

Crosslinking Reaction of Epoxy Resin (Diglycidyl Ether of Bisphenol A) by Anionically Polymerized Polycaprolactam: I. Mechanism and Optimization

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ABSTRACT: Different ratios of epoxy resin, diglycidyl ether of bisphenol A (DGEBA) and ϵ -caprolactam (starting from 10:90 DGEBA and vice versa), were used to synthesize reactive DGEBA and polycaprolactam blends by the anionic polymerization of ϵ -caprolactam at 140°C. Anionic polymerization was conducted with a strong base such as sodium hydride as a catalyst along with a cocatalyst such as *N*-acetyl caprolactam. The reaction mechanism, possible cure reactions, and reaction conditions of the reactive blends were studied with Fourier transform infrared spectroscopy and differential scanning calorimetry. The experiments were carried to study the optimization ratio and the effect of the

composition on properties such as hardness and tensile strength of the reactive blends. The DGEBA was crosslinked by polycaprolactam through the reaction of the oxirane group with the amide nitrogen, and the reaction was very fast. A ratio of 80:20 (DGEBA: ϵ -caprolactam) was optimum, and the resulting blend showed the highest tensile strength and hardness. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3237–3247, 2003

Key words: anionic polymerization; blends; crosslinking; polyamides

INTRODUCTION

Epoxy resins as a class are available in a wide range of molecular structures suitable for reaction with a large variety of different curing agents for a multitude of end uses. However, epoxy resins tend to be brittle after cure, and several approaches to the modification of epoxy resins have been tried. Many epoxy-based resin systems have been successfully toughened by the dispersion of a particulate rubbery polymer such as carboxyl terminated butadiene acrylonitrile rubbers (CTBN) with reactive end groups of either carboxyl or amine functionality.^{1–9}

Optimal performance and properties are obtained by crosslinking the epoxy resins to a three-dimensional, insoluble, and infusible network by reacting it with a curing agent. Several polyamides have been used as curing agents for epoxy resins.^{10–12} These include amidopolyamine or fatty polyamides obtained from dibasic fatty acid and primary amines such as diethylene triamine. The curing reaction takes place mainly because of the amine groups present in polyamides. Such types of curing agents provide good mechanical properties; exhibit readily workable pot lives; cure under mild conditions; and have good flexibility, toughness, corrosion resistance, and low toxicity. The main drawbacks to these curing agents are a low temperature

performance, high viscosity, and poor color. Recently, Chiang and Chang reported¹³ on polymer blends of polyamide 6 (PA6) and poly(phenylene ether) (PPE) compatibilized by a multifunctional epoxy coupler (NN N'-N'-tetraglycidyl-4,4'-diaminodiphenyl methane) (TGDDM) through the reaction of an epoxy ring with the terminal —NH₂ and —COOH groups of PA6 and the phenolic OH of PPE to form various PA6-co-GDDM-co-PPE mixed copolymers.

The object of this work was to synthesize reactive blends of epoxy resin [diglycidyl ether of bisphenol A (DGEBA) type] and polycaprolactam through the anionic polymerization of ϵ -caprolactam at 140°C. To conduct the anionic polymerization of ϵ -caprolactam, sodium hydride, a strong base, was used as catalyst along with an acylating agent, such as *N*-acetyl caprolactam, which acted as a cocatalyst. The advantages of anionic polymerization were that it provided highly reactive living ends of the growing polymer chains and required a low temperature for the reaction, whereas the hydrolytic polymerization of ϵ -caprolactam requires a polymerization temperature of around 250°C, which is not suitable for uncured DGEBA. The reaction between DGEBA and polycaprolactam was a newer area, where blends of DGEBA were crosslinked by the polycaprolactam through the reaction of the oxirane group with the amide nitrogen. The tensile strength and hardness of the reactive blends were measured to evaluate the performance and potential application of these blends.

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TABLE I
Stoichiometric Ratios of ϵ -Caprolactam and DGEBA Taken in the Synthesis of Reactive Blends for Reaction Optimization

DGEBA: ϵ -caprolactam ratio	Sample designation	DGEBA (g)	ϵ -Caprolactam (g)	Sodium hydride (g)	<i>N</i> -Acetyl caprolactam (g)
10 : 90	A	5	45	1.08	5.94
30 : 70	B	15	35	0.84	4.62
50 : 50	C	25	25	0.60	3.30
70 : 30	D	35	15	0.36	1.98
75 : 25	E	37.5	12.5	0.30	1.65
80 : 20	F	40	10	0.24	1.32
80 : 15	G	42.5	7.5	0.18	0.99
90 : 10	H	45	5	0.12	0.66

With this study, we expected to throw light on the curing reaction occurring between DGEBA and polycaprolactam and evaluate the performance of reactive blends obtained without the use of any external crosslinking agent. In this work, the optimization of the synthesis conditions of these reactive blends was performed, and a reaction mechanism is also proposed.

EXPERIMENTAL

Materials

The epoxy resin used in this study was a general purpose unmodified PG-100 DGEBA with an epoxide-equivalent weight of 185 and a viscosity of 11400 cps and was supplied by Parikh Resins and Polymers, Ltd. (India) in collaboration with F.I.C., Inc. ϵ -Caprolactam and sodium hydride were procured from Spectrochem Pvt., Ltd. (Mumbai, India). LR-grade *N*-acetyl caprolactam was supplied by Fluka Chemic AG (Switzerland).

