

Reactive Blends of Epoxy Resin (DGEBA) Crosslinked by Anionically Polymerized Polycaprolactam: Process of Epoxy Cure and Kinetics of Decomposition

Alka Gupta, Reena Singhal, A. K. Nagpal

Department of Plastic Technology, Harcourt Butler Technological Institute, Kanpur-208 002, India

Received 12 February 2003; accepted 24 September 2003

ABSTRACT: The curing reactions, kinetics, morphology, and thermal stability of the reactive blends of diglycidyl ether of bisphenol-A (DGEBA) and polycaprolactam were studied by differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and thermogravimetric analysis. DSC studies showed that the heat of reaction (ΔH) increased when the DGEBA content was increased from 50 to 80 wt % and increased drastically above 70 wt % DGEBA content because of an increase in the extent of crosslinking. The activation energy and pre-exponential factor of cure reactions increased drastically with an increase in the DGEBA content above 70 wt % because of a drastic increase in crosslink density. The extent of curing reaction of polycaprolactam with DGEBA is dependent on the blend composition. The nucleophilic attack on oxirane ring by amide nitrogen of polycaprolactam is a dominant curing reaction in low DGEBA compositions, and another type of curing reaction with relatively large activation energy and pre-expo-

nenial factor also occurred, which becomes dominant when the DGEBA content reaches above 70 wt %. FTIR studies also revealed that two types of reactions do exist during the curing of polycaprolactam with DGEBA. It was observed during SEM studies that the reactive blends show multiphase system and on increasing the DGEBA content from 50 to 80 wt %, the mixing of the two phases increased. The reactive blend Ep₈₀Ca₂₀ with 80 wt % DGEBA content exhibits a single-phase system because of better mixing of the two phases. The results of thermogravimetric analysis also indicate that the initial degradation temperature (T_i), activation energy (E), and pre-exponential factor (Z) increased with increasing DGEBA content from 50 to 80 wt % in the reactive blends and increased drastically above 70 wt % DGEBA content due to the higher crosslink density. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 687–697, 2004

Key words: epoxy resin; activation energy; cure kinetics; thermogravimetric analysis; polyamide

INTRODUCTION

Epoxy resin-derived materials play an important role when one tries to find suitable materials for different high-performance applications (e.g., adhesive, coating, insulation, molding, and composites, etc.). They offer great versatility, low shrinkage, good chemical resistance, and outstanding adhesion. Optimum performance and properties are obtained by crosslinking the epoxy resins into a three-dimensional, insoluble, and infusible network by reacting it with a curing agent. However, epoxy resins tend to be brittle after cure and several approaches for modifications on epoxy resins have been tried. Some of these include blending with elastomers in various forms.

Nowadays, thermoplastic materials are being used for toughening the epoxy resins instead of rubbers because mechanical and thermal properties are not sacrificed to the same extent as with rubbers. Therefore, more attention has recently been given to the

modification of epoxy resin by high-performance tough thermoplastics, such as polyethersulfone, polyetherimide, cardopolyimide, and polyamides.^{1–9} For these reasons, knowledge of thermal properties of epoxy resins system are very important because it can be used to determine the curing behavior and the upper temperature limit for its use.

In our previous investigation, the crosslinking reaction mechanism of epoxy resin [diglycidyl ether of bisphenol-A (DGEBA)] by anionically polymerized polycaprolactam, along with optimization of blend composition,¹⁰ were studied by using Fourier transform infrared spectroscopy (FTIR) and solvent extraction process, respectively.

The main objective of this work was to study the curing behavior of reactive blends of epoxy resin (DGEBA) and polycaprolactam by differential scanning calorimetry (DSC) and FTIR. Permanent entanglements between the DGEBA and polycaprolactam inducing strong molecular interactions are susceptible to bring significant crosslinking enhancement with increasing DGEBA content. The fracture morphology of various DGEBA/polycaprolactam reactive blends after cure was carried out to investigate the mixing and phase-separation behavior of the reactive blends.

Correspondence to: R. Singhal (reena_singhal123@rediffmail.com).

TABLE I
Stoichiometric Ratios of ϵ -Caprolactam and DGEBA Taken for Synthesis of Reactive Blends

DGEBA (epoxy resin) : ϵ -caprolactam	Blend designation	DGEBA (g)	ϵ -Caprolactam (g)	Sodium hydride (g)	N-Acetyl caprolactam (g)
50 : 50	Ep ₅₀ Ca ₅₀	25.0	25.0	0.60	3.30
70 : 30	Ep ₇₀ Ca ₃₀	35.0	15.0	0.36	1.98
75 : 25	Ep ₇₅ Ca ₂₅	37.5	12.5	0.30	1.65
80 : 20	Ep ₈₀ Ca ₂₀	40.0	10.0	0.24	1.32

Thermogravimetric analysis (TGA) is a technique to determine the weight loss of a sample, while heating it at programmed heating rate. Here, TGA is used for thermal stability and kinetics of degradation.

EXPERIMENTAL

Materials

The epoxy resin used in this study was general purpose unmodified PG-100 DGEBA with an epoxide equivalent weight of 185 and viscosity as 11,400 CPS, supplied by M/s Parikh Resins and Polymers Ltd. (Kanpur, India) in collaboration with M/s F.I.C. Inc. (USA). ϵ -Caprolactam and sodium hydride were procured from M/s Spectrochem Pvt. Ltd. (Mumbai, India). Laboratory reagent (LR) grade *N*-acetyl caprolactam was supplied by M/s Fluka Chemic AG (Buchs, Switzerland).

Synthesis of reactive blends

Reactive blends of DGEBA and polycaprolactam were prepared by anionic polymerization technique. Table I gives the details of synthesis of reactive blends of (50 : 50), (70 : 30), (75 : 25), and (80 : 20) DGEBA : ϵ -caprolactam ratio, which are designated by Ep₅₀Ca₅₀, Ep₇₀Ca₃₀, Ep₇₅Ca₂₅, and Ep₈₀Ca₂₀, respectively. Monomer ϵ -caprolactam, being a highly hygroscopic substance, was vacuum dried at room temperature for 48 h in a desiccator containing anhydrous calcium chloride. First, dried ϵ -caprolactam was taken in a three-necked round-bottom flask and to it sodium hydride was added. The lactam was melted in nitrogen atmosphere at a temperature of 69–70°C to allow the sodium hydride to react. After the hydrogen evolution ceased, *N*-acetyl caprolactam was added and mixed properly. DGEBA was added in the flask just after adding *N*-acetyl caprolactam and mixing properly (stage 1). The reaction was carried on at a temperature of 140°C with proper mixing until the products were solidified. The samples were postcured in an oven at 130–140°C for 5 h.

