

Reactive Blends of Epoxy Resin (DGEBA) Crosslinked by Anionically Polymerized Polycaprolactam. II. Mechanical and Electrical Properties

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ABSTRACT: Various reactive blends of diglycidyl ether of bisphenol A (DGEBA)/polycaprolactam were synthesized by anionic polymerization at 140°C, conducted by sodium hydride catalyst, a strong base, along with *N*-acetyl caprolactam as a cocatalyst. The experiments were performed to study the effect of composition on the mechanical and electrical properties of the reactive blends, such as tensile properties, flexural properties, Izod impact strength, Rockwell hardness, and volume resistivity. It was observed that the DGEBA was crosslinked by the polycaprolactam through the rapid reaction of the oxirane group with amide nitrogen. The heat of reaction and heat-deflection temperature of the reactive blends increased with increasing DGEBA content from 50 to 80 wt %, and increased dramatically above 70 wt % DGEBA content. The mechanical and electrical properties

of the reactive blends increased with increasing DGEBA content from 50 to 80 wt %. Substantial increases in these properties were observed above 70 wt % DGEBA content in the reactive blends. SEM studies revealed that the reactive blends show a multiphase system with an increase in the DGEBA content from 50 to 80 wt % as the mixing of the two phases increased. The reactive blend Ep₈₀Ca₂₀, with 80 wt % DGEBA content, resembles a single-phase system because of better mixing of the two phases; as a result, this reactive blend showed the highest mechanical and electrical properties. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 537–549, 2005

Key words: epoxy resin; polyamide; mechanical properties; morphology; blends

INTRODUCTION

The use of epoxy resins as high-performance structural materials has recently been increased, particularly in applications for high-performance adhesives and advanced composite matrix materials in the aerospace and electronic industries. The combined mechanical properties of high modulus and high strength at relatively high temperatures make the material suitable for such applications. However, the major drawbacks of epoxy resin are brittleness and high moisture absorption. There have been many studies on the modification of epoxy resin by the incorporation of a second component.

One of the methods used to improve the toughness is based on attaining a dispersion consisting of a particulate second phase in the thermosetting polymer. According to this procedure, a filler can consist of rigid particles (such as alumina, silica, or glass spheres), or it can be made by reactive rubbers, or by both rigid and rubbery materials. The inclusion of a second phase of dispersed rubbery particles in a ther-

moset polymer has proven to be the most effective method for toughening.^{1–4} However, the presence of the rubbery phase usually results in lowering the effective properties, such as glass-transition temperature (T_g) and elastic modulus, which are crucial performance factors under hot/wet conditions.

Another approach for the toughening of thermosets is to incorporate tough, high-performance thermoplastics into brittle thermosets, such as epoxides, cyanates, bismaleimides, and polyamides. This approach continues to receive increasing interest.^{5–10} The important features of thermoplastics include the chemical constitution, T_g , molecular weight, mechanical and thermal properties, and the presence of chemically reactive groups at the chain ends or in the polymer backbone or pendant to the backbone. The results look very promising. In fact the presence of small amounts of some thermoplastics can, in some cases, increase the fracture toughness without substantially sacrificing T_g and modulus of the resulting blend.

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 were studied by using Fourier transform infrared spectroscopy and a solvent-extraction process, respectively.¹¹ The thermal properties were stud-

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

DGEBA (epoxy resin) : caprolactam	Blend designation	DGEBA (g)	Caprolactam (g)	Sodium hydride (g)	<i>N</i> -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

ied by using differential scanning calorimetry and thermogravimetric analysis.¹²

The object of the present work was to investigate the effect of the DGEBA (epoxy resin) on the mechanical and electrical properties of reactive blends of DGEBA and polycaprolactam. For this work reactive blends of DGEBA and polycaprolactam were synthesized by carrying out anionic polymerization of caprolactam at 140°C. The anionic polymerization had the advantage of providing highly reactive living ends of the growing polymer chains, and requiring low temperature for reaction, whereas hydrolytic polymerization of caprolactam required a polymerization temperature around 250°C, which was not suitable for uncured DGEBA. To evaluate the performance and potential application of these blends, the different properties of DGEBA/polycaprolactam were studied by using various testing methods, such as heat-deflection temperature, tensile properties, flexural properties, Izod impact strength, Rockwell hardness, and volume resistivity. The fracture morphology of various DGEBA/polycaprolactam reactive blends after curing was carried out to investigate the mixing and phase-separation behavior of the reactive blends.

EXPERIMENTAL

Materials

The epoxy resin used in this study was a general-purpose unmodified PG-100 DGEBA (diglycidyl ether of bisphenol-A; M/s Parikh Resins and Polymers Ltd., Kanpur, U.P., India), with an epoxide equivalent weight of 185 and viscosity of 11,400 CPS. Caprolactam and sodium hydride (LR grade) were procured from M/s Spectrochem Pvt. Ltd. (Mumbai, Maharashtra, India). *N*-Acetyl caprolactam was supplied by Fluka Chemie (Buchs, Switzerland).

Synthesis of reactive blends

Reactive blends of DGEBA and polycaprolactam were prepared by an anionic polymerization technique. Table I provides details of the synthesis of reactive blends of 50 : 50, 70 : 30, 75 : 25, and 80 : 20 DGEBA : caprolactam ratio, which are designated by Ep₅₀Ca₅₀,

Ep₇₀Ca₃₀, Ep₇₅Ca₂₅, and Ep₈₀Ca₂₀, respectively. Because monomer caprolactam is a highly hygroscopic substance it was vacuum dried at room temperature for 48 h in a desiccator containing anhydrous calcium chloride. The dried caprolactam was charged to a three-neck round-bottom flask to which sodium hydride was added. The lactam was melted in nitrogen atmosphere at 69–70°C to allow the sodium hydride to react. After the hydrogen evolution ceased, *N*-acetyl caprolactam was added and thoroughly mixed. DGEBA was added to the flask just after adding *N*-acetyl caprolactam and mixed properly (stage 1). The reaction was carried out at 140°C with thorough mixing until the products were solidified. The samples were postcured in an oven set at 130–140°C for 5 h.

Casting of specimen

To cast a suitable specimen, the reaction mixture (stage 1) was poured into a specially designed mold. The mold consisted of two mild steel base plates and one polytetrafluoroethylene (PTFE) middle plate, which were tightened by screws. The middle plate had the shape of a rectangular bar (dimensions are given in mm as length × width × thickness: 127 × 12.7 × 3) for heat-deflection temperature; a dumbbell shape (216 × 12.7 × 3) for tensile tests; a rectangular bar (80 × 25.4 × 3) for flexural tests; a rectangular bar (63.5 × 12.7 × 3) for Izod impact tests (a notch was cut on the narrow face of the specimen); disks (25.4 mm diameter and 3 mm thickness) for Rockwell hardness; and a disk (90 mm diameter and 3 mm thickness) for volume resistivity. The mold was kept in an oven set at 140°C for curing. Samples were released from the mold and postcured for 5 h at 130–140°C. After postcuring, samples were stored in a desiccator for evaluation of various properties.

