

Toughened Cycloaliphatic Epoxy Resin for Demanding Thermal Applications and Surface Coatings

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Received 8 February 2009; accepted 26 April 2009

DOI 10.1002/app.30669

Published online 16 July 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: An epoxy resin based on nonglycidyl ether and varying content of carboxyl-terminated (poly)butadiene acrylonitrile copolymer was cured using an aromatic amine hardener. The ultimate aim of the study was to modify the brittle epoxy matrix by the liquid rubber to improve toughness characteristics. Fourier transform infrared spectroscopic analysis of the modified was performed to understand the structural transformations taking place during the uncured and cured stage of the modified systems. The decreasing trend in exothermal heat of reaction with increasing rubber content in the epoxy resin can be explained by the fact that the increase of carboxyl-terminated butadiene acrylonitrile copolymer (CTBN) modifier might induce a high reactivity of the end groups with the epoxide ring and resulting shorter curing times and, hence, the faster curing process than the unmodified resin. Tensile strength, impact strength, and elongation-at-break behaviors of neat as well as modified networks have been studied to observe the effect of rubber modification. Blends sample exhibits better properties as compared to pure epoxy resin in terms of increase in impact strength and elongation-at-

break of the casting and gloss, scratch hardness, adhesion, and flexibility of the film. The improvement in these properties indicate that the rubber-modified resin would be more durable than the epoxy based on di glycidyl ether of bis-phenol-A and other epoxies. The films of coating based on epoxy with 15 wt % CTBN offered the maximum resistance toward different concentrations of acids, alkalies, and solvents as compared to the cured films of other blend samples. The thermal stability of the cycloaliphatic-based epoxy resin was increased with the addition of 15 wt % CTBN in epoxy matrix. Cycloaliphatic-based epoxy network modified with CTBN displayed two phase separated morphology with dispersed rubber globules in the matrix resin, i.e., they revealed the presence of two phase morphological features. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2769–2776, 2009

Key words: cycloaliphatic epoxy resin; carboxyl-terminated butadiene acrylonitrile copolymer (CTBN); differential scanning calorimetry (DSC); chemical resistance; morphology

INTRODUCTION

Epoxy adhesives are currently used in various industries because of their overall performance characteristics. They can be formulated to perform adequately in extreme environments that include solvents, temperature extremes, and ultraviolet radiation and are relatively easy to process and apply. They are also easily reacted so that a wide range of curatives and catalysts can be used to initiate cure and the formation of a crosslinked three-dimensional infinite molecular weight structure.^{1–3} For higher endues temperature epoxy systems, the crosslink density must be sufficiently high to prevent thermally initiated phenomena including creep, stress relaxation, or even degradation.^{1,3–6} As a result, the cured epoxy matrices alone are somewhat brittle

and prone to flaw or crack propagation. Toughening agents, including liquid carboxyl-terminated butadiene acrylonitrile (CTBN) elastomers, are frequently added to the uncured base epoxy formulations to improve fracture characteristics. CTBN materials primarily toughen epoxy matrices through two separate mechanisms. Rubber-modified epoxy resins constitute an important class of adhesives used especially in the aeronautical and cosmonautical industries. They are characterized by a combination of high adhesion strength and toughness. One of the most important factors controlling the toughness of rubber-epoxy resins system is the size, distribution, and structure of the rubber particles.

Toughening of diglycidyl ether of bisphenol-A (DGEBA) epoxy resins with low-molecular-weight liquid rubbers has widely been studied.^{3–11} Many authors have commented on the increasingly wide use of rubber-modified epoxy resins as structural and as the matrix for fiber composition. There are several reports on DGEBA-based epoxy resins and elastomer-modified blends on immiscibility

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TABLE I
Composition of Cycloaliphatic Epoxy with CTBN
Containing DDS

S.No.	Sample code	CAE (wt %)	CTBN (wt %)	DDS (wt %)
1	CEC ₀	100	0	40
2	CEC ₅	95	5	38
3	CEC ₁₀	90	10	36
4	CEC ₁₅	85	15	34
5	CEC ₂₀	80	20	32
6	CEC ₂₅	75	25	30

depending on the structure of curing agent.^{4,9} But, there is the lack of literature on the cycloaliphatic epoxy (CAE) resin modification.

CAE resins have been applied in a variety of industrial applications, such as paints, coatings, inks, reactive diluents, and so on, because of their good heat and chemical resistance, superior mechanical and electrical properties, as well as excellent processability.^{12–16}

CAE resins have high heat deflection temperature and good high temperature electrical properties.¹⁷ This article reports on the modification of amine-cured CAE resin by CTBN copolymer. The change in the behavior of macro and microstructure with the addition of CTBN having acrylonitrile content at the level of 27% was examined during the investigation.