Characterizations

Differential scanning calorimetry

Thermal Analyst 2000 (TA Instruments), equipped with a 2910 differential scanning calorimeter, was

used to study the curing behavior of reactive blends under nitrogen atmosphere. Scans were obtained under dynamic conditions with program heating rates of 5, 10, 15, 20, and 25°C min⁻¹ from 40°C to the temperature at which the exothermic reactions were completed. The samples were taken just after all reactants were added and mixed properly (stage 1) and weighed accurately in an aluminum pan and crimped, by using the cover (upper lid) of the pan. From the peak exotherm temperature (T_p) and the heating rate (β), we can obtain the kinetic parameters of cure reaction, such as activation energy (E) and the pre-exponential factor (Z). Activation energy was calculated according to work by Ozawa,^{11,12} Prime,¹³ and Peyser and Bascon.¹⁴ The relationship of E , β , and T_p can be described as

$$E \cong -2.19 R \frac{\Delta \log \beta}{\Delta (1/T_p)} \quad (1)$$

where R is the gas constant, β is the heating rate, and T is the peak temperature. Kissinger¹⁵ derived an expression for the pre-exponential factor (frequency factor) for n th order reactions:

$$Z (\text{min}^{-1}) = \frac{\beta E e^{E/RT_p}}{RT^2} \quad (2)$$

Rearrangement of eq. (2) results in

$$\log \beta = \log (ZR/E) + 2 \log T_p - E/RT_p \quad (3)$$

Fourier transform infrared spectroscopy

An MB-100 Fourier transform infrared spectrometer (BOMEM, Japan) was used to study the curing reaction of polycaprolactam with DGEBA in KBr pellet form in cesium chloride cells.

Morphological observations

Scanning electron micrographs were taken by a JEOL 35 CF scanning electron microscope. The samples were cryogenically fractured in liquid nitrogen and scanned up to suitable magnification to get an appropriate image of fracture surface of samples. A thin uniform gold film was sputtered on samples by using

an ion sputter. Changes in surface morphology were examined from the micrographs taken.

Thermogravimetric analysis

Thermogravimetric analysis of the DGEBA/polycaprolactam reactive blends were carried out on Thermal Analyst 2000 (TA Instruments) system. The thermal stability and the degradation kinetics of different samples were evaluated from the obtained thermograms at $20^\circ\text{C min}^{-1}$ heating rate under nitrogen atmosphere. Thermogravimetric analysis is also used as a fast and exact method for determination of the kinetics of thermal degradation of polymers. The kinetic parameters such as activation energy (E), pre-exponential factor (Z), and order of reaction were determined by Coats and Redfern method¹⁶

$$\log_{10} \left[\frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} \right] = \log_{10} \frac{ZR}{\beta E} \left[1 - \frac{2RT}{E} \right] - \frac{E}{2.3RT} \quad (4)$$

for all values of n except $n = 1$; for the situation where $n = 1$, this equation becomes

$$\log_{10} \left[\frac{-\log_{10}(1 - \alpha)}{T^2} \right] = \log_{10} \frac{ZR}{\beta E} \left[1 - \frac{2RT}{E} \right] - \frac{E}{2.3RT} \quad (5)$$

where α is the fraction decomposed, β is the heating rate, R is the gas constant, T is the absolute temperature, n is the order of reaction, E is the activation energy, and Z is the pre-exponential factor.

Thus, a plot of either

$$\log_{10} \left[\frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} \right] \quad (6)$$

against $1/T$ or

$$\log_{10} \left[\frac{-\log_{10}(1 - \alpha)}{T^2} \right] \quad (7)$$

against $1/T$ (when $n = 1$) should result in a straight line of slope $-(E/2.3R)$. By using a computational technique, the best fit value of n for all the reactive blends was calculated in the range of 0–2.

RESULTS AND DISCUSSION

Cure kinetics of the DGEBA/polycaprolactam reactive blends

DSC is a valuable technique used for determining the curing rate constant and the resulting kinetic parameters.^{17–19} Typical dynamic DSC scans at $10^\circ\text{C min}^{-1}$ heating rate and in nitrogen atmosphere for the curing

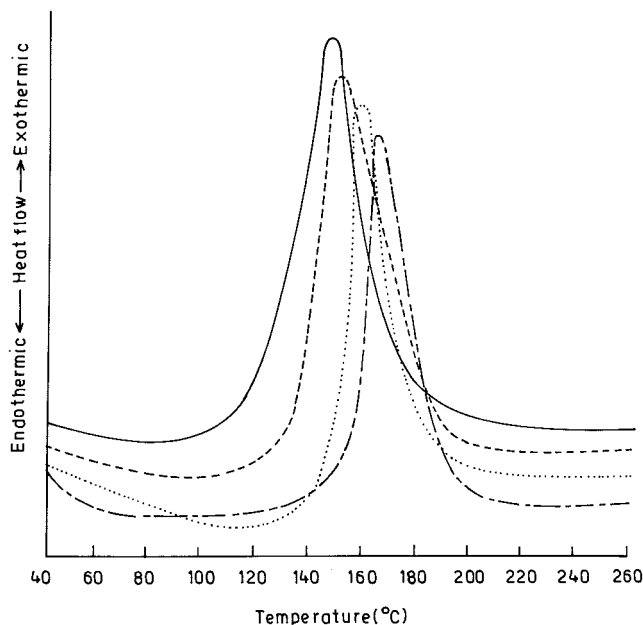


Figure 1 Dynamic DSC scans for the curing of DGEBA/polycaprolactam reactive blends at heating rate of $10^\circ\text{C min}^{-1}$ (—) Ep₅₀Ca₅₀; (---) Ep₇₀Ca₃₀; (···) Ep₇₅Ca₂₅; (-·-·) Ep₈₀Ca₂₀.

of reaction mixture (stage 1) of various reactive blends (Ep₅₀Ca₅₀, Ep₇₀Ca₃₀, Ep₇₅Ca₂₅, and Ep₈₀Ca₂₀) are shown in Figure 1. From these DSC scans, the onset temperature of curing (T_o), the exothermic peak position (T_p), final temperature of curing (T_f), and heat of curing reaction are determined and are summarized in Table II. It was observed that T_o and T_p are increasing with an increase in DGEBA content from 50 to 80 wt % in the reactive blends, whereas the curing temperature T_f remained almost the same for all the reactive blends. DSC scans at 5, 15, 20, and $25^\circ\text{C min}^{-1}$ also showed a similar trend. This indicates that the reactive blends prepared in different stoichiometric ratios show variation in their curing behavior.