Characterizations

Solvent extraction

Several solvent-extraction techniques^{13–15} have been reported to give successful separation of the blended components of immiscible polymer blends. To isolate and identify the formed DGEBA/polycaprolactam re-

active blends solvent extractions were carried out. The unreacted DGEBA was removed by agitating crosslinked polymer in powder form in acetone for 24 h at room temperature. The solid polymer was dried in oven after filtration at 60°C. The extraction process was repeated five times. The unreacted cap-

rolactam or polycaprolactam homopolymer was removed by agitating the above solid polymer in formic acid for 24 h at room temperature. After filtration the solid polymer was dried in oven at 105°C. The extent of cure of the reactive blends was determined by use of the following equation:

$$\text{Extent of cure (\%)} = 100 - \text{percentage of unreacted polymers}$$

$$\text{Percentage of unreacted polymers} = \frac{\left(\text{Weight of sample after reaction} \right) - \left(\text{Weight of sample after final extraction} \right)}{\text{Weight of sample after reaction}} \times 100$$

Gel time

The gel time of reactive blends was determined at different temperatures using a digital gel timer (Techno Cambridge Ltd., Duxford, U.K.).

Fourier transform infrared spectroscopy

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

Differential scanning calorimetry

A Thermal Analyst 2000 apparatus (TA Instruments, New Castle, DE), equipped with 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 10°C/min from 40°C to the temperature at which the exothermic reactions were completed.

Heat-deflection temperature (HDT) studies

Heat-deflection temperature of reactive blends was determined by using Vicat softening point-*cum*-temperature of deflection under load (multistation) (M/s Prolific Engineers, D-91, Sector-2, Noida, India).

Study of mechanical properties

Tensile tests and flexural tests were conducted at ambient conditions using a universal testing machine (Star Testing Machine, Mumbai, India), according to ASTM D-638 and D-790, respectively, at a crosshead speed of 25 mm/min. The results were calculated from the stress-strain curves on an average of five specimens for each reactive blend composition. The Izod impact strength of a notched specimen having a 2-mm-deep triangular notch of 45° was measured by a CEAST® Resil 25 impact tester at ambient conditions,

according to ASTM D-256. Rockwell hardness of each reactive blend was measured on the R-scale in accordance to ASTM D-785, using a Rockwell hardness tester [RAS; M/s. Saroj Engg. Udyog (P) Ltd., Maharashtra, India]. Results of Izod impact strength and Rockwell hardness are expressed as means \pm SD for five determinations.

Study of electrical property

Volume resistivity was measured according to ASTM D-257, on a Model SM 8220 electrometer (TOA Electronics Ltd., Khome, Takadoanobaba, Tokyo, Japan) at room temperature (25 \pm 2°C).

Morphological observations

Scanning electron micrographs were taken on a model 35 CF scanning electron microscope (JEOL, Tokyo, Japan). The samples were cryogenically fractured in liquid nitrogen and scanned to suitable magnification to obtain appropriate images of the fracture surfaces 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.

RESULTS AND DISCUSSION

Various reactive blends, Ep₅₀Ca₅₀, Ep₇₀Ca₃₀, Ep₇₅Ca₂₅, and Ep₈₀Ca₂₀, synthesized by using different ratios of caprolactam and DGEBA (Table I), varied widely from rubbery to hard crosslinked solids. Therefore it became important to study the different properties of reactive blends to obtain a blend having properties suitable for commercial applications. The extent of cure was determined by the solvent-extraction process by using solvents for unreacted DGEBA and caprolactam. Results of the solvent-extraction process indicate that the extent of cure for the reactive blends Ep₅₀Ca₅₀, Ep₇₀Ca₃₀, Ep₇₅Ca₂₅, and Ep₈₀Ca₂₀ was 76.99, 92.98, 97.05, and 98.20%, respectively. It is clear from these

TABLE II
Determination of Gel Time for Various DGEBA/Polycaprolactam Reactive Blends at Different Temperatures

Temperature (°C)	Gel time (s)			
	Ep ₅₀ Ca ₅₀	Ep ₇₀ Ca ₃₀	Ep ₇₅ Ca ₂₅	Ep ₈₀ Ca ₂₀
130	72	88	179	195
140	62	80	150	163
150	55	71	125	145
160	41	63	103	121
170	30	51	73	99

results that the values of reactive blends Ep₇₅Ca₂₅ and Ep₈₀Ca₂₀ are very close and can give reactive blends of practical utility.

Gel time

The important observation during synthesis of reactive blends was the extremely fast reaction, which completed in just a few minutes, depending on the blend composition. The gel time of reactive blends Ep₅₀Ca₅₀, Ep₇₀Ca₃₀, Ep₇₅Ca₂₅, and Ep₈₀Ca₂₀ was measured at temperatures ranging from 130 to 170°C (Table II). It is clear from Table II that by increasing the DGEBA content from 50 to 80 wt %, the gel time increased considerably at constant temperature. Gel times for reactive blends Ep₅₀Ca₅₀ and Ep₇₀Ca₃₀ with 50 and 70 wt % DGEBA content, respectively, were considerably less compared to those for reactive blends Ep₇₅Ca₂₅ and Ep₈₀Ca₂₀ with 75 and 80 wt % DGEBA content, respectively. These facts were supported by the solvent-extraction results, as explained earlier, that the reactive blends prepared with lower DGEBA ratios were not properly crosslinked and the reaction was not complete. Reactive blends Ep₇₅Ca₂₅ and Ep₈₀Ca₂₀ had approximately equal gel time, which reveals that reaction was complete in both compositions.

The results indicate that by increasing the temperature from 130 to 170°C, the gel time of the reaction mixture was decreased by half, as shown in Figure 1. The reactive blends Ep₇₅Ca₂₅ and Ep₈₀Ca₂₀ have a gel time approximately between 2 and 4 min, and thus these blends have potential application in reaction injection molding (RIM). Nylon 6 is also processed on rotational molding and RIM because anionic polymerization is carried out at considerably reduced temperatures and at rapid rates.

Speculative mechanism

The mechanism of the anionic polymerization of caprolactam is shown in Scheme 1(a).¹¹ In this case, the attacking anionic species is the caprolactam an-

ion (I) formed by the reaction of sodium hydride, caprolactam, and *N*-acetyl caprolactam. The anion attacks a caprolactam molecule and extracts a proton, generating a new caprolactam anion (II). This new anion opens up the ring in the dimer (III) formed between sodium caprolactam and *N*-acetyl caprolactam and becomes attached, forming a trimer that is an anion (IV). The anion on the trimer now carries on the attack on a fresh caprolactam molecule and extracts a proton, generating a new monomeric anion. Propagation of the polymer chain continues by repeated and successive opening of the activated rings by the monomeric anion, which in turn is followed by the proton activation. Two types of curing reactions occur during the curing of polycaprolactam with DGEBA, as shown in Scheme 1(b). The first type of reaction [eq. (1) in Scheme 1(b)] is a nucleophilic attack on the oxirane ring by the amide nitrogen of polycaprolactam, which is expected to be the dominant reaction, and another type of reaction also occurs during curing [eq. (2) in Scheme 1(b)].