Synthesis of reactive blends

Reactive blends of DGEBA and polycaprolactam were prepared by the anionic polymerization technique. Table I gives the details of the synthesis of reactive blends with 10:90, 30:70, 50:50, 70:30, 75:25, 80:20, 85:15, and 90:10 DGEBA: ϵ -caprolactam ratios, which are designated as samples A, B, C, D, E, F, G, and H, respectively. The monomer ϵ -caprolactam, 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 put in a three-necked round-bottom flask, and then, sodium hydride was added to it. The lactam was melted under a nitrogen atmosphere at 69–70°C to allow the sodium hydride to react. After the hydrogen evolution ceased, *N*-acetyl caprolactam was added and mixed properly [the anionic polymerization of ϵ -caprolactam is shown in Scheme 1(a)] DGEBA was added to the flask just after the addition of *N*-acetyl caprolactam and mixed properly (stage 1). The reac-

tion was carried out at 130–140°C with proper mixing until the products were solidified. The samples were postcured in an oven at 130°C for 5 h.

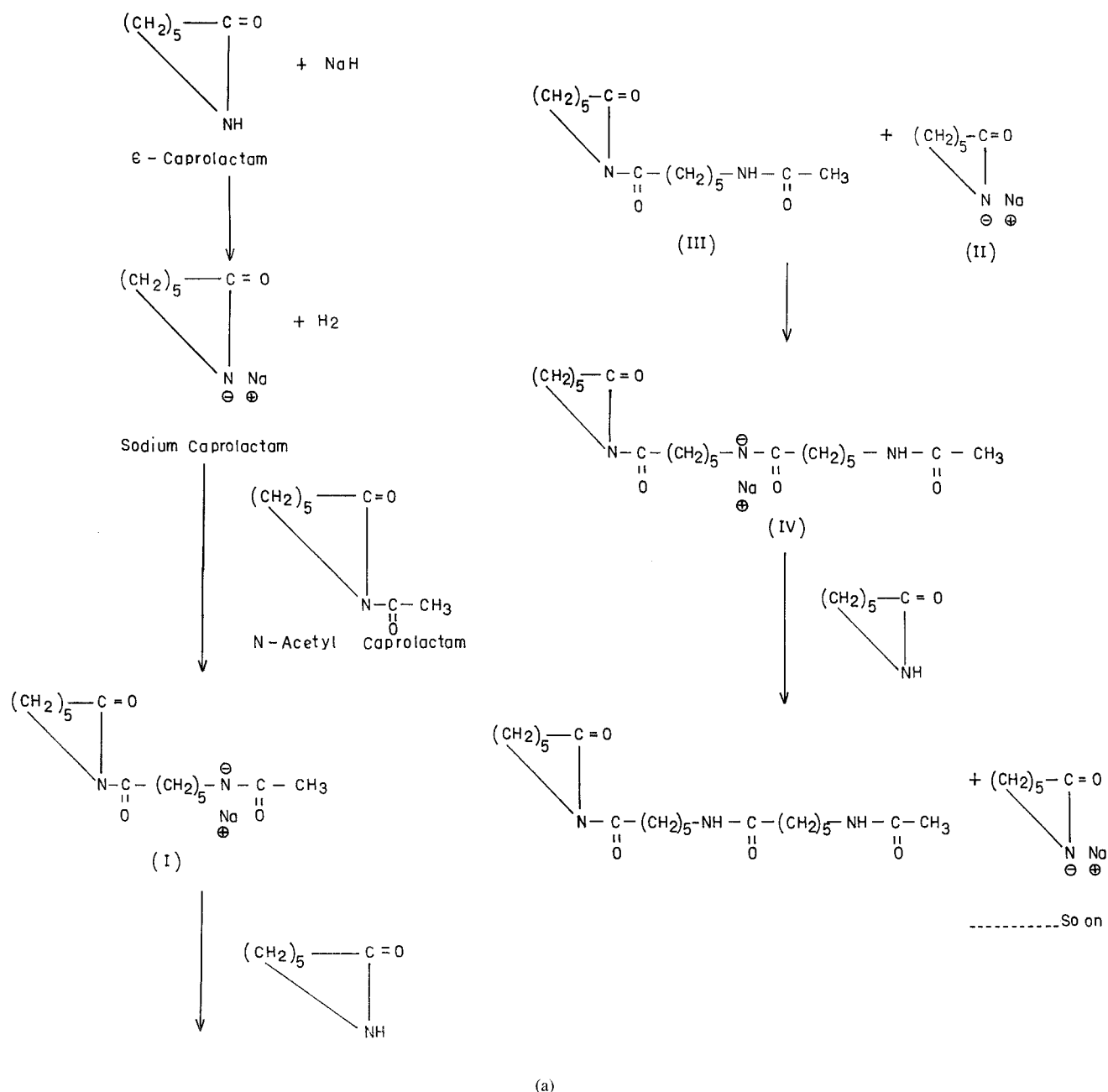
Casting of specimens

In casting, the reaction mixture (stage 1) was poured into a specially designed mold. The mold consisted of two mild steel base plates and one polytetrafluoroethylene middle plate, which were tightened by screws. The middle plate was dumbbell-shaped (8½ in. long, ½ in. wide, and ⅛ in. thick) for the tensile tests and disk-shaped (1 in. in diameter and ⅛ in. thick) for hardness and water absorption tests. The mold was kept in oven at 140°C for curing. Samples were released from the mold and postcured for 5 h at 130°C. After postcuring, the samples were stored in a desiccator for the evaluation of water absorption and mechanical properties.