T_o and T_p for reactive blend Ep₅₀Ca₅₀ was lower than reactive blends Ep₇₀Ca₃₀, Ep₇₅Ca₂₅, and Ep₈₀Ca₂₀. Thus, the reactive blend Ep₅₀Ca₅₀ requires more time for the completion of reaction. The area under the exotherm in between T_o and T_f gives the value of heat of reaction (ΔH); the values are summarized in Table II. From Table II, it is clear that the value of heat of reaction increases from 1530.14 to 1715.25 J g^{-1} as increasing the 50–70 wt % DGEBA content in the reactive blends. When the DGEBA content increases from 70 to 75 wt % in the reactive blends, the heat of reaction increases drastically from 1715.25 to 2071.25 J g^{-1} . On increasing the DGEBA content from 75 to 80 wt % in the reactive blends, the heat of reaction increases marginally, which proves that the extent of crosslinking increases as the DGEBA content increases from 50 to 80 wt %. Thus, because of the presence of lower content of DGEBA (50 wt %) in the reactive

TABLE II
Curing Behavior of Various DGEBA/Polycaprolactam Reactive Blends at a Heating Rate of $10^{\circ}\text{C min}^{-1}$

Blend	DGEBA content (Wt %)	T_o ($^{\circ}\text{C}$)	T_p ($^{\circ}\text{C}$)	T_f ($^{\circ}\text{C}$)	ΔH (J g^{-1})	E (K J mol^{-1})	Z (min^{-1})
Ep ₅₀ Ca ₅₀	50	94.56	144.42	208.21	1530.14	34.84	4.15×10^6
Ep ₇₀ Ca ₃₀	70	106.08	149.46	206.17	1715.25	48.24	2.38×10^8
Ep ₇₅ Ca ₂₅	75	128.67	156.13	208.98	2071.25	60.74	8.53×10^9
Ep ₈₀ Ca ₂₀	80	135.91	161.26	210.79	2184.52	64.33	2.11×10^{10}

T_o is the temperature of onset of exotherm; T_p is the temperature of peak; T_f is the temperature of completion of exotherm; ΔH is the heat of exotherm; E is the activation energy; Z is the preexponential factor.

blend Ep₅₀Ca₅₀, less DGEBA is polymerized and less heat is generated. The extent of crosslinking increases drastically above 70 wt % DGEBA content in the reactive blends.

By using the Ozawa,^{11,12} Prime,¹³ and Peyser and Bascon¹⁴ method and plotting $1000/T_p$ versus $\log \beta$ (Fig. 2), the values of activation energy (E) of curing reaction calculated for reactive blends Ep₅₀Ca₅₀, Ep₇₀Ca₃₀, Ep₇₅Ca₂₅, and Ep₈₀Ca₂₀ are given in Table II. By using the resulting E from the above method, plotting $(2 \log T_p - E/RT_p)$ versus $\log \beta$ (Fig. 3), the values of the preexponential factor of various reactive blends can be obtained and are also listed in Table II. The activation energy increases considerably from 34.84 to 48.24 K J mol⁻¹ as the DGEBA content increases from

50 to 70 wt %. When the DGEBA content increases from 70 to 75 wt % in the reactive blends, the activation energy increases drastically from 48.24 to 60.74 K J mol⁻¹. On increasing the DGEBA content from 75 to 80 wt %, it was found that activation energy increases marginally from 60.74 to 64.33 K J mol⁻¹.

On increasing the DGEBA content from 50 to 80 wt %, the preexponential factor of various reactive blends increases from 4.15×10^6 to $2.11 \times 10^{10} \text{ min}^{-1}$ in a similar trend, as followed by activation energy. These results are consistent with the variation of T_p against

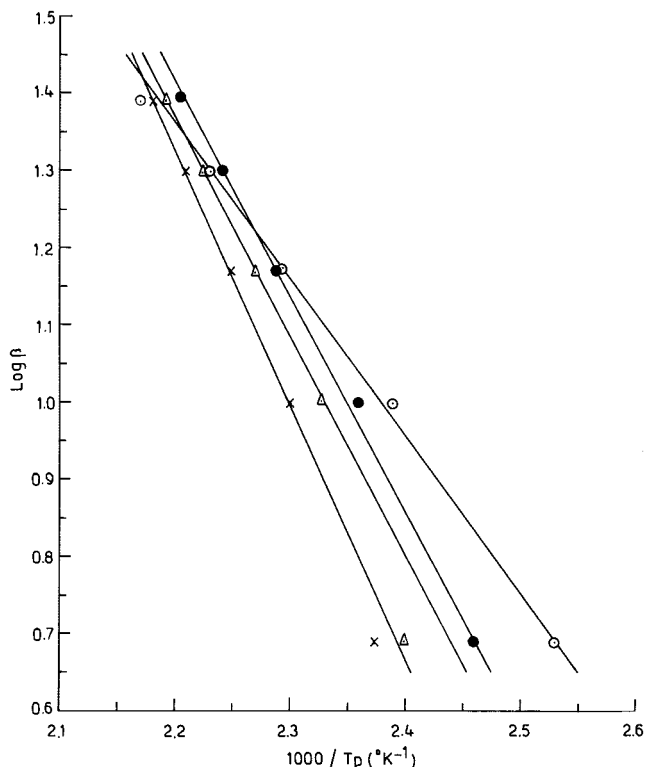


Figure 2 Plot for activation energy of cure reaction of reactive blends (○) Ep₅₀Ca₅₀; (●) Ep₇₀Ca₃₀; (△) Ep₇₅Ca₂₅; (+) Ep₈₀Ca₂₀.

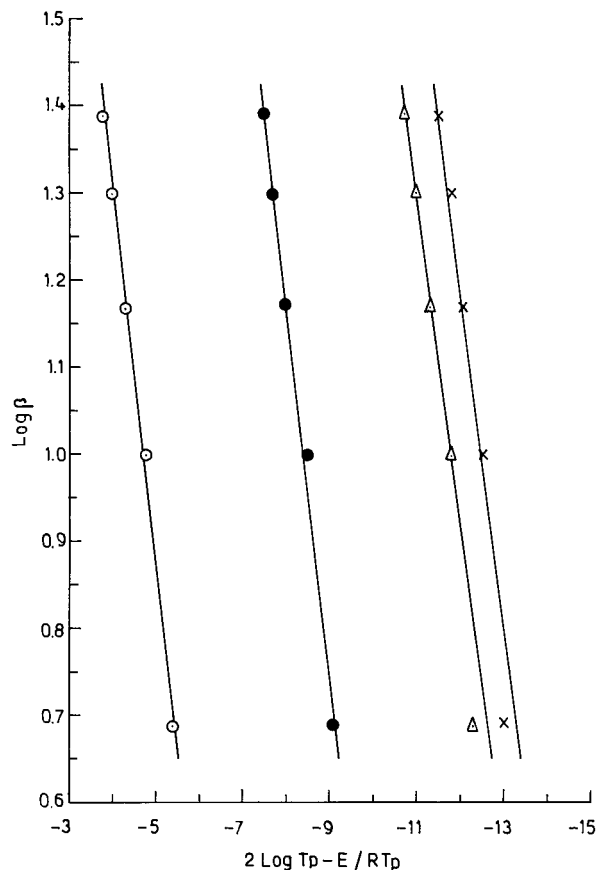


Figure 3 Plot for preexponential factor of cure reaction of reactive blends (○) Ep₅₀Ca₅₀; (●) Ep₇₀Ca₃₀; (△) Ep₇₅Ca₂₅; (+) Ep₈₀Ca₂₀.