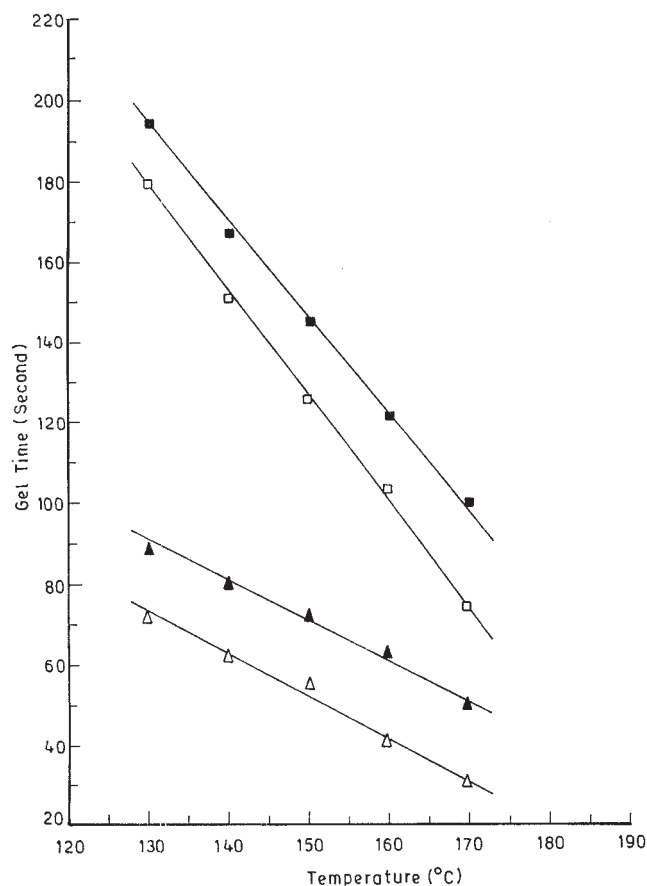
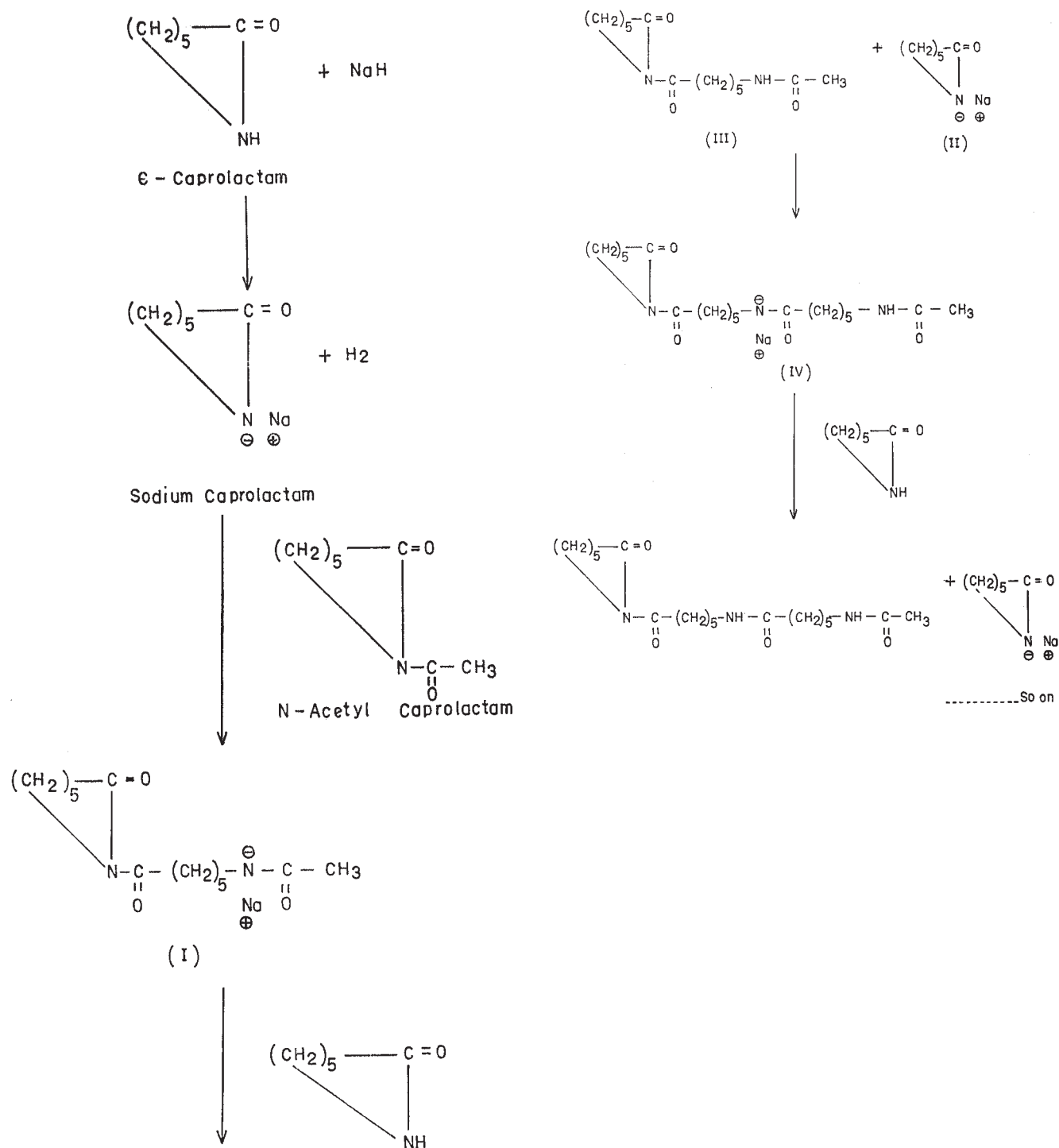


Figure 1 Plot of the gel time at different temperatures for various DGEBA/polycaprolactam reactive blends: (Δ) Ep₅₀Ca₅₀; (▲) Ep₇₀Ca₃₀; (□) Ep₇₅Ca₂₅; (■) Ep₈₀Ca₂₀.

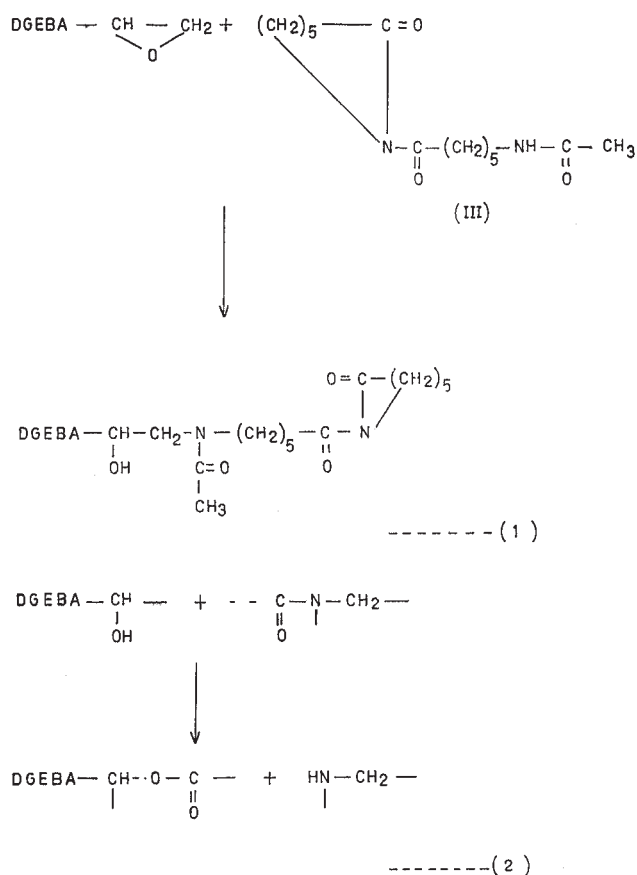


Scheme 1 Reactions of DGEBA and polycaprolactam during the synthesis of reactive blend (a) anionic polymerization of caprolactam and (b) mechanism of the cure reactions of polycaprolactam with DGEBA.