EXPERIMENTAL

Materials

Nonglycidyl type CAE resin, i.e., 3,4-epoxy cyclohexylmethyl, 3',4'-epoxycyclohexane carboxylate (viscosity: 1300–1800 mPa s at 27°C) used in all experiments was ERL-4221 (epoxide equivalent weight: 145 eq/g) and cure agent 4,4'-diamino diphenyl sulphone (DDS) (HT 976) were procured

from M/s Ciba Specialty Chemicals, Mumbai, India. The elastomer used was CTBN copolymer (Viscosity: 625,000 mPa s at 27°C) (Trade name: Hycar 1300×13) and was kindly supplied by M/s Emerald Performance Materials, LLC, Hong Kong with molecular weight \overline{M}_n of 3500, containing 27% acrylonitrile content and 32% carboxyl content.

Preparation of samples

Six samples containing 0–25 wt % CTBN were prepared according to the procedure as reported in our previous publication for DGEBA epoxy resin.¹¹ The calculated quantity of CAE epoxy resin (as per formulation given in Table I) was, firstly, stirred at 120°C for 1 h to entrap out all air bubbles from the resin. To this homogeneous resin system, the calculated quantity of DDS was added and stirred at 150–155°C for 45 min to get clear homogeneous mixture.

Curing of blend samples

The cure process of all blend samples followed four steps: First, the epoxy resin was degassed followed by the addition of 0–25 wt % CTBN in the epoxy resin. To this mixture 36 phr DDS was added and finally, the whole mixture degassed again. The mixture was poured into preheated iron mold and cured into hot air oven at 170°C for 1 h and then postcured for 2 h at 200°C. Specimens for the entire test were cut from this block.

Characterization of samples

Fourier-transform infrared spectroscopy

Fourier transform infrared (FTIR) spectroscopy has been used to monitor the chemical reactions between CAE resin/CTBN/DDS blend systems. For the

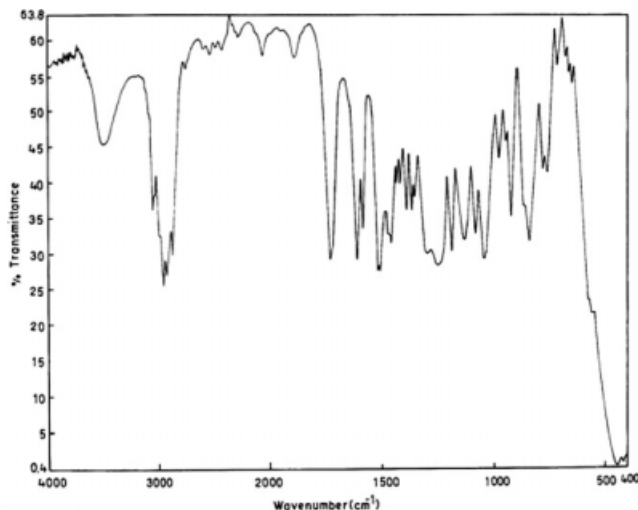


Figure 1 FTIR spectra of sample CEC₀.