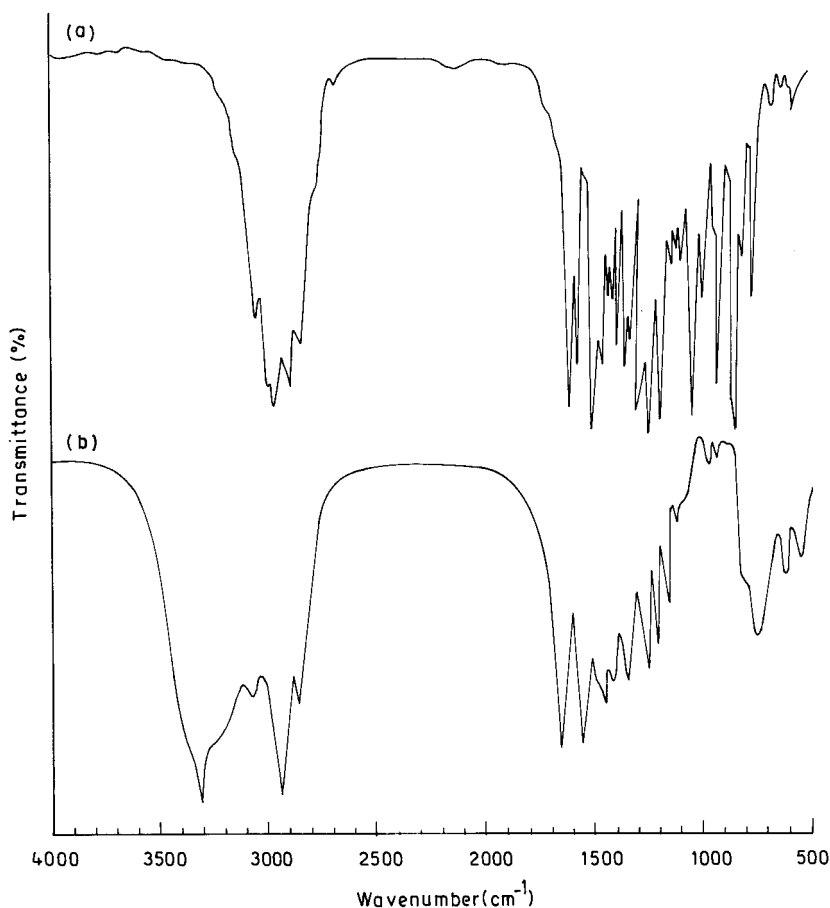


Figure 4 FTIR spectrum of (a) Diglycidyl ether of bisphenol-A (DGEBA, $n = 0$), (b) polycaprolactam.

a considerably smaller peak of epoxy ring at 910.64 cm^{-1} , indicating that a major portion of the epoxy ring was consumed in the reaction, which is in support of Scheme 1 [eq. (1)]. The FTIR spectrum of the reactive blend after complete solvent extraction is shown in Figure 5(b). This figure shows that after solvent extraction the peak of oxirane ring (910.64 cm^{-1}) and N—H group (3304.24 cm^{-1}) has disappeared completely. This shows that these peaks are found in the blend $\text{Ep}_{70}\text{Ca}_{30}$ because of the presence of unreacted DGEBA and polycaprolactam in the blend. This is also confirmed by FTIR spectrum of residue obtained on drying the solvents after solvent extractions [Fig. 6(a, b)].

FTIR spectrum of residue obtained on drying the solvent after extraction of acetone [Fig. 6(a)] shows the same type of peaks as observed in FTIR spectrum of neat DGEBA resin [Fig. 4(a)], except certain minor variations in the intensities of band and sharpness of the peaks because of the impurities, which proves that the unreacted DGEBA has been removed by acetone. The FTIR spectrum of residue obtained on drying the solvent after extraction (acetone extracted reactive blend) by formic acid [Fig. 6(b)] exhibits the same type of peaks as observed in FTIR spectrum of polycapro-

lactam [Fig. 4(b)] except certain minor variations in the intensities of band and sharpness of the peaks due to the impurities, which proves that the unreacted ϵ -caprolactam and polycaprolactam homopolymer were removed by solvent extraction of reactive blend with formic acid.

The main reaction is a nucleophilic attack on the oxirane ring by the amide nitrogen of polycaprolactam, which produces a hydroxyl group [Scheme 1, eq. (1)]; this reaction is a typical curing reaction of epoxy resin with an amine hardener.¹⁹ In addition, a new peak at 1720.4 cm^{-1} appeared after curing, which is present in both spectra [Fig. 5(a, b)], indicating another type of reaction occurred during the curing. The peak of 1720.4 cm^{-1} is the absorption of carbonyl ($\text{C}=\text{O}$) of the ester group. This suggests that the second type of reaction occurs through eq. (2) [Scheme 1, eq. (2)]. The resulted secondary amine group can react further with the epoxide group. Reactive blends contained linkages with chemical bonds in amide group and epoxy ring because of the presence of basic functional groups belonging to DGEBA and polycaprolactam, as confirmed by FTIR. The FTIR spectrum of other reactive blends such as $\text{Ep}_{50}\text{Ca}_{50}$, $\text{Ep}_{75}\text{Ca}_{25}$, and $\text{Ep}_{80}\text{Ca}_{20}$ showed the same types of peaks as observed