FTIR studies

The curing reaction of polycaprolactam with DGEBA can result in significant changes of the chemical structure of the molecule and this is reflected in the IR spectrum of the reactive blend. The FTIR spectrum of the reactive blend Ep₈₀Ca₂₀ [Fig. 2(b)] exhibits a peak at 3478.6 cm⁻¹, attributed to the stretching vibration of the O—H group. 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)] and this reaction is a typical curing reaction of epoxy resin with an amine hardener.¹⁶ The FTIR spectrum of DGEBA shows the peak of the oxirane ring at 910.64 cm⁻¹ [Fig. 2(a)], which disappears completely after curing [Fig. 2(b)].



Scheme 1 (Continued from the previous page)

In addition a new peak at 1724.8 cm^{-1} appeared after curing, which was presented in this spectrum, indicating that another type of reaction occurred during the curing. The peak at 1724.8 cm^{-1} is attributed to the absorption of carbonyl ($\text{C}=\text{O}$) of the ester group. This suggests that the second type of reaction occurs through eq. (2). The resulting secondary amine group can react further with the epoxide group. Reactive blends contained linkages with chemical bonds in the amide group and the epoxy ring attributed to the presence of basic functional groups belonging to DGEBA and polycaprolactam were confirmed by FTIR.

DSC studies

Typical dynamic DSC scans at $10^\circ\text{C}/\text{min}$ heating rate and nitrogen atmosphere for the curing of reaction mixture (stage 1) of various reactive blends ($\text{Ep}_{50}\text{Ca}_{50}$, $\text{Ep}_{70}\text{Ca}_{30}$, $\text{Ep}_{75}\text{Ca}_{25}$, and $\text{Ep}_{80}\text{Ca}_{20}$) are shown in Figure 3. From these DSC scans, the onset temperature of curing (T_0), the exothermic peak position (T_p), and final temperature of curing (T_f) were noted and are summarized in Table III. It was observed that T_0 and T_p increase with increasing 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. T_0 and T_p values for the reactive blend $\text{Ep}_{50}\text{Ca}_{50}$ were lower than those for reactive blends $\text{Ep}_{70}\text{Ca}_{30}$, $\text{Ep}_{75}\text{Ca}_{25}$, and $\text{Ep}_{80}\text{Ca}_{20}$. Thus the reactive blend $\text{Ep}_{50}\text{Ca}_{50}$ requires more time for the completion of reaction. The area under the exotherm between T_0 and T_f gives the value of heat of reaction (ΔH) and the values are summarized in Table III.

From Table III it is clear that the value of heat of reaction increases from 1530.14 to 1715.25 J g^{-1} concomitantly with the increase from 50 to 70 wt % DGEBA content in the reactive blends. When the DGEBA content increases from 70 to 75 wt %, the heat of reaction of reactive blends increases dramatically from 1715.25 to 2071.25 J g^{-1} . By increasing the DGEBA content from 75 to 80 wt %, the heat of reaction increases marginally, which proves that the crosslinking density 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 blend $\text{Ep}_{50}\text{Ca}_{50}$, less DGEBA is polymerized and less heat is generated. The crosslinking density increases drastically above 70 wt % DGEBA content in the reactive blends because more DGEBA is polymerized and a greater amount heat is generated.

HDT studies

Heat-deflection temperature tests are useful in determining the highest application temperature of materials and in assessing the degree of cure, plasticization, or copolymerization effects.¹⁷ The HDT results are given in Table IV, which shows that the heat-deflection temperature increases from 63 to 90°C as the DGEBA content in the reactive blends increases from 50 to 70 wt %. By increasing the DGEBA content from 70 to 75 wt % in the reactive blends, the heat-deflection temperature increases dramatically from 90 to 108°C . As the DGEBA content increases from 75 to 80 wt %, the heat-deflection temperature increases marginally, which proves that the degree of cure increases as the DGEBA content increases from 50 to 80 wt % and increases substantially above 70 wt % DGEBA content in the reactive blends. Heat-deflection temperatures of all the reactive blends are greater than that of DGEBA cured with polyamide, which has been reported to vary from 40 to 60°C .¹⁸ All the reactive blends except $\text{Ep}_{50}\text{Ca}_{50}$ are comparable to DGEBA cured with aliphatic polyamine, which has been reported to vary from 80 to 120°C .¹⁸

Mechanical properties of DGEBA/polycaprolactam reactive blends

Mechanical properties were determined in tension, flexure, under impact loading, and hardness. All me-

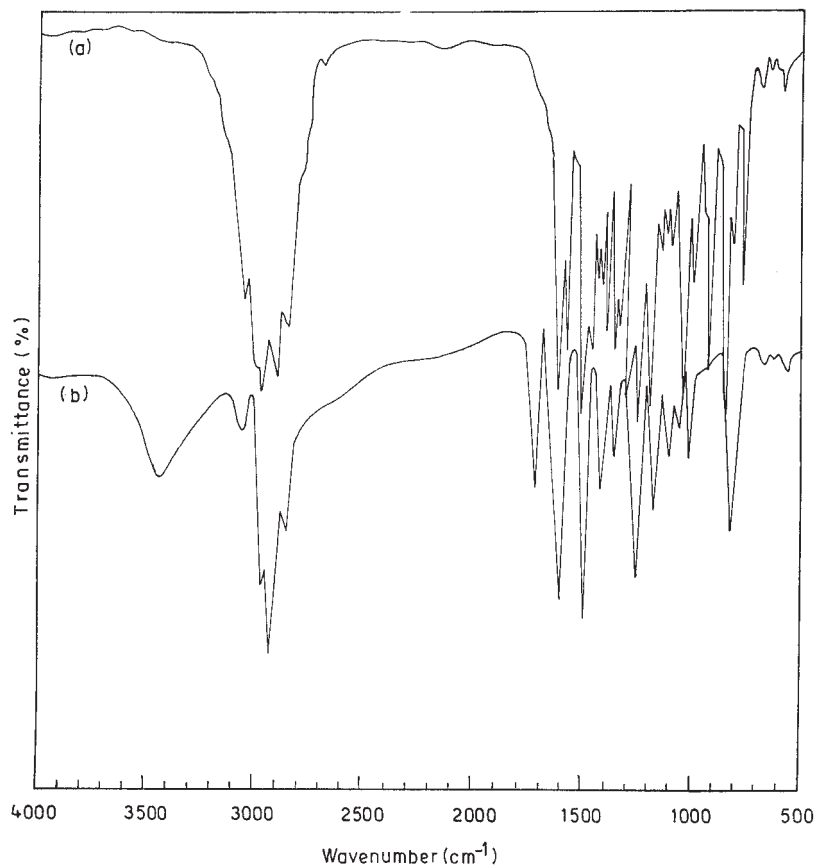


Figure 2 FTIR spectrum of (a) DGEBA (epoxy resin) and (b) reactive blend $Ep_{80}Ca_{20}$.

chanical testings were carried out at room temperature ($25 \pm 2^\circ C$).