Characterization

Solvent extraction

Several solvent extraction techniques^{14–16} have been reported to give successful separation of the blended components of immiscible polymer blends. To isolate and identify the formed DGEBA/polycaprolactam reactive blends, solvent extractions were carried out. The unreacted DGEBA was removed by the agitation of the crosslinked polymer in powder form in acetone for 24 h at room temperature. The solid polymer was dried in an oven after filtration at 60°C. The extraction process was repeated five times. The unreacted ϵ -caprolactam or polycaprolactam homopolymer was removed by agitation of the same solid polymer in formic acid for 24 h at ambient temperature. After filtration, the solid polymer was dried in an oven at 105°C. The optimum ratio of the DGEBA/polycaprolactam reactive blend was determined from percentage weight loss studies with the following equation:



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

Percentage water loss =

$$\frac{\text{Weight of sample after reaction} - \text{Weight of sample after final extraction}}{\text{Weight of sample after extraction}} \times 100$$

Gel time

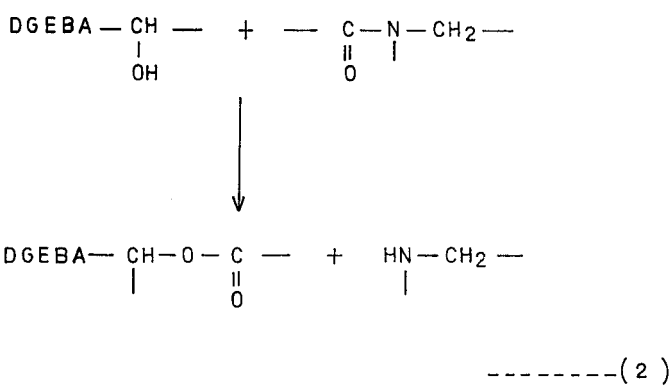
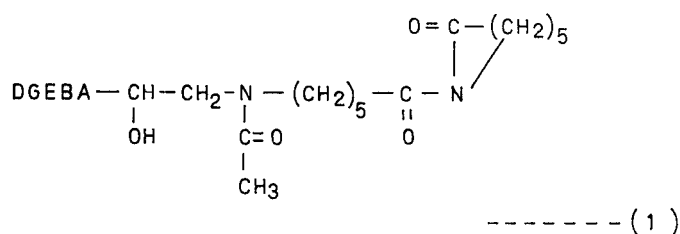
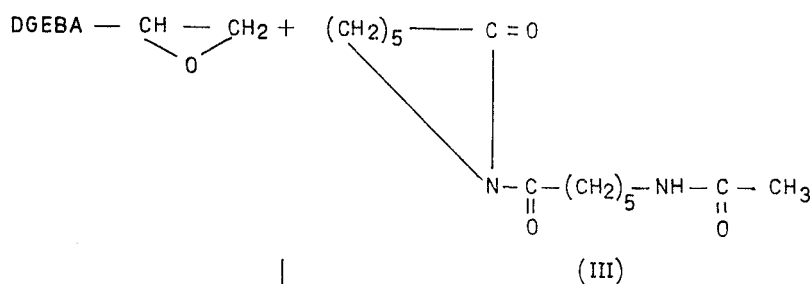
The gel times of the reactive blends were determined at different temperatures with a gel timer [Techno Cambridge, Ltd. (Ducx Ford, United Kingdom)].

Fourier transform infrared (FTIR) spectroscopy

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

Differential scanning calorimetry (DSC)

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



(b)

Scheme 1 (Continued)

used to study the curing behavior of the reactive blends under a nitrogen atmosphere. Scans were obtained under dynamic conditions with program heating rates of $10^\circ\text{C min}^{-1}$ from 40°C to the temperatures at which the exothermic reactions were completed.

Water absorption

Water absorption was determined by placement of the disc samples in distilled water for 8 days at room temperature. The difference between final weight and initial weight was used to calculate the water absorption with the following equation:

Percentage water absorption =

$$\frac{\text{Final weight} - \text{Initial weight}}{\text{Initial weight}} \times 100$$

Mechanical tests

Tensile tests were conducted at ambient conditions with a universal testing machine (Star Testing Machine, Mumbai, India) according to ASTM D 638. The crosshead speed was 25 mm/min. The results were calculated from the stress-strain curves of an average of five specimens for each reactive blend composition. The Rockwell hardnesses of the samples were measured on an R scale according to ASTM D 785.

RESULTS AND DISCUSSION

Ratio optimization

Reactive blends A to H, synthesized with different ratios of ϵ -caprolactam and DGEBA (Table I), varied

TABLE II
Results of Solvent Extraction for the Determination of the Extent of the Reaction

Sample	Weight of sample after reaction (g)	Weight of sample after final extraction (g)	Percentage weight loss in sample
A	5.5409	CS	—
B	8.6541	CS	—
C	5.8608	4.5120	23.01
D	7.7245	7.1825	7.02
E	7.1223	6.9120	2.95
F	6.5687	6.4502	1.80
G	NC	NC	—
H	NC	NC	—

CS = was completely soluble in both solvents, indicating the absence of any crosslinking reactions; NC = was not crosslinked at all as the reaction mixture remained a liquid and was discarded.

widely from liquid to rubbery to hard crosslinked solids. Therefore, it was important for us to find the optimum ratio of reactants to obtain a blend with properties suitable for commercial applications. The optimum ratio was determined by the solvent extraction process with solvents for unreacted DGEBA and ϵ -caprolactam. The data of solvent extraction is given in Table II, which indicates the extent of the reaction for all of the eight samples.