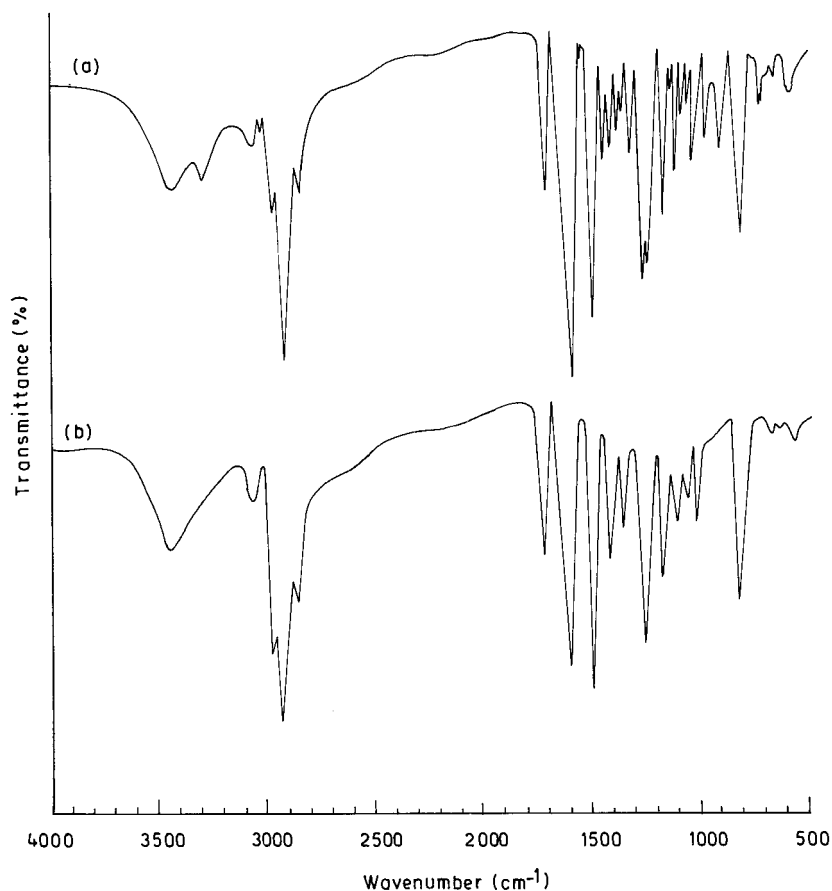


Figure 5 FTIR spectrum of reactive blend of DGEBA and polycaprolactam ($\text{Ep}_{70}\text{Ca}_{30}$) (a) before solvent extraction; (b) after complete solvent extraction.

in reactive blend $\text{Ep}_{70}\text{Ca}_{30}$, except certain minor variations in the intensities of bands and sharpness of the peaks. These minor variations in peaks are due to the difference in stoichiometric ratios of ϵ -caprolactam and DGEBA in the reactive blends.

Scanning electron microscopy

The fracture morphology of various DGEBA/polycaprolactam reactive blends after cure revealed the mixing and phase-separation behavior of the reactive blends. Considering the various DGEBA/polycaprolactam reactive blends with permanent entanglements between the DGEBA and polycaprolactam, inducing strong molecular interactions is susceptible to bring significant crosslinking enhancement with increasing DGEBA content. Scanning electron micrographs of fracture surfaces of the reactive blends at the same magnification are shown in Figure 7. The black space visible in these micrographs represents the DGEBA polymer and white space represents the polycaprolactam polymer. Various DGEBA/polycaprolactam reactive blends show multiphase system.

The micrograph of reactive blend $\text{Ep}_{50}\text{Ca}_{50}$ [Fig. 7(a)] shows poor mixing of two phases and minor

black spots of unreacted DGEBA and white spots of the unreacted polycaprolactam. The increase of the DGEBA content in the reactive blends from 50 to 80 wt % increases the diffusion of DGEBA into the polycaprolactam-rich phase and increases the mixing of two phases, as shown in the micrographs of reactive blends $\text{Ep}_{50}\text{Ca}_{50}$, $\text{Ep}_{70}\text{Ca}_{30}$, $\text{Ep}_{75}\text{Ca}_{25}$, and $\text{Ep}_{80}\text{Ca}_{20}$ [Fig. 7(a–d)], which increases the crosslink density of the reactive blends, as already proven by DSC studies. The micrographs of the reactive blends with 50–80 wt % DGEBA content shows that the increase in the DGEBA content in the reactive blends reduces the extent of unreacted DGEBA and polycaprolactam polymers as are shown by reduction in minor black and white spots in the micrographs on increasing the DGEBA content from 50 to 80 wt %. The presence of unreacted DGEBA and polycaprolactam is already proven by FTIR studies. Thus, the micrograph of reactive blend $\text{Ep}_{80}\text{Ca}_{20}$ [Fig. 7(d)] shows better mixing of polycaprolactam with DGEBA similar to single-phase system as expected. The same type of morphology was seen earlier in the SEM micrograph of the fully miscible polyimide–epoxy system.⁸ The reduction in minor spots shows the poor extent of unreacted polymers.

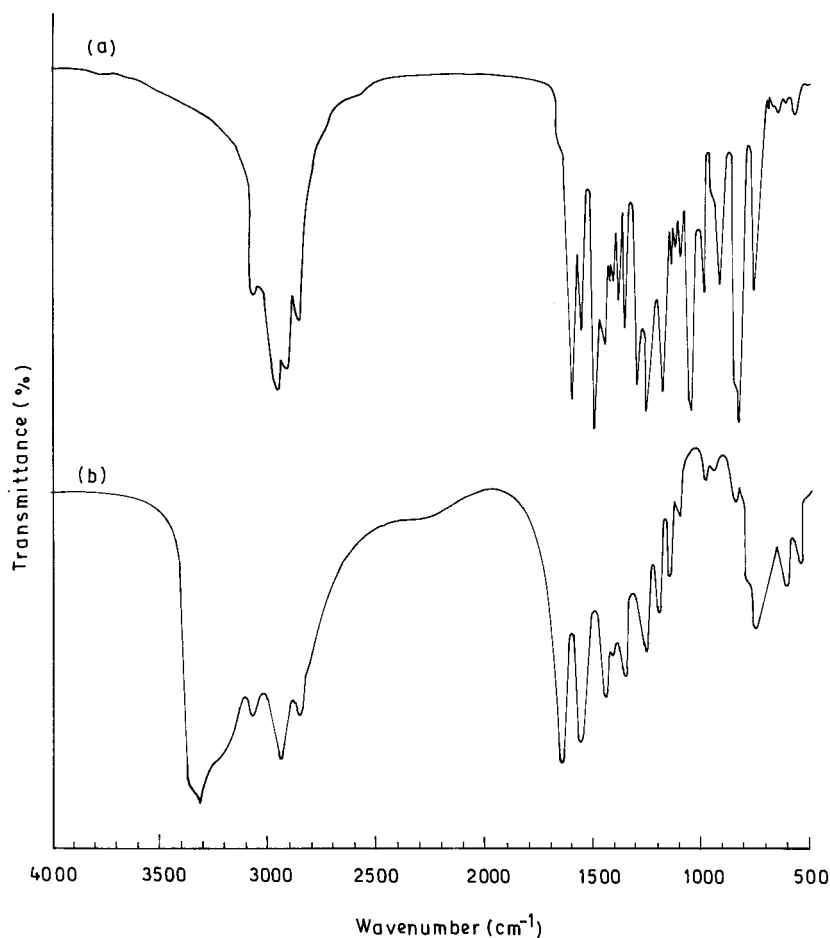


Figure 6 FTIR spectrum of residue obtained on drying the solvent (a) after extraction by acetone; (b) after extraction (acetone extracted reactive blend) by formic acid.