Tensile properties

Tensile properties were evaluated by measuring stress at break and corresponding elongations as a function of blend composition. The results of various tensile tests of DGEBA/polycaprolactam reactive blends are given in Table V and shown in Figure 4, where tensile strength and tensile modulus are plotted as functions of reactive blend composition. The data points in this figure represent the mean values of several samples tested for each reactive blend composition.

Tensile strength, an important mechanical property, is the measure of the strength of the reactive blend. Figure 4 indicates that as the DGEBA content in the reactive blends increases from 50 to 70 wt %, the tensile strength of the reactive blend $Ep_{70}Ca_{30}$ increases considerably (9.84–31.36 MPa), approximately threefold that of the tensile strength value for the reactive blend $Ep_{50}Ca_{50}$. When the DGEBA content increases from 70 to 75 wt % in the reactive blends, the tensile strength increases dramatically from 31.36 to 43.04 MPa. A further increase in DGEBA content from 75 to 80 wt % shows a marginal increase in tensile

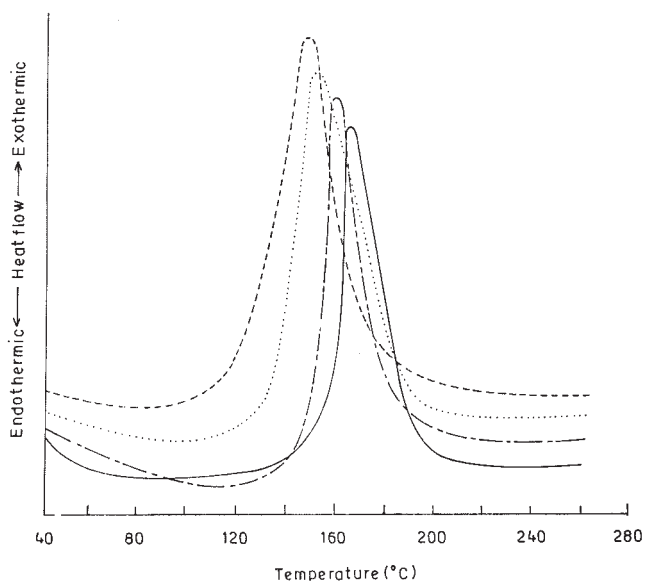


Figure 3 Dynamic DSC scans for the curing of DGEBA/polycaprolactam reactive blends at $10^\circ C/min$: (---) $Ep_{50}Ca_{50}$; (···) $Ep_{70}Ca_{30}$; (-·-) $Ep_{75}Ca_{25}$; (—) $Ep_{80}Ca_{20}$.

TABLE III
Curing Behavior of DGEBA/Polycaprolactam Blends at Heating Rate of 10°C/min

Blend	Temperature of onset of exotherm (T_0) (°C)	Temperature of peak (T_p) (°C)	Temperature of completion of exotherm (T_f) (°C)	Heat of reaction, ΔH (J g ⁻¹)
Ep ₅₀ Ca ₅₀	94.56	144.42	208.21	1530.14
Ep ₇₀ Ca ₃₀	106.08	149.46	206.17	1715.25
Ep ₇₅ Ca ₂₅	128.67	156.13	208.98	2071.25
Ep ₈₀ Ca ₂₀	135.91	161.26	210.79	2184.52

strength. Figure 4 also indicates that, as the DGEBA content increases from 50 to 70 wt %, the tensile modulus of the reactive blend Ep₇₀Ca₃₀ increases considerably from 695 to 1308 MPa, approximately double the tensile modulus value of the reactive blend Ep₅₀Ca₅₀. Tensile modulus increases sharply from 1308 to 1635 MPa, with the increase in DGEBA content from 70 to 75 wt % in the reactive blends. With a further increase in DGEBA content from 75 to 80 wt %, a marginal increase in tensile modulus was observed. Variation in elongation with increasing DGEBA content in the reactive blends is given in Table V, which indicates that as the DGEBA content increases from 50 to 80 wt % in the reactive blends, the elongation increases from 1.5 to 4.9% in a trend similar to that followed by the tensile modulus (Fig. 4).

Tensile strength increases on increasing the DGEBA content from 50 to 80 wt %. A substantial increase in tensile strength was observed above 70 wt % DGEBA content as a result of the higher crosslinking density of the reactive blends, as proved by DSC studies. The observed behavior can be analyzed as a combined effect of both components of the reactive blend. Tensile strength of DGEBA/polycaprolactam reactive blends increases with increasing DGEBA content because of the rigid nature of epoxy resin (DGEBA) as proved by Rockwell hardness, which increases with increasing DGEBA content. The reactive blends Ep₇₅Ca₂₅ and Ep₈₀Ca₂₀, above 70 wt % DGEBA content, have comparatively higher modulus and elongation than those of the reactive blends Ep₅₀Ca₅₀ and Ep₇₀Ca₃₀ with DGEBA content 50 and 70 wt %, which shows that these reactive blends can sustain higher stresses for long periods, attributed to the higher extent of cure, as proved by results of solvent extractions. The tensile strengths of the reactive blends Ep₇₅Ca₂₅ and Ep₈₀Ca₂₀ above 70 wt % DGEBA content (43.04 and 45.97 MPa) are comparable to that of the DGEBA cured with polyamide, which has been reported to vary from 35 to 55 MPa.¹⁸

Flexural properties

Flexural properties express the stiffness and bending strength of a material with respect to its ability to

withstand loads. Data for various DGEBA/polycaprolactam reactive blends are given in Table V and their variations of flexural strength and flexural modulus as a function of blend composition are shown in Figure 5, which indicates that as the DGEBA content in the reactive blends increases from 50 to 70 wt %, the flexural strength of the reactive blend Ep₇₀Ca₃₀ increases considerably (15.77 to 58.56 MPa), approximately fourfold that of the flexural strength value of the reactive blend Ep₅₀Ca₅₀. When the DGEBA content increases from 70 to 75 wt % in the reactive blends, the flexural strength increases drastically from 58.56 to 81.08 MPa. The flexural strength increases marginally on increasing the DGEBA content from 75 to 80 wt %.

Figure 5 also indicates that as the DGEBA content increases from 50 to 70 wt % in the reactive blends, the flexural modulus of the reactive blend Ep₇₀Ca₃₀ increases considerably (766 to 1423 MPa), which is approximately double the flexural modulus value of the reactive blend Ep₅₀Ca₅₀. By increasing the DGEBA content from 70 to 75 wt % in the reactive blends, a sharp increase in flexural modulus value, from 1423 to 1839 MPa, is observed. A marginal increase in flexural modulus value, from 1839 to 1928 MPa, was observed when the DGEBA content increased from 75 to 80 wt % in the reactive blends.