Samples A and B with DGEBA contents of 10 and 30% were completely soluble in solvents; therefore, no solid polymer was obtained after extraction. This indicated that no crosslinking occurred at low DGEBA contents in the composition. A reaction occurred in sample C, as the percentage weight loss was 23.01%, indicating that nearly 76.99% of the epoxy was crosslinked at a 50% DGEBA ratio. For samples D, E, and F, the percentage weight loss decreased tremendously to 7.02, 2.95, and 1.80%, respectively, indicating that a reasonably good amount of DGEBA was cured during the reaction. As shown in Table II, it was clear that for samples E and F, 97.05 and 98.20% crosslinking, respectively, occurred, and these values were also very close and could give the reactive blends practical utility. Therefore, our further studies were based only on samples C, D, E, and F samples. With the increase in DGEBA content from 50% (sample C) to 80% (sample F), the extent of crosslinking increased considerably. However, blends with more than 80% DGEBA, that is, 85 and 90%, did not crosslink, as the reaction mixture remained liquid. The results of solvent extraction showed that the reaction was at a maximum at the 80:20 ratio composition; that is, sample F was optimum because only 1.80% unreacted DGEBA and ϵ -caprolactam remained unreacted. Because the curing of DGEBA with ϵ -caprolactam involves multiple reactions, it was difficult to measure the extent of each reaction separately; therefore, the optimum ratio could not be calculated stoichiometrically.

Gel time

A very important observation we made during synthesis of the reactive blend was that the reaction was extremely fast; it was completed in a few minutes, depending on the blend composition. Therefore, the gel times of samples C, D, E, and F were measured at 130–170°C (Table III). It is clear from Table III that with an increase of DGEBA from 50 to 80%, the gel time increased considerably at a constant temperature. The gel times for samples with DGEBA contents of 50% (sample C) and 70% (sample D) were much lower compared with the gel times for 75% (sample E) and 80% (sample F) DGEBA samples. These facts were supported by the solvent extraction results, as explained earlier, where the samples prepared with lower DGEBA ratios were not properly crosslinked and the reactions were not complete. Samples E and F had approximately equal gel times, which revealed that the reaction was complete in both of the compositions. Thus, the reactive blend containing 80% DGEBA content (sample F) had an optimum ratio of DGEBA and polycaprolactam for curing, as supported by solvent extraction process.

The results indicated that with increasing temperature from 130 to 170°C, the gel time of the reaction mixture decreased properly by half, as shown in Figure 1. Samples E and F had approximate gel times

TABLE III
Determination of the Gel Time for Different Reactive Blends at Various Temperatures

Temperature (°C)	Gel time of reactive blends (seconds)			
	C	D	E	F
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

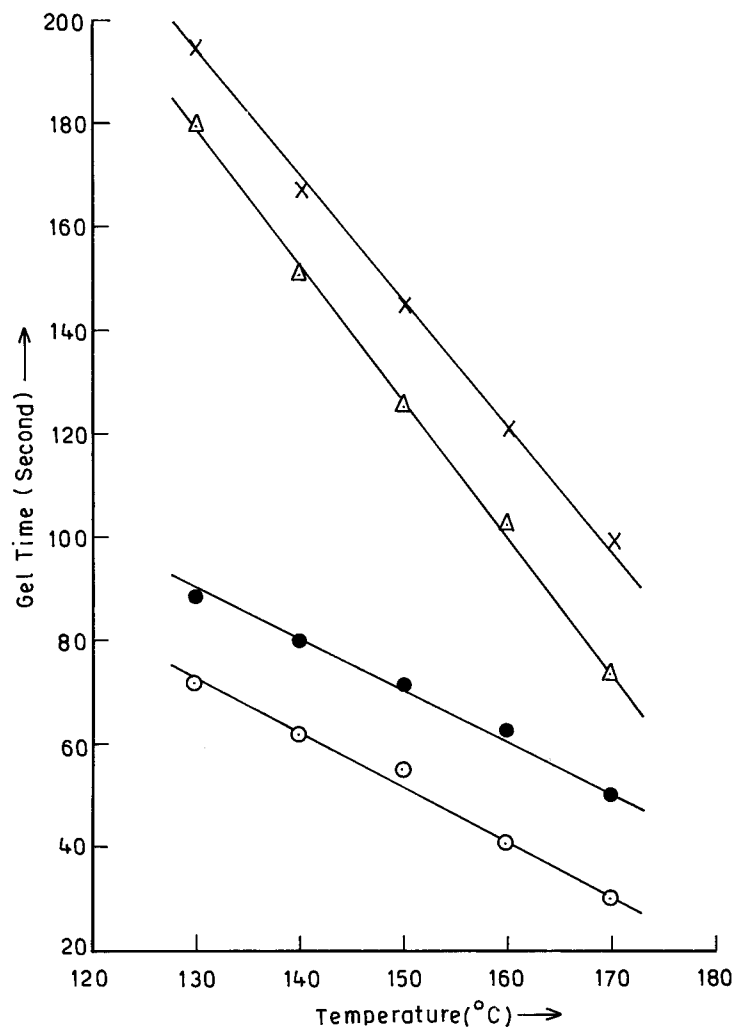


Figure 1 Plot of the gel time at various temperatures for different reactive blends: samples (○) C, (●) D, (Δ) E, and (×) F.

between 2 and 4 min, due to which these blends have potential applications in reaction injection molding (RIM). Nylon 6 is also processed on rotational molding and RIM, as anionic polymerization is carried out at considerably reduced temperatures and at faster rates.