Thermal stability of DGEBA/polycaprolactam reactive blends

The initial degradation temperature generally represents the stability of the material. It is also recognized that the anhydrides are generally better curing agents than the amines. It was reported that the presence of the residual chlorine adversely affected the thermal stability, especially when an amine was used as a curing agent. Undoubtedly there are other variables, such as curing schedules, type of curing agent, and structure of epoxy resin, which can affect the thermal stability of epoxy resins.^{23–25} The initial degradation temperature is to be considered at 1% weight loss of DGEBA/polycaprolactam reactive blend after removal of unreacted polymers and impurities by solvent extractions.

Thermal stability of the DGEBA/polycaprolactam system is of great importance and is dependent in part on the chemical structure and bonds as well as the crosslink density of the system. Neiman et al.²⁶ were perhaps the first to attempt to relate the stability of epoxy resins to chemical structure. Thermal degradation behavior of the reactive blends under dynamic mode at a program heating rate of $20^{\circ}\text{C min}^{-1}$ in

nitrogen atmosphere and the plot of percentage weight loss versus temperature ($^{\circ}\text{C}$) were obtained by using a thermogravimetric analyzer (TA 2000) and are shown in Figure 8.

On examining the thermograms (Fig. 8), it is observed that one-step reaction mechanism is operative during the degradation of various DGEBA/polycaprolactam reactive blends. It is apparent that the shape of the thermograms is not linear throughout the degradation reaction in all cases. It was seen that there are some points in the thermogram at which the degradation reaction changes its mechanism. In the initial stages (1–5% weight loss), the rate of weight loss was comparatively very slow from initial degradation temperature of 197, 231, 248, and 255°C to temperatures at 5% weight loss 353, 370, 38, and 384°C for the reactive blends $\text{Ep}_{50}\text{Ca}_{50}$, $\text{Ep}_{70}\text{Ca}_{30}$, $\text{Ep}_{75}\text{Ca}_{25}$, and $\text{Ep}_{80}\text{Ca}_{20}$, respectively. Rate of weight loss (5–85%) was significant at higher temperatures, whereas later on after higher weight loss (85.1%), the rate of weight loss was again very slow up to final decomposition temperature of 529, 535, 546, and 549°C for the reactive blends $\text{Ep}_{50}\text{Ca}_{50}$, $\text{Ep}_{70}\text{Ca}_{30}$, $\text{Ep}_{75}\text{Ca}_{25}$, and $\text{Ep}_{80}\text{Ca}_{20}$, respectively. This indicates that, in the initial stage of poly-

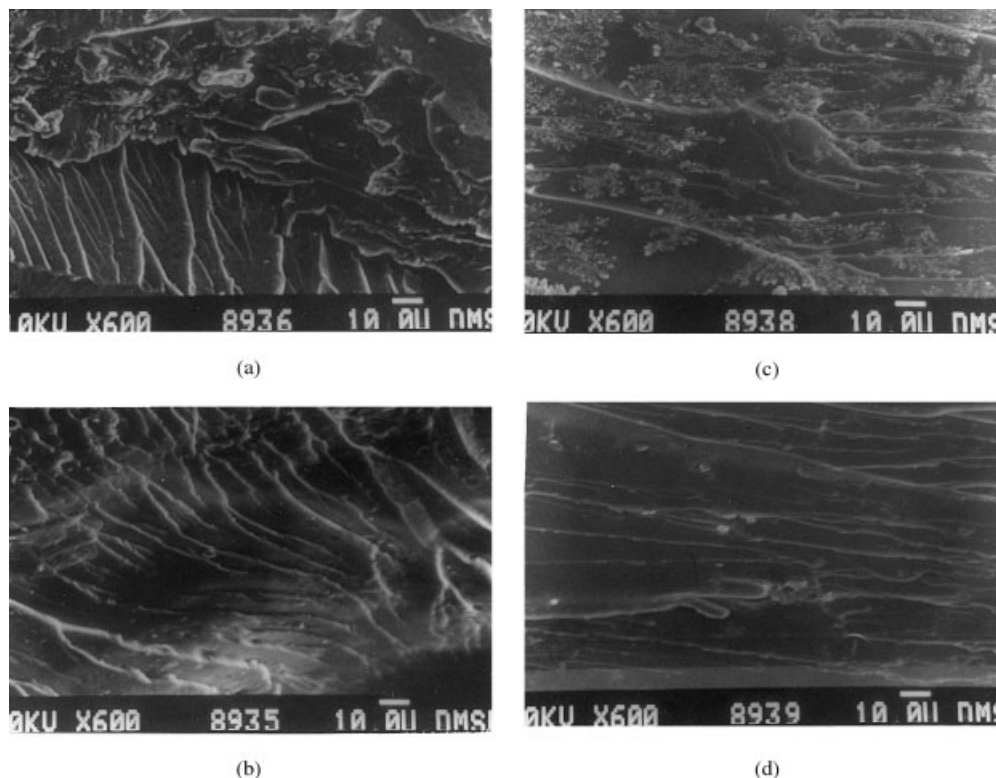


Figure 7 Scanning electron micrograph of DGEBA/polycaprolactam reactive blends (a) $\text{Ep}_{50}\text{Ca}_{50}$; (b) $\text{Ep}_{70}\text{Ca}_{30}$; (c) $\text{Ep}_{75}\text{Ca}_{25}$; (d) $\text{Ep}_{80}\text{Ca}_{20}$.

mer decomposition, the extent of crosslinking is greater than the extent of bond rupture. However, at the middle stage of decomposition, the trend is reversed and decomposition rate is high. In the last stage of decomposition, a similar trend was found to the initial stage.

The temperature of initial decomposition (T_i), the temperature of maximum decomposition (T_m), the

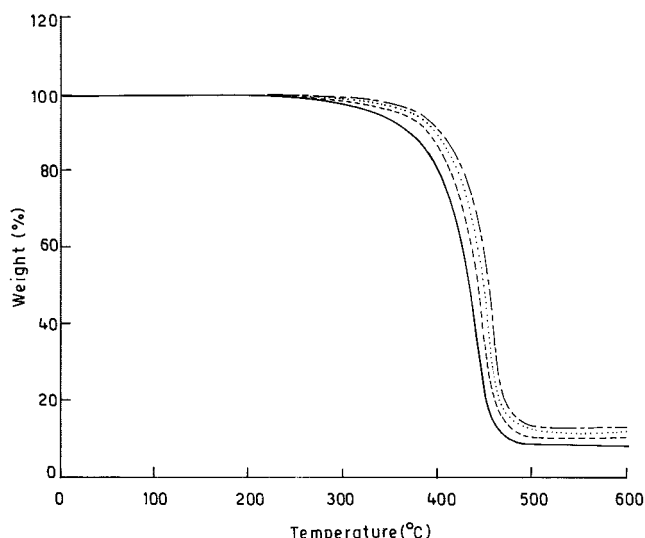


Figure 8 Thermal degradation by thermogravimetric analysis (TGA) in nitrogen atmosphere of reactive blends (—) $\text{Ep}_{50}\text{Ca}_{50}$; (---) $\text{Ep}_{70}\text{Ca}_{30}$; (···) $\text{Ep}_{75}\text{Ca}_{25}$; (- · - ·) $\text{Ep}_{80}\text{Ca}_{20}$.