Flexural strength and flexural modulus of the reactive blends increase with increasing DGEBA content in the reactive blends. The drastic increases in flexural strength and flexural modulus above 70 wt % DGEBA content were attributed to the higher extent of cure in reactive blends, as proved by solvent-extraction results. The flexural strength and

TABLE IV
Heat-Deflection Temperature and Volume Resistivity of Various DGEBA/Polycaprolactam Reactive Blends

Blend	DGEBA content (wt %)	Heat-deflection temperature (°C)	Volume resistivity (ohm-cm)
Ep ₅₀ Ca ₅₀	50	63	2.09 × 10 ¹¹
Ep ₇₀ Ca ₃₀	70	90	7.38 × 10 ¹³
Ep ₇₅ Ca ₂₅	75	108	1.95 × 10 ¹⁵
Ep ₈₀ Ca ₂₀	80	114	5.57 × 10 ¹⁵

TABLE V
Mechanical Properties of Various DGEBA/Polycaprolactam Reactive Blends

Blend	DGEBA content (wt %)	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation (%)	Flexural strength (MPa)	Flexural modulus (MPa)	Izod impact strength; notched ($J m^{-1}$)	Rockwell hardness (R-scale)
Ep ₅₀ Ca ₅₀	50	9.84	695	1.5	15.77	766	67.79	25.8
Ep ₇₀ Ca ₃₀	70	31.36	1308	3.4	58.56	1423	216.94	79.9
Ep ₇₅ Ca ₂₅	75	43.04	1635	4.6	81.08	1839	305.07	114.2
Ep ₈₀ Ca ₂₀	80	45.97	1783	4.9	87.84	1928	338.96	119.5

flexural modulus of the reactive blend Ep₅₀Ca₅₀ with 50 wt % DGEBA content are extremely small because of the poor extent of cure and the presence of higher extent of unreacted polymers, as also proved by solvent-extraction results. The observed behavior can be analyzed as a combined effect of both components of the reactive blend. Flexural strength increases with increasing DGEBA content in the reactive blends. DGEBA content increases the rigidity and stiffness in the reactive blends, which reduces the bending properties of the system. However, flexural strength and flexural modulus increase with increasing DGEBA content. This can be attributed to the fact that as the DGEBA content (rigid molecules) decreases in the reactive blend, the extent of cure and hardness also decreases and increases the extent of unreacted polymers, as con-

firmed by solvent-extraction results and Rockwell hardness testing. Thus an increase in DGEBA content increases the extent of cure and hardness and decreases the extent of unreacted polymers by which flexural strength and flexural modulus values are increased. Flexural strengths of the reactive blends Ep₇₅Ca₂₅ and Ep₈₀Ca₂₀ are greater than that of the DGEBA cured with polyamide, which has been reported to vary from 48 to 62 MPa.¹⁸ The flexural strength of the reactive blend Ep₇₀Ca₃₀ with 70 wt % DGEBA content is comparable to that of polyamide-cured DGEBA system, reported earlier.¹⁸

Izod impact strength (notched)

The important mechanical property for the application of this type of reactive blends, Izod impact strength is

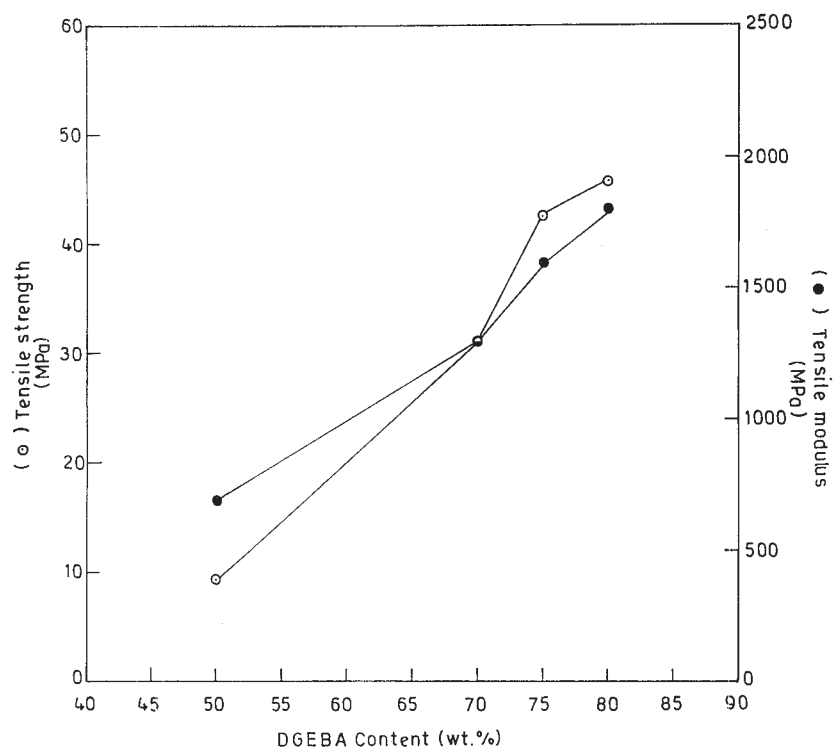


Figure 4 Variation of tensile properties with blend composition for DGEBA/polycaprolactam reactive blends: (○) tensile strength; (●) tensile modulus.

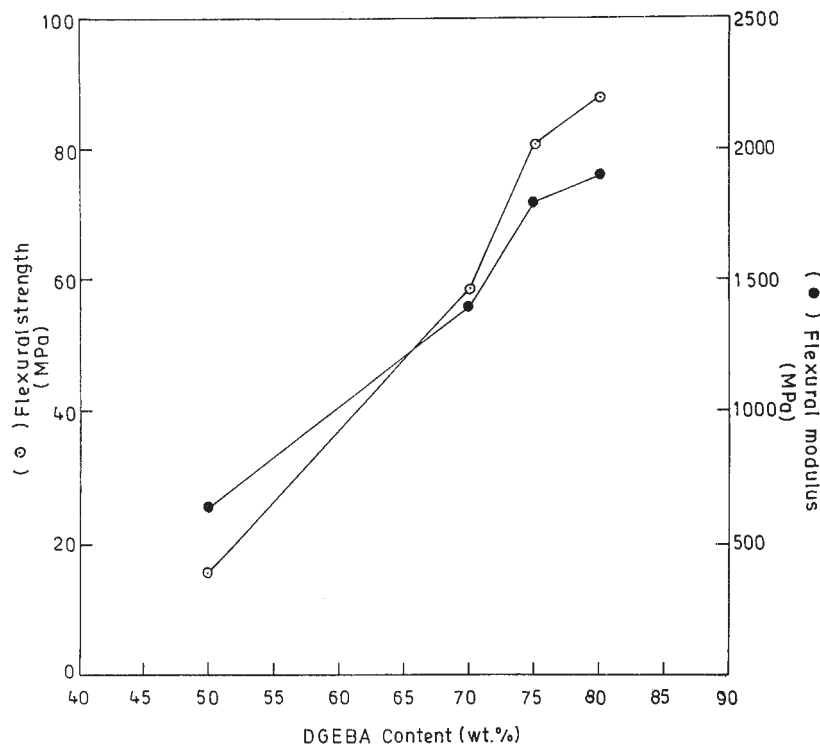


Figure 5 Variation of flexural properties with blend composition for DGEBA/polycaprolactam reactive blends: (○) flexural strength; (●) flexural modulus.

displayed as a function of DGEBA content in Figure 6. The variation in results of Izod impact strength (notched) with blend composition for DGEBA/polycaprolactam reactive blends are presented in Table V. Izod impact strength of the reactive blend $Ep_{70}Ca_{30}$ increases considerably (67.79 to 216.94 J m^{-1}), approximately threefold that of the reactive blend $Ep_{50}Ca_{50}$. When the DGEBA content increases from 70 to 75 wt % in the reactive blends, Izod impact strength increases rapidly from 216.94 to 305.07 J m^{-1} . By increasing the DGEBA content from 75 to 80 wt %, it is found that the Izod impact strength increases only marginally.