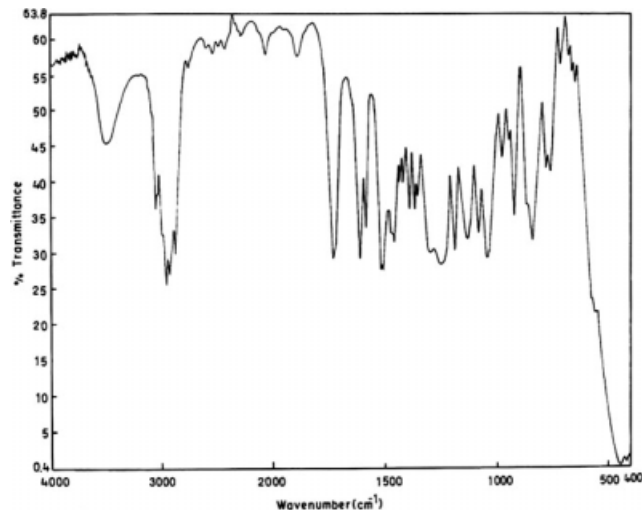
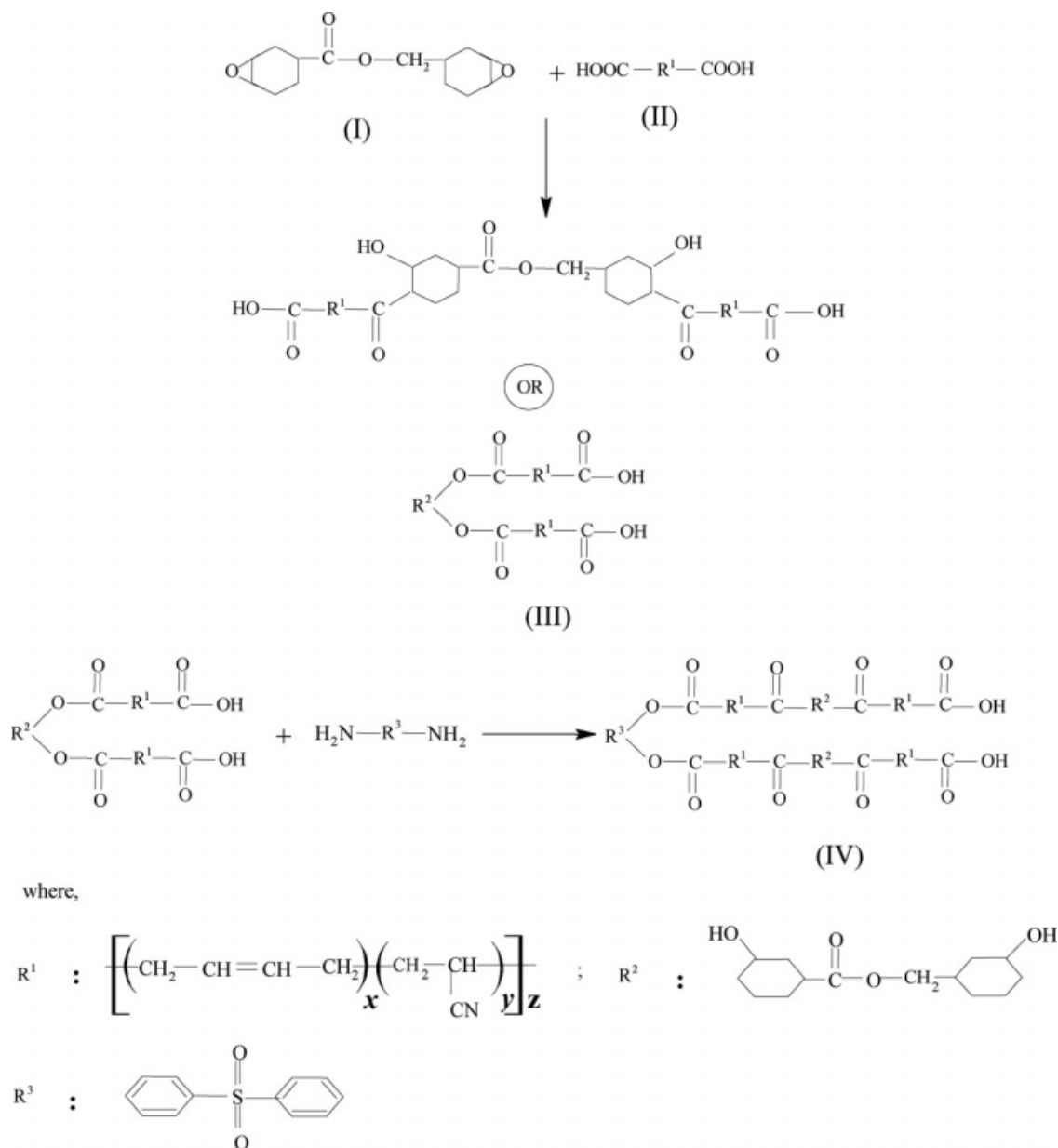


Figure 2 FTIR spectra of sample CEC₁₀.



Scheme 1 Reaction mechanism for the formation of prepolymer and cured product.

infrared (IR) measurement, a small portion of the cured epoxy system was grind to a fine powder, mixed with potassium bromide (KBr) powder, and pressed into a pellet by hand press. For the liquid (uncured) samples, sodium chloride pellets were used and a very little quantity of the material was kept in between them. FTIR were recorded by Nicolet Magna 750 spectrophotometer in the wavelength range of 4000–400 cm^{-1} .

Differential scanning calorimetric analysis

Cure temperature of the prepared samples were observed by taking very little quantity of blend samples into shallow aluminum pan of DSC (TA Instru-

ment, USA; Model DSC 2920), which was sealed by an aluminum cover. This was placed in sample cell of the instrument. The starting temperature was ambient, programmed rate was 10°C/min, and the final temperature was 350°C. Dynamic scans were obtained which were used for assuming the cure temperature.

