBA blends are shown in *Figure 10*, and the results are summarized in *Table 2*. *Figure 11* shows the plot of T_g, T_m and T_c against the blend composition. From *Figures 10 and 11*, we can see that all the cured blends exhibit a single T_g, strongly suggesting that the cured blends have a single amorphous phase. As we have discussed, the curing reaction between nylon and DGEBA occurs in the nylon-rich phase, and the DGEBA molecule in the DGEBA phase diffuses into the nylon-rich phase to react with nylon. With reaction of nylon with DGEBA, the DGEBA phase becomes smaller and smaller, and finally disappears. Thus the cured blends show only one amorphous phase, which consists of the cured nylon–DGEBA network. The curing reaction causes the linkage of nylon macromolecules with DGEBA molecules to form a network, and this limits the segment motion and results in the increase of T_g after curing. It is also noted, from *Figures 10 and 11*, that all the cured blends are uncrystallizable except for the 90/10 and 80/20 nylon/DGEBA blends, indicating that the curing greatly destroys the crystallinity of the blends. For the 90/10 and the 80/20 nylon/DGEBA blends, as mentioned above, there still exist enough amido groups after curing, which can form intermolecular hydrogen bonds. Therefore, these two cured blends remain crystallizable. In view of the fact that curing reduces the chain mobility and the perfection of the crystallization, the decrease of T_m and the increase of T_c comparing to the uncured blends are expected. The lower T_m and T_c of the 80/20 cured nylon/DGEBA blend compared with those of the 90/10 cured nylon/DGEBA blend are also understandable.

CONCLUSION

From the results presented here, it can be concluded that:

(1) Nylon is partially miscible with DGEBA in the entire composition range. The extent of miscibility in the

low-DGEBA compositions is lower than that in the high-DGEBA compositions. All the uncured nylon/DGEBA blends are crystallizable and have two amorphous phases: a nylon-rich phase which consists mainly of nylon with some DGEBA incorporated, and a pure DGEBA phase.

(2) The curing reaction of nylon with DGEBA is dependent on the blend composition. For low-DGEBA compositions, nucleophilic attack on the oxirane ring of epoxide by the amide nitrogens of the nylon is dominant. Another type of reaction with a relatively large activation energy and frequency factor also occurs during the curing reaction, and this reaction becomes predominant when the DGEBA content is in stoichiometric excess, i.e. more than 63 wt%.

(3) All the cured nylon/DGEBA blends have a single amorphous phase. Except for the 90/10 and the 80/20 cured nylon/DGEBA blends, all other blends are uncrystallizable after curing. The curing destroys the crystallinity of the blends.

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