Speculative mechanism

The mechanism of the anionic polymerization of ϵ -caprolactam is shown in Scheme 1(a). In this case, the attacking anionic species is the ϵ -caprolactam anion (I) formed by the reaction of sodium hydride, ϵ -caprolactam, and *N*-acetyl caprolactam. The anion attacks a ϵ -caprolactam molecule and extracts a proton, generating a new ϵ -caprolactam anion (II). This new anion opens up the ring in the dimer (III) formed between sodium caprolactam and *N*-acetyl caprolactam and gets itself attached, forming a trimer that is an anion (IV). The anion on the trimer now carries on the attack on a fresh ϵ -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 and is expected to be the dominant reaction, and another type of reaction also occurs during curing [eq. (2) in Scheme 1(b)].

FTIR studies

The curing reaction of polycaprolactam with DGEBA resulted in significant changes of the chemical structure of the molecule, which was reflected in the IR spectrum of the blend. FTIR spectra of polycaprolactam, a reactive blend of DGEBA and polycaprolactam (sample D), and after solvent extraction of the reactive blend are shown in Figure 2.

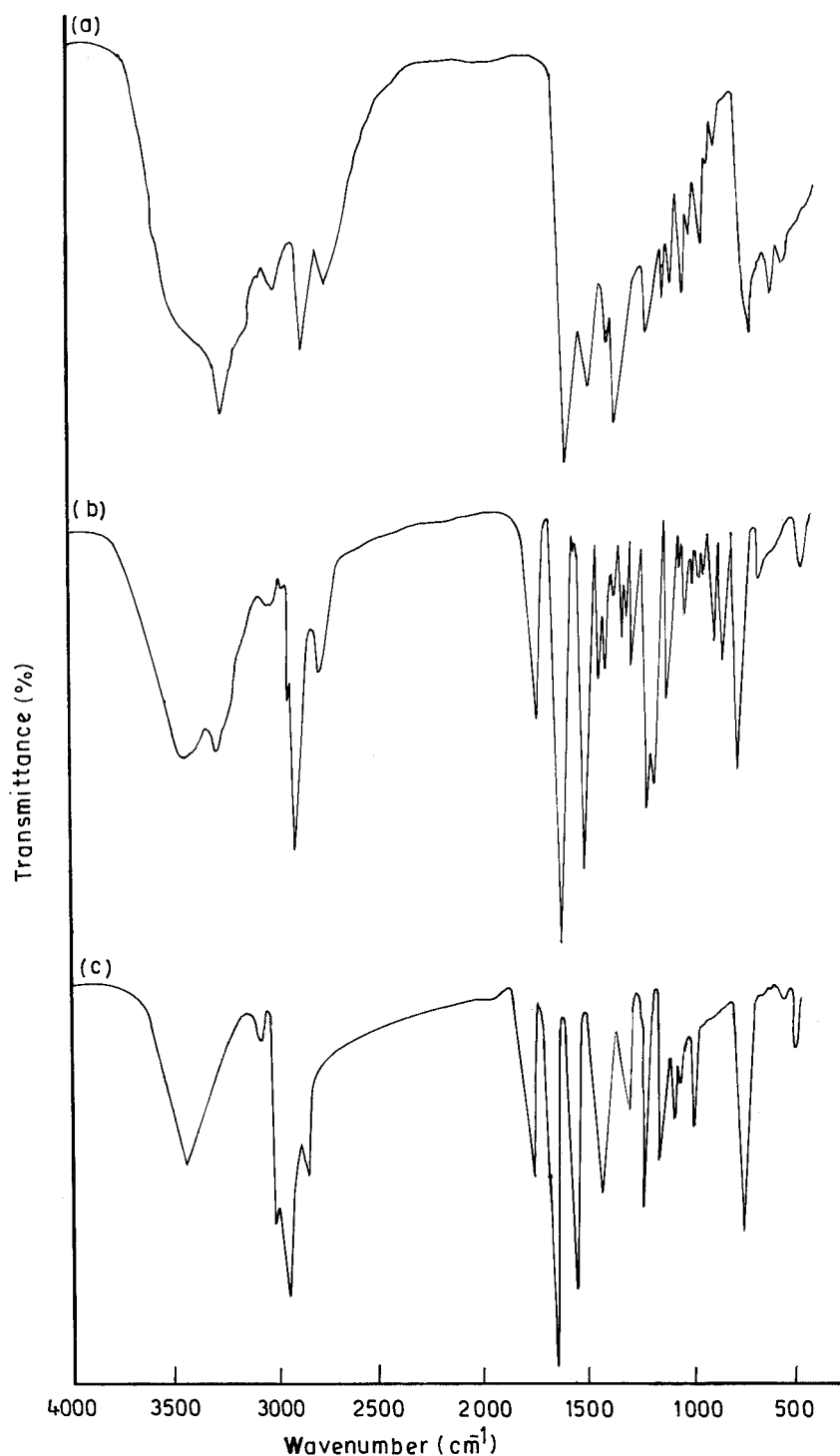
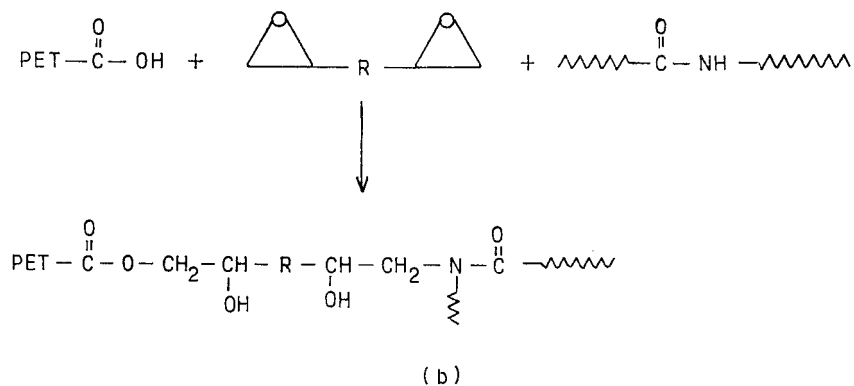
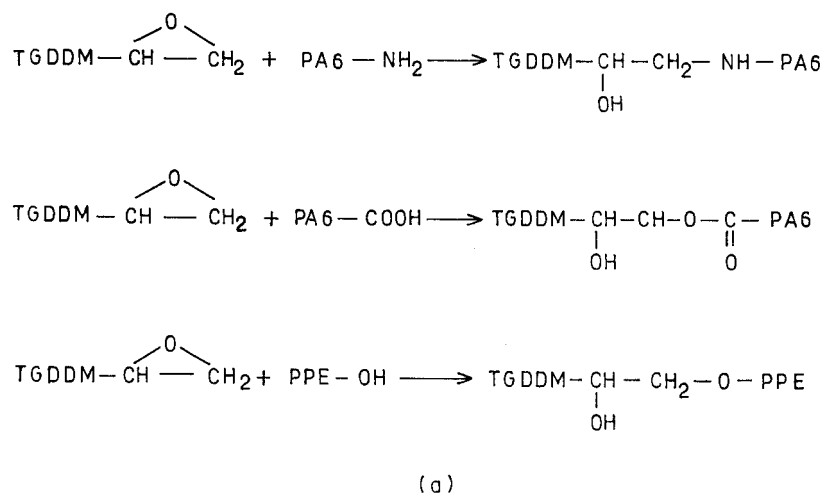