Mechanical and chemical properties

The panels were prepared by applying the blend samples on sand-blasted steel sheet and glass panels of sized 150 × 100 × 1.25 mm with a Bird Film Applicator (M/s Sheen Instruments, UK). These panels were sealed on three sides with molten paraffin wax. A dry film thickness of about 150 μm was

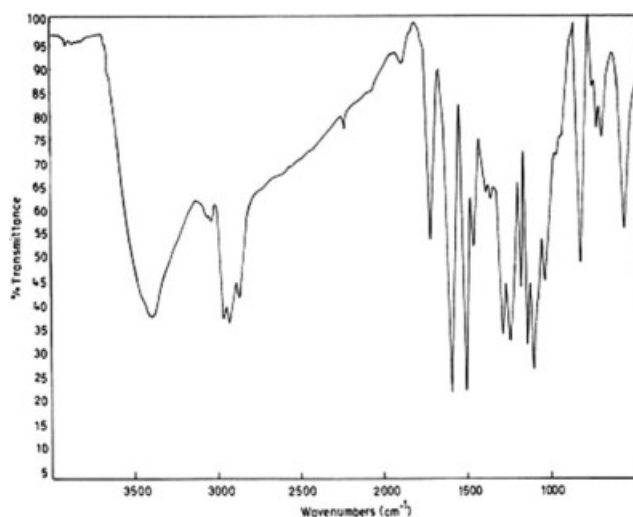


Figure 3 FTIR spectra of sample CEC₁₀ (cured).

maintained on all the panels. These films were then cured at 170°C. The adhesion and flexibility of the cured films of the resin was tested by putting the prepared steel panels into a 1/4 inch mandrel keeping the coated side downward. Then the two plates, connected to the mandrel, were readily bent. The bent portion of the panel was examined for any damage in the film. The impact resistance of the cured film samples was conducted by dropping a hemispherical shaped two-pound weight from 25 inch height over the panels. The tests were carried out with the uncoated side of the panel facing the falling weights. Gloss was measured using Triglossometer (Sheen). After watching the films from 60° angle, it had been observed that all the coating films had good gloss. Dumbbell-shaped cured samples (size: 7.5 × 3/4 × 1/8 inch) of blend samples were used for the determination of tensile strength and elongation-at-break according to the ASTM D 638 standard on a Universal Testing Machine (UTM) (M/s Patiwana Group, Star Testing Systems, Mumbai, India). The crosshead speed of the machine was kept at 25 mm/min.

Scanning electron microscopic analysis

The fractured samples under mechanical analysis were sputter-coated with gold before scanning electron microscopy (SEM) examination. Joel JSM 5800 model was used to view the specimen; several micrographs were taken for each sample.

RESULTS AND DISCUSSION

Fourier transform infrared spectroscopic analysis

Figure 1 showed the FTIR spectrum of cycloaliphatic epoxy resin (sample CEC₀). Absorption peaks at 772.1 and 915.5 cm⁻¹ characterized the presence of oxirane group in the resin. Absorption peak near 1075 cm⁻¹

indicated the asymmetric C—O—C stretching which did not react with either epoxy composition or CTBN. It has been reported^{18,19} that the C—O—C group, present between the cycloaliphatic ring, was found to be inert to epoxy curing because of the presence of fairly chemically stable carbonate linkage.

The disappearance of peak at 772.1 cm⁻¹ in the spectra of blend samples containing 10 wt % CTBN, i.e., samples CEC₁₀ (Fig. 2) indicated the opening of epoxy groups from CAE which further reacted with carboxylic group of CTBN (Scheme 1).

The increase in the intensity of peak near 1725 cm⁻¹ might be due to the increase in the concentration of carboxylic group which might further indicate the formation of functional group ester.

The broad strong band near 3400 cm⁻¹ in the case of cured blend samples CEC₁₀ suggested (Fig. 3) that there was certain number of hydroxyl groups on the surface of the sample that might establish intermolecular hydrogen bond with other nucleophilic groups.^{20,21} Indeed, the absorption band corresponding to carbonyl group in the epoxy monomer, broadened and shifted to lower wave number as a result of hydrogen bonding. These hydroxyl groups were generated as a result of the initiation step of the curing process as reported in the literature.

Differential scanning calorimetry

Figures 4 and 5 showed the traces of dynamic DSC, conducted from ambient to 325°C with a heating rate of 10°C min⁻¹, for all investigated samples. Also, the related data analyzed from the DSC traces are given in Table II. From the results, it can be observed that the cure temperature (*T_c*) shifted to lower temperature side with the increasing level of CTBN (i.e., upto 15 wt % addition). This behavior can be interpreted in terms of intermolecular transition state of epoxy-amine systems, according to this mechanism¹⁶ strong hydrogen bonding species, such as acids and alcohols, stabilized the transition stage and strongly accelerated the reaction.