Izod impact strength increases drastically above 70 wt % DGEBA content because of the higher extent of cure and higher crosslinking density, as proved by solvent-extraction results and DSC studies. Izod impact strength of the reactive blend $Ep_{50}Ca_{50}$ with 50 wt % DGEBA content is very small because of the poor extent of cure, which increases the unreacted polymers, as already verified by solvent-extraction results. The decrease in Izod impact strength of the reactive blend $Ep_{50}Ca_{50}$ is also attributed to the poor crosslinking density, proved by DSC studies.

Rockwell hardness

Hardness also depicts the extent of cure and the hardness values on an R-scale for DGEBA/polycaprolac-

tam reactive blends are depicted in Table V; their variations with DGEBA content in the reactive blend composition are shown in Figure 7, indicating that the hardness of the reactive blend $Ep_{50}Ca_{50}$ is very poor and showing that the reactive blend $Ep_{50}Ca_{50}$ was rubbery in nature because of the poor extent of cure. Rockwell hardness of the reactive blend $Ep_{70}Ca_{30}$ increases considerably (25.8 – 79.9 on the R-scale), approximately threefold the value for reactive blend $Ep_{50}Ca_{50}$ as the DGEBA content increases from 50 to 70 wt % in the reactive blend. Rockwell hardness increases rapidly from 79.9 to 114.2 on the R-scale as DGEBA content increases from 70 to 75 wt %. By increasing the DGEBA content from 75 to 80 wt %, Rockwell hardness increases only marginally.

Rockwell hardness of reactive blends increases with increasing DGEBA content from 50 to 80 wt %. The drastic increase in Rockwell hardness was observed above 70 wt % DGEBA content because of the increase in crosslinking density, as proved by DSC studies. The observed behavior can be analyzed as a combined effect of both components of the reactive blend. Rockwell hardness of the DGEBA/polycaprolactam reactive blends increases with increasing DGEBA content as a result of the rigid nature of epoxy resin (DGEBA).

The results of mechanical properties confirm that the extent of cure and crosslinking density increases drastically above 70 wt % DGEBA content in the reactive blends. As a result of this, mechanical properties such as tensile, flexural, Izod impact strength, and

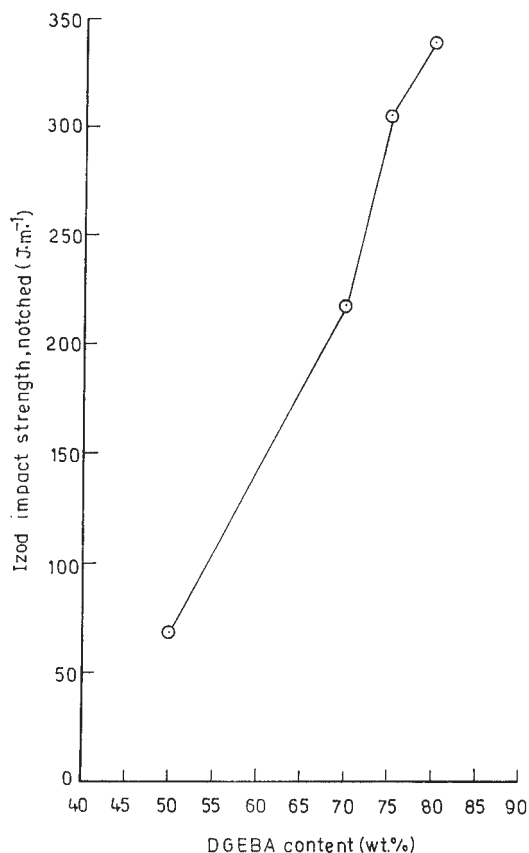


Figure 6 Variation of Izod impact strength (notched) with blend composition for DGEBA/polycaprolactam reactive blends.

Rockwell hardness increase drastically above 70 wt % DGEBA content in the reactive blends. This has already been proved by solvent-extraction results and DSC studies, which reveal drastic increases in extent of cure and crosslinking density.

Electrical property of DGEBA/polycaprolactam reactive blends

Various epoxy formulations are used in many electrical applications, often as primary electrical insulation. As electrical insulation, epoxy resins are used in a wide variety of devices ranging from tiny electronic devices to large reinforced structures.¹⁹ In materials used to insulate and support components of an electrical network, it is generally desirable to have insulation resistance as high as possible. Knowing the volume resistivity of an insulating material makes it possible to design an insulator for a specific application.

Volume resistivity

The volume resistivity measurement is useful in studying the resin cure and determining the presence of impurities. The results of volume resistivity for the

DGEBA/polycaprolactam reactive blends are shown in Table IV. Figure 8 indicates that with increasing DGEBA content in the reactive blends from 50 to 70 wt % the volume resistivity of reactive blends increases considerably, from 2.09×10^{11} to 7.38×10^{13} ohm-cm. The lower value of volume resistivity for the reactive blend Ep₅₀Ca₅₀ is attributed to the presence of an abundance of unreacted polymers, as confirmed by solvent-extraction results and poor crosslinking density and as proved by DSC studies. When the DGEBA content increases from 70 to 75 wt % in the reactive blend, the volume resistivity increases rapidly from 7.38×10^{13} to 1.95×10^{15} ohm-cm and the volume resistivity increases marginally.

When the DGEBA content is increased in the reactive blends above 70 wt %, a dramatic increase in volume resistivity was observed. This can be the result of the presence of a relatively small amount of unreacted polymers in the reactive blends above 70 wt % DGEBA content, as already confirmed by solvent-extraction results, and a drastic increase in crosslinking density of the reactive blends above 70 wt % DGEBA content, as already proved by DSC studies. The observed behavior can be analyzed as a combined effect of both components of the reactive blend. With a decrease in the polycaprolactam component in the reactive blends, the volume resistivity increases because of the decrease of polar molecules in the reactive blends. The volume resistivity of the reactive blends Ep₇₅Ca₂₅ and Ep₈₀Ca₂₀ (1.95×10^{15} and 5.57×10^{15}

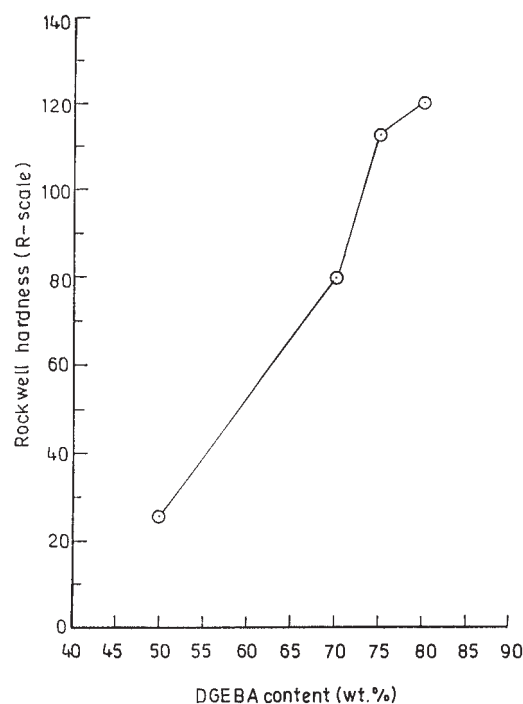


Figure 7 Variation of Rockwell hardness with blend composition for DGEBA/polycaprolactam reactive blends.