temperature of completion of decomposition reaction (T_f), and the percentage char yield (Y_c) at 500°C were determined from the TGA curves and are given in Table III. Comparison of data for various reactive blends with increasing 50–80 wt % DGEBA content shows that reactive blends $\text{Ep}_{75}\text{Ca}_{25}$ and $\text{Ep}_{80}\text{Ca}_{20}$ above 70 wt % DGEBA content have better thermal stability than $\text{Ep}_{50}\text{Ca}_{50}$, and $\text{Ep}_{70}\text{Ca}_{30}$ with 50 and 70 wt % DGEBA content. This is due to high crosslink density of the reactive blends as proven by DSC studies, which restrict the mobility of chains. Initial thermal decomposition temperature of various reactive blends are shown in Figure 9, which indicates that initial decomposition temperature increases from 197 to 255°C with increasing DGEBA content from 50 to 80 wt % in the reactive blends. Drastic increases in initial decomposition temperature are observed above 70 wt % DGEBA content in the reactive blends. Initial thermal decomposition temperature of the reactive blends $\text{Ep}_{75}\text{Ca}_{25}$ and $\text{Ep}_{80}\text{Ca}_{20}$ (248°C and 255°C) was comparable to the epoxy cured with anhydride, which has been reported to vary from 240 to 250°C, with the evolution of predominantly carbon monoxide and methane.²³

Degradation kinetics of various DGEBA/polycaprolactam reactive blends

Thermogravimetric analysis is also used as a fast and exact method for determination of the kinetics of ther-

TABLE III
Decomposition Behavior of Various DGEBA/ Polycaprolactam Reactive Blends at a Heating Rate of 20°C min⁻¹

Blend	DGEBA content (wt %)	T_i (°C)	T_m (°C)	T_f (°C)	Y_c (%)	E (K J mol ⁻¹)	Z (min ⁻¹)
Ep ₅₀ Ca ₅₀	50	197	437	529	9.6	91.84	2.32×10^7
Ep ₇₀ Ca ₃₀	70	231	442	535	10.5	125.47	7.49×10^9
Ep ₇₅ Ca ₂₅	75	248	445	546	11.9	139.66	8.37×10^{10}
Ep ₈₀ Ca ₂₀	80	255	444	549	12.5	144.91	2.12×10^{11}

T_i is the Initial decomposition temperature; T_m is the Maximum decomposition temperature; T_f is the Final decomposition temperature; Y_c is the Char yield at 500°C; E is the Activation energy; Z is the Pre-exponential factor.

mal degradation of polymers. The statistical analysis of the TGA data in accordance with the Coats and Redfern equation, done by linear regression, provided the best fit value of n ,²⁷ where the n was taken as 0, 0.5, 0.67, 1.0, 1.5, and 2. Analysis was done by using the above order of reaction for reactive blends containing 50–80 wt % DGEBA content in the range of 5 to 85% weight loss of thermogram. The results revealed that degradation follows zero-order kinetics as best correlation coefficients were obtained for it. The reactive blends show zero order of reaction with correlation coefficient values of 0.9866, 0.9735, 0.9859, and 0.9821

for 50–80 wt % DGEBA content in the reactive blends. The values of correlation coefficients, close to unity, indicate near perfect fit. Plots of

$$\log_{10} \left(\frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} \right) \quad (8)$$

against $1000/T$ obtained from the data have been shown in Figure 10. From the slope of the respective plots and its intercept, the values of activation energy (E) and preexponential factor (Z) are calculated and summarized in Table III.

The kinetic parameters including activation energy and preexponential factor are the other major factors for determining the thermal stability of reactive blends. Table III shows that the activation energy increases considerably from 91.84 to 125.47 K J mol⁻¹ as the DGEBA content increases from 50 to 70 wt %.

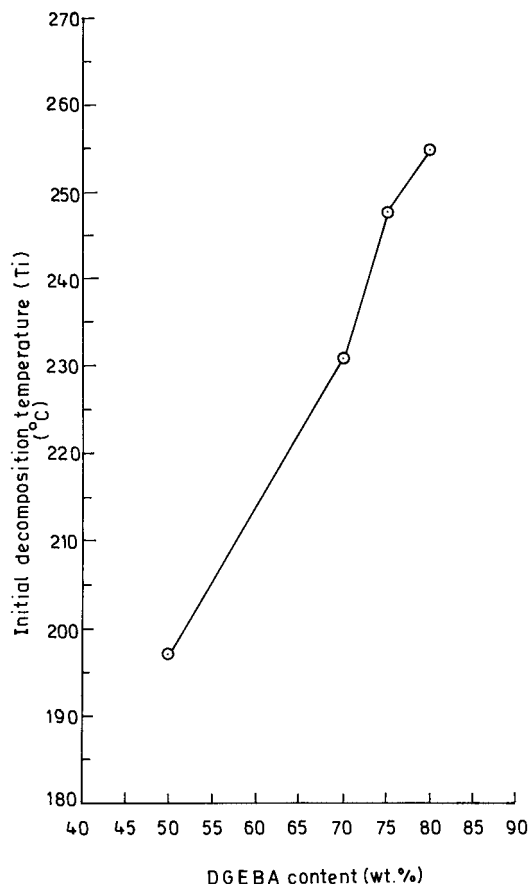


Figure 9 Variation of initial decomposition temperature at 1% weight loss with blend composition for DGEBA/polycaprolactam reactive blends.

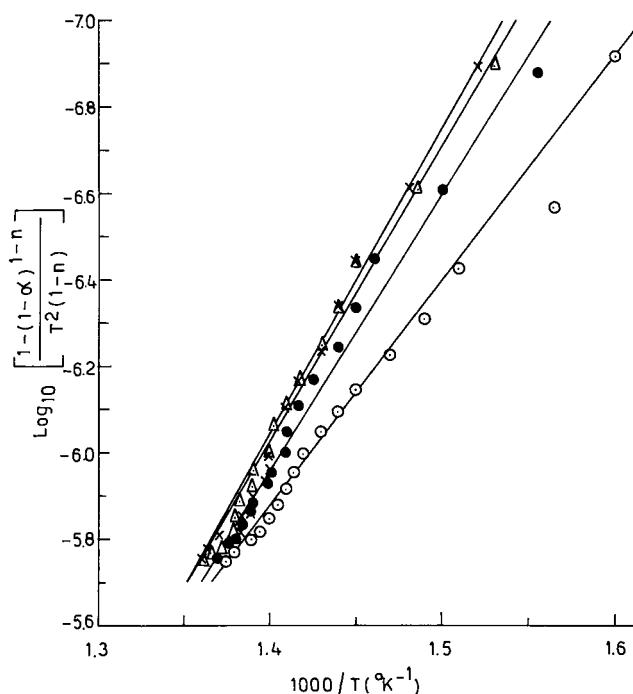


Figure 10 Plot for decomposition of reactive blends (○) Ep₅₀Ca₅₀; (△) Ep₇₀Ca₃₀; (Δ) Ep₇₅Ca₂₅; (+) Ep₈₀Ca₂₀.