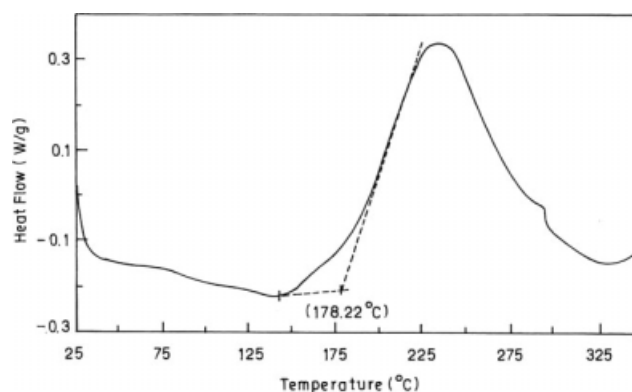


Figure 4 Dynamic DSC trace of sample CEC₀.

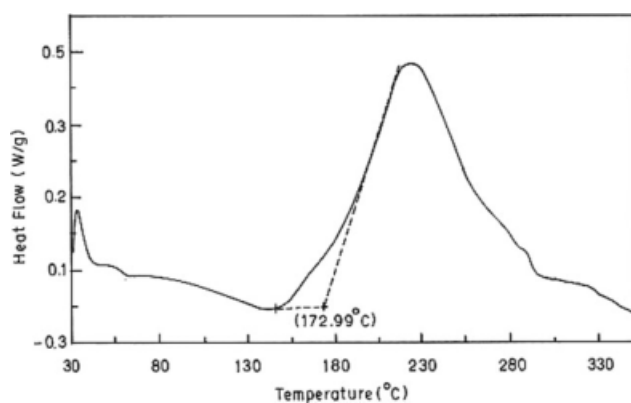


Figure 5 Dynamic DSC trace of sample CEC₁₀.

The total reaction heat values, ΔH , related to the cure process were determined from the area of the exothermic peak obtained from DSC analysis, taken in the dynamic mode, were found in the range of 168–288 J/g and decreased with the increasing content of CTBN in the blend systems (refer Table II). The decrease in the ΔH values might be attributed to the fact that the increase of CTBN modifier might induce a high reactivity of the end groups with the epoxide ring and resulting shorter curing times and, hence, the faster curing process than the unmodified resin. The decrease of cure time data revealed the same (Table II). A similar conclusion was also given by Wise et al.²² in their work based on the modification of DGEBA epoxy resin with CTBN or amine-terminated butadiene–acrylonitrile copolymer (ATBN) and cured with diamino diphenyl methane (DDM) and aniline. This may also be attributed to the formation of adduct between the resin and liquid elastomer resulting in a concomitant decrease in the net volume fraction of epoxy with increasing CTBN, which ultimately caused the reduction of ΔH values for epoxy crosslinking.

Tensile strength, elongation-at-break, and impact strength of castings of blend samples

The variation of tensile strength and elongation-at-break with CTBN contents in the castings of the

TABLE II
Data Obtained from Dynamic DSC Runs

S.No.	Sample	T_O (°C)	T_P (°C)	Heat of reaction ΔH	Cure time (min)
1	CEC ₀	178.2	232.7	288.8	17.8
2	CEC ₅	176.6	231.3	278.8	17.0
3	CEC ₁₀	172.9	230.2	232.4	16.2
4	CEC ₁₅	181.4	223.9	187.8	18.7
5	CEC ₂₀	183.2	222.7	175.3	19.0
6	CEC ₂₅	186.5	217.8	168.1	21.6

T_O , cure temperature; T_P , peak temperature of cure.

blend samples of epoxy and CTBN cured with diamine has been shown in Table III. A gradual fall in tensile strength (Fig. 6) was noted as the concentration of the elastomer phase increased. This may be due to the increase in the relative amount of dissolved rubber as the rubber content increases. The percent elongation-at-break of the blend samples increased continuously with CTBN content in the blend. The formulation with 15 wt % of CTBN showed greater impact strength, which means that it likely absorbed greater impact energies. The impact behavior of the cured epoxy could be explained on the two phase nature of the system. Similar behavior has also been reported in other rubber-modified epoxy systems and attributed to the agglomeration of the rubber particles with the increase in the rubber concentration.^{7,22–26} The presence of agglomerates acts as defect and initiates catastrophic failure. The difference in mechanical behavior can be associated with the morphological characteristics.