Figure 2 FTIR spectra of (a) polycaprolactam, (b) a reactive blend of DGEBA and polycaprolactam (sample D), and (c) the reactive blend after extraction.

The polycaprolactam exhibited a peak at 3304.24 cm^{-1} . The peak in this range was due mainly to the N—H group. After curing, the blend exhibited a sharp peak at 3480.38 cm^{-1} and a shoulder peak at about 3304.24 cm^{-1} . The absorptive peak in this range was mainly due to the stretching vibration of the O—H group (3480.38 cm^{-1}) and the stretching vibration of

the N—H group (3304.24 cm^{-1}). The spectrum of the unextracted sample [Fig. 2(b)] showed a considerably smaller peak of the epoxy ring at 910.64 cm^{-1} , indicating that a major portion of the epoxy ring was consumed in the reaction, which further supports Scheme 1(b) in verifying the presence of any unreacted epoxy ring in the reactive blend. The FTIR spectrum of



Scheme 2 Reactions between the epoxy ring and amide group in the area of compatibilization of polymer blends: (a) reactions of PA6, PPE, and TGDDM components¹³ and (b) reactions among PET, PA6, and the epoxy compatibilizer.¹⁸

the reaction product after complete solvent extraction is also shown in Figure 2(c). This figure shows that after solvent extraction, the peak for the oxirane ring (910.64 cm^{-1}) and N—H group (3304.24 cm^{-1}) disappeared completely. This shows that these peaks were found in the blend (sample D) due to the presence of unreacted DGEBA and polycaprolactam in the blend, which was also confirmed by the solvent extraction process. The main reaction was the nucleophilic attack on the oxirane ring by the amide nitrogen of polycaprolactam, which produced a hydroxyl group, and this reaction was a typical curing reaction of epoxy resin with an amine hardener.¹⁷ In addition, a new peak at 1720.4 cm^{-1} appeared after curing, which was present in both Figure 2(b) and 2(c), indicating another type of reaction occurred during the curing. The peak at 1720.4 cm^{-1} was the absorption of the carbonyl (C=O) of the ester group. This suggested that the second type of reaction occurred through eq. (2). The resulting secondary amine group could react further with the epoxide group. Samples contained linkages 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.

A very new and interesting application of the reaction between the epoxy ring and the amide group was reported by several researchers in the area of the compatibilization of polymer blends. Chiang and Chang¹³ reported the use of a multifunctional epoxy coupler (TGDDM) to compatibilize the polymer blends of PA6 and PPE, as shown in Scheme 2(a). A reactive compatibilizer (low-molecular-weight bisphenol A epoxy resin E-44)¹⁸ was used to compatibilize the polymer blends incorporating poly(ethylene terephthalate) (PET) and PA6. Because E-44 was reactive, there was an equilibrium between the reaction of the epoxy groups with PA6 and PET. The probable reaction on the interface between PET and PA6 during melt mixing is shown in Scheme 2(b).

DSC studies

Typical dynamic DSC scans at a heating rate of $10^\circ\text{C min}^{-1}$ under a nitrogen atmosphere for the curing of the reaction mixtures (stage 1) of different ratios (sam-