When the DGEBA content increases from 70 to 75 wt %, in the reactive blends, the activation energy increases drastically from 125.47 to 139.66 K J mol⁻¹. On increasing the DGEBA content from 75 to 80 wt %, the activation energy increases marginally. As the DGEBA content was increased from 50 to 80 wt %, the preexponential factor of the various reactive blends increases from 2.32×10^7 to 2.12×10^{11} min⁻¹ in a similar trend, as followed by activation energy.

When the DGEBA content increases from 50 to 80 wt %, the activation energy and preexponential factor increases because of an increase in crosslink density, which causes chain stiffening and results in increased thermal stability. Thermal stability of the epoxy resin cured with aromatic polyamide²⁸ increases because of an increase in the crosslink density and the introduction of stiff aramid segment into the epoxy network. This is already proven by DSC studies that on increasing the DGEBA content in the reactive blends, the crosslink density of reactive blends increases. The activation energies of the reactive blends Ep₇₅Ca₂₅ and Ep₈₀Ca₂₀ (139.66 and 144.91 K J mol⁻¹, respectively) are comparable to the epoxy cured with anhydride,²³ which has been reported in literature (34 K Cal mol⁻¹ or 142.36 K J mol⁻¹) and have better thermal stability than the diglycidyl ether of bisphenol-A with epoxy aniline cured by triethylenetetramine system²⁹ (DGEBA/EA/TETA) (96.46 K J mol⁻¹).

CONCLUSION

The following conclusions may be drawn from the work carried out in the present investigation.

1. The value of heat of reaction (ΔH), activation energy (E), and preexponential factor (Z) increased with increasing DGEBA content from 50 to 80 wt % in the reactive blends due to the increase in extent of crosslinking and crosslink density.

2. Reactive blends contained linkage with chemical bonds in the amide group and epoxy ring due to the presence of basic functional groups belonging to DGEBA and polycaprolactam, as confirmed by FTIR studies. DGEBA is crosslinked by the polycaprolactam through the reaction of oxirane group with amide nitrogen.

3. The morphological study of various DGEBA/polycaprolactam reactive blends show multiphase system. On increasing the DGEBA content in the reactive blends, the mixing of polycaprolactam with DGEBA increased. The micrograph of reactive blend

Ep₈₀Ca₂₀ is similar to a single-phase system due to better mixing of polycaprolactam with DGEBA.

4. Thermal stability studies revealed that the initial degradation temperature (T_i), activation energy (E), and preexponential factor (Z) increased with an increase in the DGEBA content from 50 to 80 wt % in the reactive blends.

The authors acknowledge the support of Dr. K. P. Singh, Director, H.B.T.I., Kanpur, and Dr. G. N. Mathur, Director, DMSRDE, Kanpur, toward this work. We are also thankful to Dr. A. K. Srivastava, H.B.T.I., for valuable discussions in FTIR analysis.

References

1. Yamanaka, K.; Inoue, T. *Polymer* 1989, 30, 662.
2. Bucknall, C. B.; Gilbert, A. H. *Polymer* 1989, 30, 213.
3. Bucknall, C. B.; Partridge, I. K. *Polymer* 1983, 24, 639.
4. Kim, S.; Kim, J.; Lim, S. H.; Jo, W. H.; Choe, C. R. *J Appl Polym Sci* 1999, 72, 1055.
5. Carfagna, C.; Nicolais, L.; Admendola, E.; Carfagna, C., Jr.; Filipov, A. G. *J Appl Polym Sci* 1992, 44, 1465.
6. Hedrick, J. L.; Yilgor, I.; Jurek, M.; Hedrick, J. C.; Wilkes, G. L.; McGrath, J. E. *Polymer* 1991, 32, 2020.
7. McGrail, P. T.; Jenkins, S. D. *Polymer* 1993, 34, 677.
8. Pascal, T.; Bonneau, J. L.; Biolley, N.; Mercier, R.; Sillion, B. *Polym Adv Tech* 1995, 6, 219.
9. Jang, K.; Cho, W. J.; Ha, C. S. *Compos Sci Technol* 1999, 59, 995.
10. Gupta, A.; Singhal, R.; Nagpal, A. K. *J Appl Polym Sci* 2003, 89, 3237.
11. Ozawa, T. *Bull Chem Soc Jpn* 1965, 38, 1881.
12. Ozawa, T. *J Therm Anal* 1970, 2, 301.
13. Prime, R. B. *Polym Eng Sci* 1973, 13, 365.
14. Peyser, P.; Bascon, W. D. *Analyst Calorim* 1974, 3, 537.
15. Kissinger, H. E. *Anal Chem* 1957, 29, 1702.
16. Coats, A. W.; Redfern, J. P. *Nature* 1964, 201, 68.
17. Acitelli, M. A.; Prime, R. B.; Sacher, E. *Polymer* 1971, 12, 133.
18. Schneider, N. S.; Sprouse, J. E.; Hagman, I. F.; Gillham, J. K. *Polym Eng Sci* 1979, 19, 304.
19. Prime, R. B. in *Thermal Characterization of Polymeric Materials*; Turi, E., Ed.; Academic Press: London, 1981.
20. Zvetkov, V. L. *Polymer* 2001, 42, 6687.
21. Horie, K.; Hiura, H.; Sawada, M.; Mita, I.; Kambe, H. *J Polym Sci, Part A-1* 1970, 8, 1357.
22. Zhang, S.; Guo, Q. *Polymer* 1998, 39, 3451.
23. Conley R. T. *Thermal Stability of Polymers*; Marcel Dekker: New York, 1970; Vol. 1, p 512.
24. Delmonte, J. *Chem Eng Progr* 1962, 58, 51.
25. Belanger, W. J.; Schulte, S. A. *Mod Plast* 1959, 37, 154.
26. Neiman, M. B.; Golubenkova, L. I.; Kovarskaya, B. M.; Strizhkova, A. S.; Levantovskaya, I. I.; Akutin, M. S.; Moiseev, V. D. *Vysokomol Soedin* 1959, 1, 1531.
27. Raj, H.; Nigam, D.; Mathur, G. N. *J Propulsion Power* 1989, 5, 561.
28. Ochi, M.; Koyama, C.; Tanaka, S.; Matsuo, K. *Nippon Setchaku Gakkaishi* 2001, 37, 133 [in Japanese].
29. Mustata, F.; Bicu, I. *Polym Testing* 2001, 20, 533.