Scratch hardness, adhesion, flexibility, gloss, and impact resistance of cured films of blend samples

Table III showed the surface and mechanical properties of cured films of blend samples. The table clearly indicated that the cured films of all blend samples containing 5–25 wt % CTBN showed smooth and uniform with glossy surfaces. The blend samples showed improved impact resistance than that of pure epoxy resin. The adhesion and flexibility

TABLE III
Mechanical Properties of Pure Epoxy and its Blend with CTBN

Sample code	Properties of castings			Properties of films			
	Tensile strength (MPa)	Impact strength (kJ/m ²)	Elongation-at-break(%)	Gloss (60° angle)	Scratch hardness	Adhesion and flexibility	Impact resistance (kg cm)
CEC ₀	270.7	15.4	8.5	86.7	4.4	Pass	99.0
CEC ₅	258.9	20.8	9.8	88.0	4.6	Pass	112.0
CEC ₁₀	250.6	26.1	10.6	92.6	4.3	Pass	126.0
CEC ₁₅	232.1	35.9	14.9	94.8	3.8	Pass	128.0
CEC ₂₀	210.4	24.8	20.8	96.8	3.5	Pass	130.0
CEC ₂₅	198.6	18.8	24.8	87.2	3.2	Pass	98.0

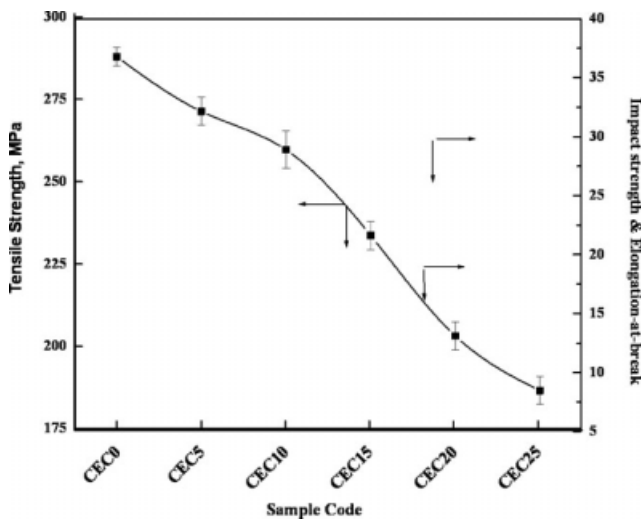


Figure 6 Graphical view of mechanical test data of samples CEC₀–CEC₂₅.

improvement may be thought due to the presence of some dissolved rubber particles inside the epoxy matrix. The decrease of crosslink density might also be an indicative of improved flexibility whereas cavitations of rubber particles inside the epoxy matrix improved the impact resistance of the films of blend samples. The addition of CTBN decreased the hardness due to increase in the flexibility of resin films. This is further clear from SEM micrographs in the proceeding paragraphs.

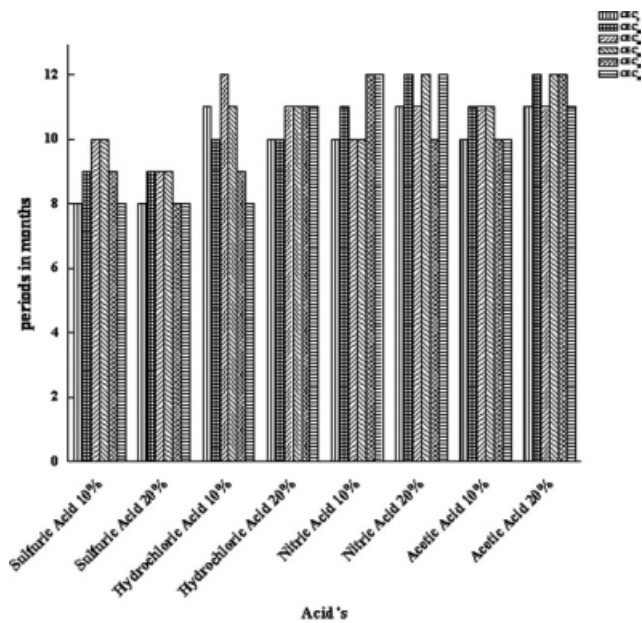


Figure 7 Comparative acid resistance of epoxy and epoxy/CTBN film showing the period after which the first effect was detected when immersed for 12 months at ambient temperature.