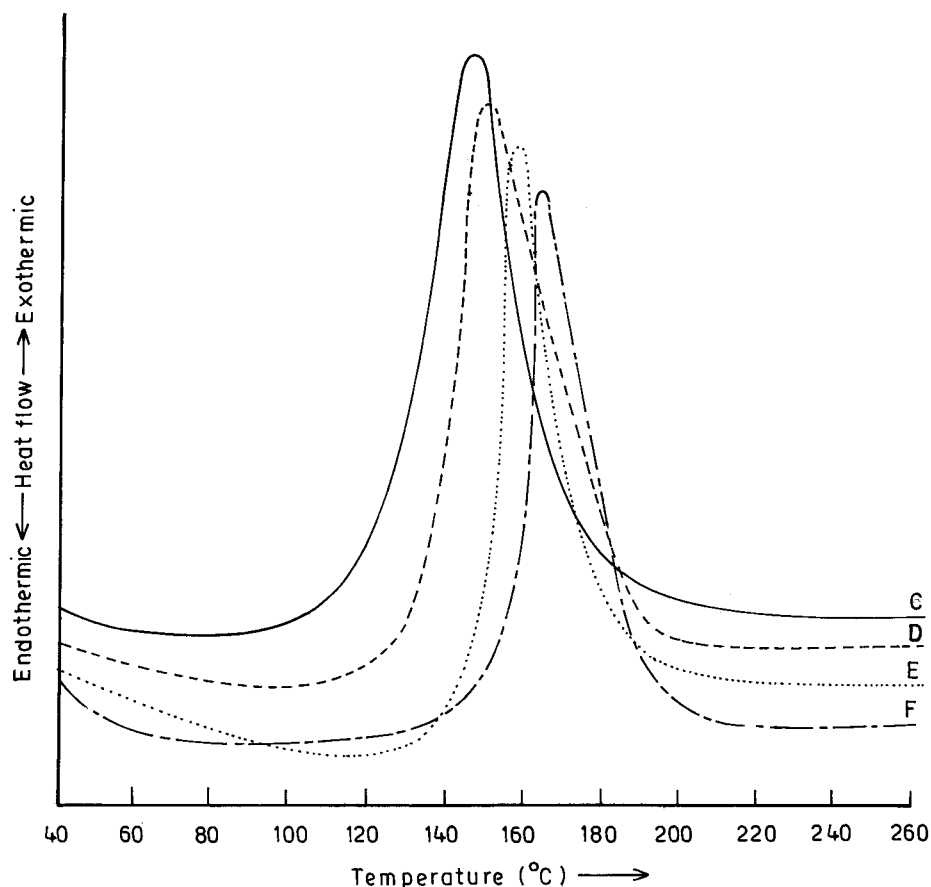


Figure 3 Dynamic DSC scans for the curing of polycaprolactam and DGEBA reactive blends at $10^{\circ}\text{C min}^{-1}$: samples (—) C, (---) D, (···) E, and (-·-) F.

ples C, D, E, and F) are given in Figure 3. From these DSC scans, the onset temperature of curing (T_o), the exothermic peak position (T_p), and the final temperature of curing (T_f) were noted and are summarized in Table IV. T_o and T_p increased from samples C to F, whereas the curing temperature (T_f) remained almost the same for all of the samples. This indicated that T_o and T_p for sample C were lower than for samples D, E, and F; thus, C required more time for the completion of reactions. The heat of the curing reaction for all of the samples were also calculated, which increased from samples C to F. The results revealed that extent of the reaction was poor in sample C, and as the

DGEBA content increased from 50 to 80%, the extent increased considerably, which could be explained on the basis of the solvent extraction process. The data indicated when the DGEBA content increased from 50 to 80%, the weight loss decreased from 23.01 to 1.80% and the extent of the reaction increased considerably, which was proven by the heat of the curing reactions of the reactive blends, which increased from 1530.14 to 2184.52 J g^{-1} for samples C to F.

Water absorption

The data for percentage water absorption for samples (C to F) before and after postcuring are listed in Table V. The results indicated that as the ϵ -caprolactam:DGEBA ratio decreased, the water absorption tendency decreased. The absorption was reduced from 6.24 to 1.46% as the DGEBA content increased from 50 to 80%. This could have been due to the fact that the samples prepared with lower DGEBA ratios were not properly crosslinked. This fact was supported by the results of the solvent extraction process (Table II) and postcuring studies. After postcuring, the water absorption decreased, as shown in Table V.

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

Sample	T_o ($^{\circ}\text{C}$)	T_p ($^{\circ}\text{C}$)	T_f ($^{\circ}\text{C}$)	ΔH Jg^{-1}
C	94.56	144.42	208.21	1530.14
D	106.08	149.46	206.17	1715.25
E	128.67	156.13	208.98	2071.25
F	135.91	161.26	210.79	2184.52

ΔH = heat of reaction.

TABLE V
Water Absorption Studies of Cured and Postcured Reactive Blends

Sample	Postcure	Initial weight (g)	Final weight (g)	Water absorption (%)
C		3.9876	4.2893	7.57
	5 hr at 130°C	3.3822	3.5934	6.24
D		3.4351	3.5649	3.78
	5 h at 130°C	3.7498	3.8625	3.01
E		3.2165	3.2911	2.32
	5 h at 130°C	3.3458	3.4120	1.98
F		3.2199	3.2736	1.67
	5 h at 130°C	3.6214	3.6741	1.46

It is well known that nylons are moisture sensitive and have high water absorptions, varying from 2.7 to 10%.¹⁹ Hence, it could be concluded that as the polycaprolactam component increased, the water absorption tendency increased due to the polar nature of polycaprolactam. The pure epoxy sample had the lowest water absorption (0.71%) due to its rigidity.