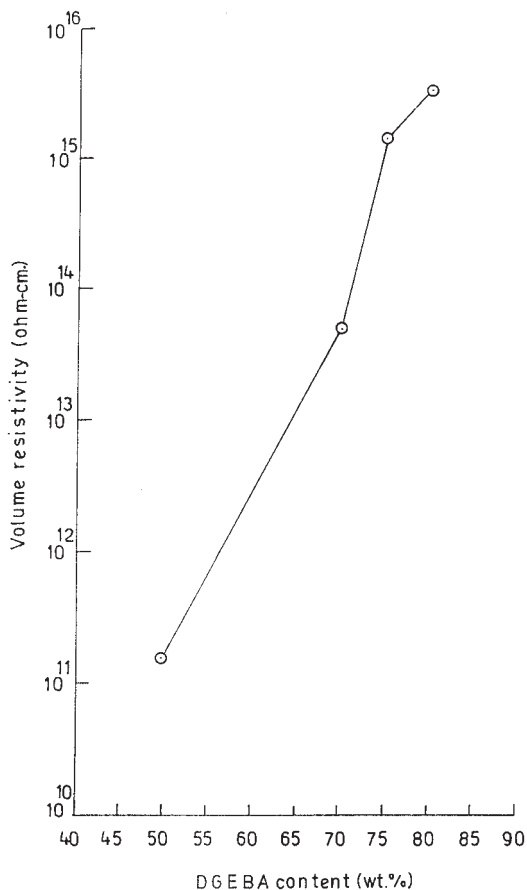


Figure 8 Variation of volume resistivity with blend composition for DGEBA/polycaprolactam reactive blends.

ohm-cm, respectively) are comparable to that of the DGEBA cured with polyamide, which has been reported to vary from 4.5×10^{15} to 10^{16} ohm-cm.^{18,20}

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, the blends are susceptible to significant crosslinking enhancement with increasing DGEBA content. Scanning electron micrographs of the fracture surfaces of the reactive blends at the same magnification are shown in Figure 9. Various DGEBA/polycaprolactam reactive blends show a multiphase system. The black space visible in these micrographs represents the DGEBA polymer and the white space represents the polycaprolactam polymer.

The micrograph of reactive blend $Ep_{50}Ca_{50}$ [Fig. 9(a)] shows poor mixing of the two phases and minor black spots of unreacted DGEBA, and the white spots

of the untreated polycaprolactam. With increasing DGEBA content in the reactive blends from 50 to 80 wt % the diffusion of DGEBA increases into the polycaprolactam-rich phase and increases the mixing of the two phases, as shown in micrographs of reactive blends $Ep_{50}Ca_{50}$, $Ep_{70}Ca_{30}$, $Ep_{75}Ca_{25}$, and $Ep_{80}Ca_{20}$ [Fig. 9(a)–(d)], which increases the crosslinking density of the reactive blends, as already confirmed by DSC studies. The micrographs of the reactive blends with 50–80 wt % DGEBA content show that with increasing DGEBA content in the reactive blends, the extent of unreacted DGEBA decreases and polycaprolactam polymers are shown by the reduction in minor black and white spots in the micrographs on increasing the DGEBA content from 50 to 80 wt %.

Thus the micrograph of reactive blend $Ep_{80}Ca_{20}$ [Fig. 9(d)] shows better mixing of polycaprolactam with DGEBA, similar to that of a single-phase system, as expected. As a result of this, the mechanical properties of the reactive blend $Ep_{80}Ca_{20}$ were maximum. The same type of morphology was seen earlier in the SEM micrograph of a fully miscible polyamide–epoxy system.⁸

CONCLUSIONS

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

1. Diglycidyl ether of bisphenol A (DGEBA) is crosslinked by polycaprolactam through the reaction of the oxirane group with amide nitrogen. The rapid reaction rates observed in the experiments at different temperatures suggest the application in the epoxy–polyamide reaction injection molding (RIM) process.
2. The degree of cure and crosslink density of the reactive blends increased with increasing DGEBA content from 50 to 80 wt %. Because of this, the heat of reaction and heat deflection temperature increased concomitantly with increasing DGEBA content in the reactive blends.
3. Tensile properties, flexural properties, Izod impact strength, Rockwell hardness, and volume resistivity of the reactive blends increased with increasing DGEBA content from 50 to 80 wt % in the reactive blends.
4. The morphological study of DGEBA/polycaprolactam reactive blends, having 50–75 wt % DGEBA content, showed a multiphase system, whereas the micrograph of the reactive blend $Ep_{80}Ca_{20}$, with 80 wt % DGEBA content, is similar to a single-phase system as a result of better mixing of polycaprolactam with DGEBA, which was also supported by thermomechanical studies.

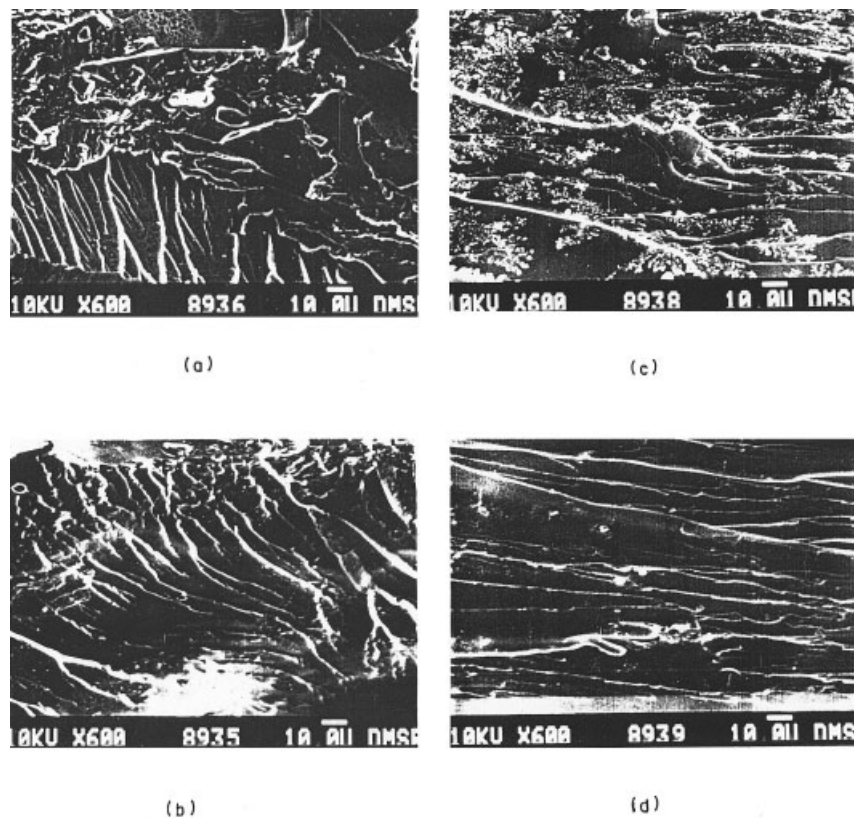


Figure 9 Scanning electron micrographs of DGEBA/polycaprolactam reactive blends: (a) Ep₅₀Ca₅₀; (b) Ep₇₀Ca₃₀; (c) Ep₇₅Ca₂₅; (d) Ep₈₀Ca₂₀.

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