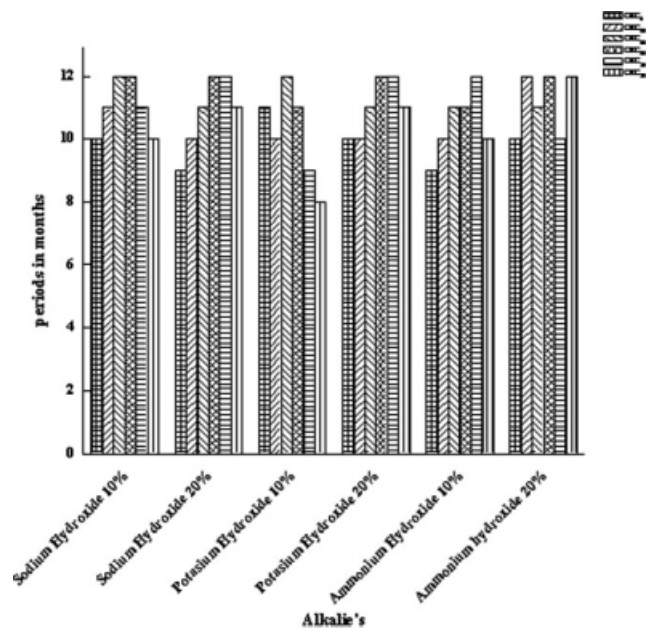


Figure 8 Comparative alkali resistance of epoxy and epoxy/CTBN film showing the period after which the first effect was detected when immersed for 12 months at ambient temperature.

Chemical resistance of the films of prepared blend compositions

The comparative acids and alkali resistance of the films of prepared blends with varying weight ratios of CTBN are summarized in Figures 7–9. A quick perusal of figures clearly illustrated that the film based on blends of CAE and CTBN has offered the

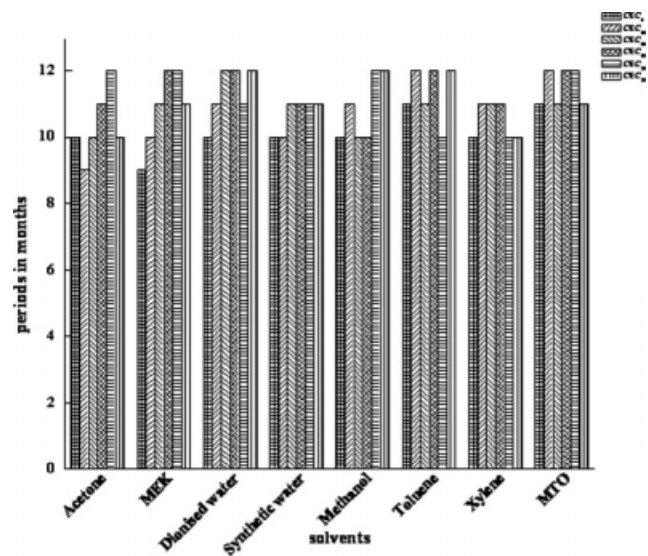


Figure 9 Comparative solvent resistance of epoxy and epoxy/CTBN film showing the period after which the first effect was detected when immersed for 12 months at ambient temperature.