Mechanical tests

Tensile strength is an important mechanical property as it is the measure of the strength of a blend. The tensile strengths for the reactive blends (samples C, D, E, and F) are shown in Figure 4, which indicates that as the DGEBA content in the reactive blends increased from 50% (sample C) to 70% (sample D), the tensile

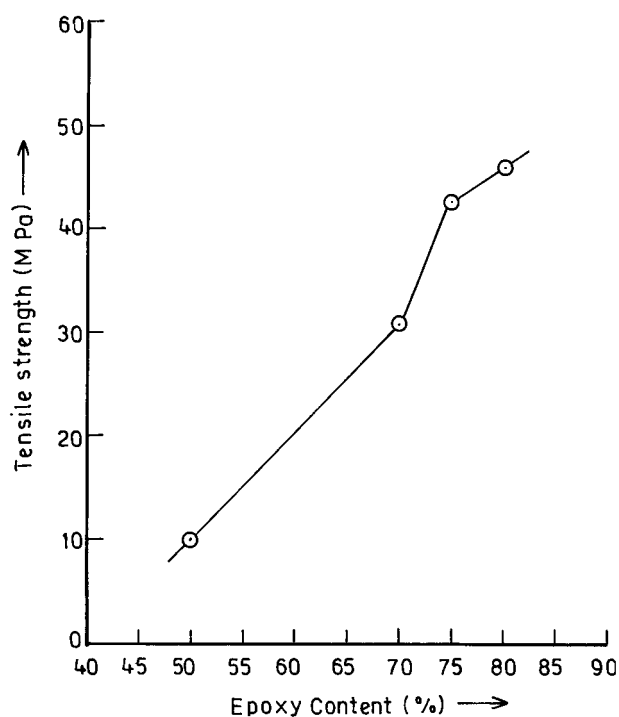


Figure 4 Effect of DGEBA content on the tensile strength of the reactive blends.

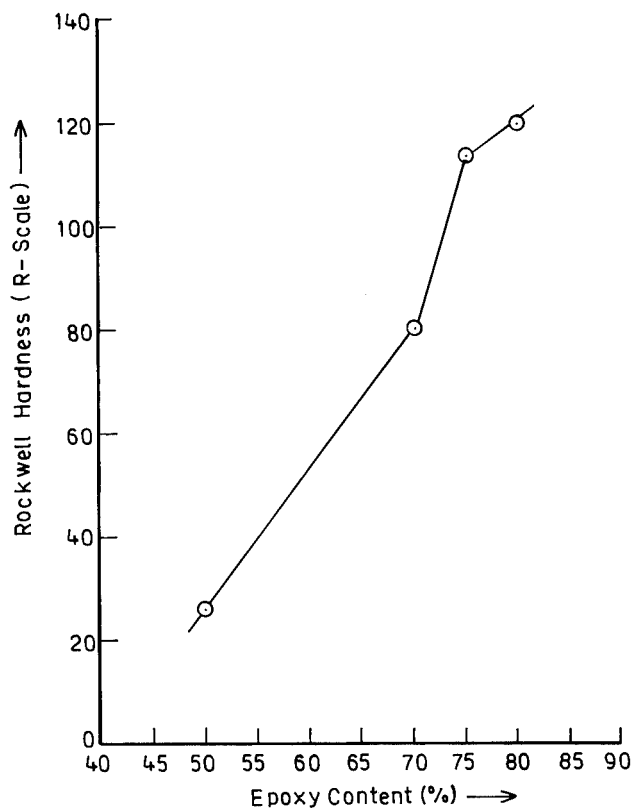


Figure 5 Effect of DGEBA content on the Rockwell hardness of the reactive blends.

strength increased considerably (9.84 to 31.36 MPa); the tensile strength of sample D was approximately three times that of sample C. The tensile strength of the sample C was very much lower due to an incomplete crosslinking reaction, as proven by the solvent extraction process. When the DGEBA content increased from 70 to 75% in the reactive blends, the tensile strength increased drastically from 31.36 to 43.04 MPa. With increasing epoxy content from 75 to 80%, the tensile strength increased marginally. This indicated that maximum crosslinking reaction had taken place in sample F.

Hardness also depicts the extent of cure. The Rockwell hardnesses for the reactive blends C, D, E, and F are shown in Figure 5. This figure shows that the hardness of sample C was very poor, which indicates that blend C was rubbery in nature due to the poor extent of cure. Figure 5 also shows that as the epoxy content increased from 50 to 80%, the hardness of the reactive blends increased from 25.8 to 119.5 on the R scale, a similar trend as followed by tensile strength (Fig. 4). These results confirmed that the extent of cure was at a maximum at an 80:20 ratio (Sample F) and that it was optimal. The hardness and tensile strength values increased due to the enhanced extent of crosslinking in the reactive blends with increasing epoxy content. This was also confirmed by DSC stud-

ies (Table IV), which exhibited a considerable increase in the heat of reaction for samples E and F as compared to samples C and D. The tensile strength of reactive blend F (45.97 MPa) was comparable to the DGEBA cured with polyamide, which was reported to vary from 35 to 55 MPa.²⁰

It could be concluded that a crosslinking reaction in DGEBA and polycaprolactam took place, and the rapid reaction rates observed in the experiments suggest applications in the epoxy-polyamide RIM process. Due to this crosslinking reaction, the product cannot be termed an interpenetrating network (IPN), but it happens to be a close relative of the IPN, known as an AB crosslinked copolymer (or joined IPN). To confirm this structural configuration, further morphological and other studies are required.

CONCLUSIONS

It may be concluded from this study that

1. DGEBA was crosslinked by polycaprolactam through the reaction of the oxirane group with the amide nitrogen.
2. The nature of the product varied from rubbery to a hard and brittle solid (depending on the reactant ratio). An 80:20 DGEBA: ϵ -caprolactam ratio was the optimum ratio of the DGEBA/polycaprolactam reactive blend.
3. As the DGEBA component increased, the hardness and tensile strength of the blends also increased.

4. The rapid reaction rates observed in the experiments at different temperatures suggest application in epoxy-polyamide RIM process.

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