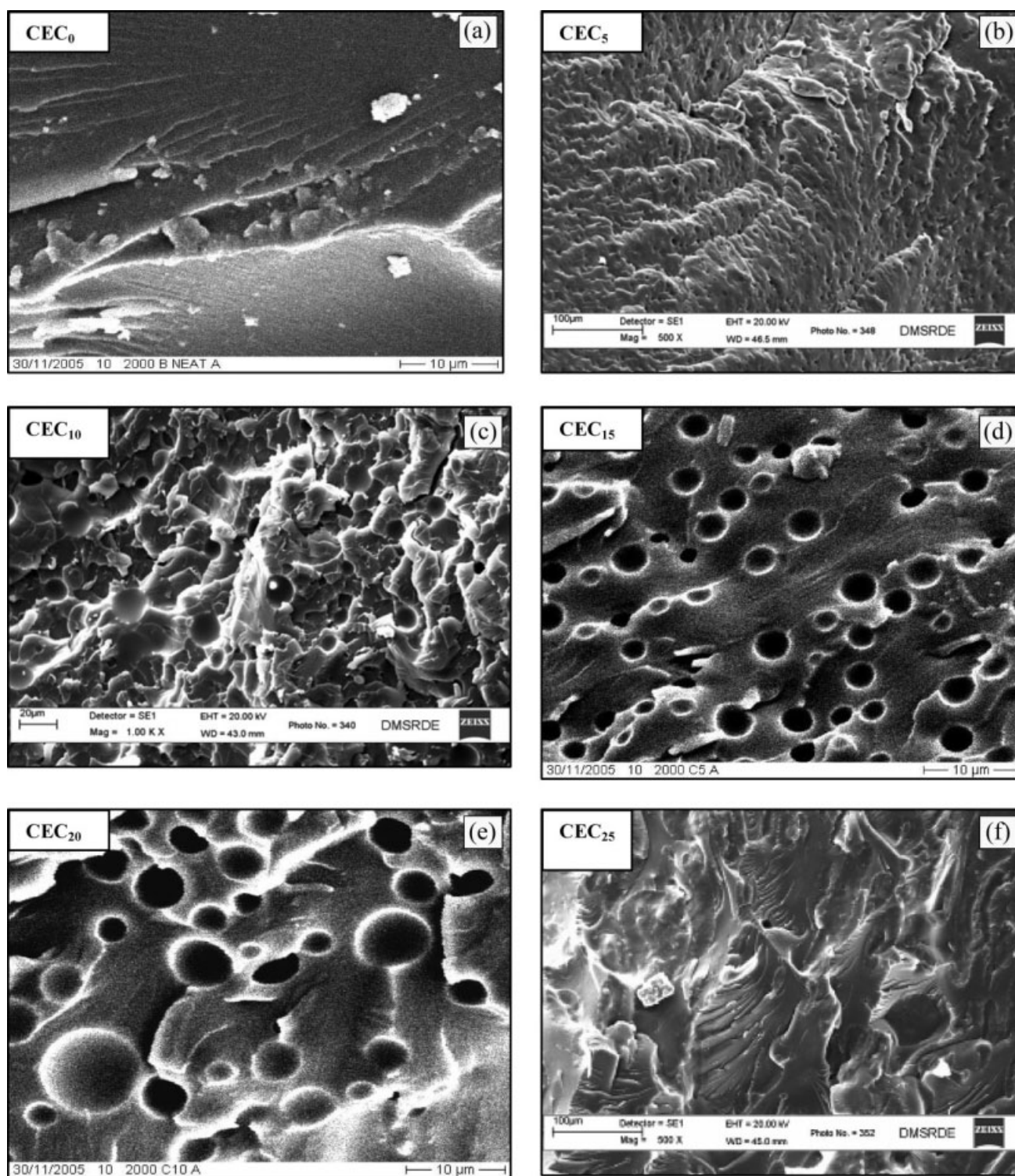


Figure 10 Scanning electron microscopic views of fractured samples, (a)–(f).

more resistance toward different concentrations of acids and alkalis as compared to films having neat compositions. This behavior can be attributed to the behavior of CAE and CTBN. At concentration more than 15 wt % CTBN might show dispersed phase

morphology between the ingredients in a slightly inferior performance.

The comparative resistances of films against different solvents are shown in Figure 9. This revealed almost similar behavior as shown with acids and

alkalis except for hydrocarbon solvents, such as MTO, toluene, and xylene.

Scanning electron microscopic analysis

Scanning electron microscopy (SEM) was used to examine the cryogenically fractured surfaces of the neat and rubber-modified epoxy blends to reveal the texture and morphology of the phase separated system. Figure 10(a)–(f) showed SEM micrographs of typical fractured surfaces of prepared sample CEC₀ and modified with 5–25 wt % of CTBN with the interval of 5 wt %.

In the micrograph of blend sample CEC₀ [Fig. 10(a)], there appeared ripples that might be due to brittle fracture surfaces of the blend system. The fractured surfaces of all modified epoxies with CTBN incorporation showed two phase morphology with a rigid continuous phase and a dispersed rubbery phase of isolated spherical particles.

As the concentration of CTBN was increased the domain size increased. A similar pattern was followed to other epoxy–rubber blends.^{27–32} Initially, CTBN was immiscible with epoxy and as the curing reaction preceded the molecular weight of the system increased and a situation was reached where CTBN got phase separated from the epoxy matrix at the onset of gelation process—a reaction induced phase separated system.

Although there were some deformation lines, the relative smoothness of these fractured surfaces indicated that the significant plastic deformation occurred. Complete phase separation was observed after curing in the samples containing 10, 15, and 20 wt % CTBN (i.e., samples CEC₁₀, CEC₁₅, and CEC₂₀). The fractured surfaces of the particular zone were shown to be characterized by numerous cavities and appreciable plastic deformation in the surrounding matrix. The fractured surfaces of blend sample with 10–20 wt % of CTBN [Fig. 10(b)–(d)] showed that the cavity wall were actually lined with a layer of rubber [Fig. 10(c)] and the cavity in this region were larger than those in the fast crack growth region [Fig. 10(e)].

The fractured surfaces of most of the rubber-toughened epoxy systems have a rigid continuous epoxy matrix with a dispersed rubbery phase as isolated particles.^{28–32} As the CTBN content was increased up to 25 wt % in the blend matrix of epoxy, the rubbery phase got more and more aggregated leading to that phase being distinguishable from the epoxy matrix. This mechanism led to the flexibilization of the matrix resulting in the reduction of mechanical properties, impact strength, and toughness.

The authors are thankful to Ciba Speciality Chemicals, Mumbai, India, for providing cycloaliphatic epoxy resin as free sample.

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