

Chemical Toughening of Epoxies. II. Mechanical, Thermal, and Microscopic Studies of Epoxies Toughened with Hydroxyl-Terminated Poly(butadiene-co-Acrylonitrile)

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Synopsis

Diglycidyl ether-bisphenol-A-based epoxies toughened with various levels (0–12%) of chemically reacted liquid rubber, hydroxyl-terminated poly(butadiene-co-acrylonitrile) (HTBN) were studied for some of the mechanical and thermal properties. Although the ultimate tensile strength showed a continuous decrease with increasing rubber content, the toughness as measured by the area under the stress-vs.-strain curve and flexural strength reach a maximum around an optimum rubber concentration of 3% before decreasing. Tensile modulus was found to increase for concentrations below 6%. The glass transition temperature T_g as measured by DTA showed no variation for the toughened formulations. The TGA showed no variations in the pattern of decomposition. The weight losses for the toughened epoxies at elevated temperatures compare well with that of the neat epoxy. Scanning electron microscopy revealed the presence of a dual phase morphology with the spherical rubber particles precipitating out in the cured resin with diameter varying between 0.33 and 6.3 μm . In contrast, a physically blended rubber-epoxy showed much less effect towards toughening with the precipitated rubber particles of much bigger diameter (0.6–21.3 μm).

INTRODUCTION

In a previous paper¹ a chemical modification procedure of a bisphenol-A diglycidyl ether with HTBN (hydroxyl-terminated copolymer of butadiene-acrylonitrile) and TDI was reported in an attempt to toughen the resin matrix for the fiber-reinforced composite applications. The structural changes were followed by infrared spectra and chemical analysis. The establishment of urethane and oxazolidone linkages were proposed under the reaction conditions employed for the purpose. A conspicuous attempt to elucidate the chemical linkages established during the reaction was made since most of the published work in the area of rubber toughening of epoxies describe procedures without conclusive evidence for the establishment of chemical linkages, though proposing simple reaction type and prereaction type in the modification process² and also mechanisms involving chemical reactions.³

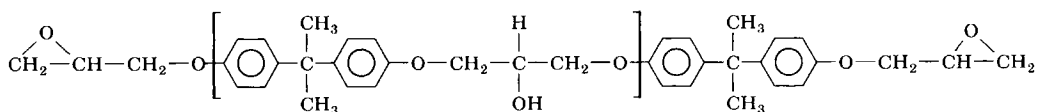
In this paper the HTBN/TDI-toughened epoxy has been evaluated for some of its mechanical and thermal properties for various levels of the elastomer (0–12%) and a comparison is made with a representative specimen

of a physically blended HTBN/epoxy mixture to bring out the advantages of chemically reacting the rubber with the epoxy resin.

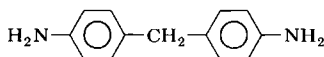
EXPERIMENTAL

Materials

The bisphenol-A-based epoxy resin system Araldite LY 556/Hardener HT 972 supplied by the Hindustan Ciba-Geigy, (Bombay, India) was used for toughening in this work. The epoxy resin had an epoxy equivalent weight of 190. The hardener is a high temperature curing aromatic diamine, diaminodiphenyl methane. The resin and hardener can be represented by the structural formulae shown below:



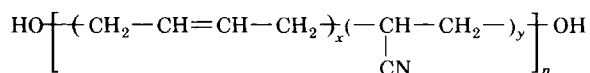
Araldite LY 556



Diaminodiphenylmethane

The tetrafunctionality of the hardener was considered for the stoichiometry of mixing resin and hardener.

The liquid rubber-HTBN (hydroxyl-terminated copolymer of butadiene and acrylonitrile) with a molecular weight of 4500 from Aldrich Chemical (U.S.A.) was used in the work. The acrylonitrile content of HTBN was 15%. The generalized structural formula can be written as



HTBN

Preparation of Cast Resin

The preparation of chemically modified Araldite LY 556 with HTBN/TDI was already presented in a prior paper.¹ The modified epoxy resin was suitably diluted with excess of Araldite LY 556 to give a composition of known (18%) rubber concentration and also of known epoxy equivalent weight. Cast resin specimens of different compositions varying in their rubber content from 0 to 12% were prepared. The compositions and the notations of these specimens are shown in Table I. The following procedure was adopted in each case to get a defect-free specimen.

The epoxy resin Araldite LY 556 was degassed under vacuum at a temperature of 100°C to remove any volatiles. To this was added the correct quantity of chemically reacted rubber/epoxy mixture of known rubber content. The mixture was heated to 120°C and stoichiometric quantities of the hardener

TABLE I
Compositions and Notations of the Toughened Epoxy Formulations

No.	Weight percentage of		Notation ^a
	Epoxy	Rubber	
1	100.0	—	EP-NEAT
2	98.5	1.5	EP-CRR-1.5
3	97.0	3.0	EP-CRR-3.0
4	94.0	6.0	EP-CRR-6.0
5	91.0	9.0	EP-CRR-9.0
6	88.0	12.0	EP-CRR-12.0
7	95.0	5.0	EP-PBR-5.0

^aEP stands for epoxy resin LY 556; CRR stands for chemically reacted rubber and PBR stands for physically blended rubber.

HT 972 in powder form was added in lots and stirred well till the hardener was completely dissolved. The mixture was poured to fill a metallic mold with a teflon releasing surface preheated to a temperature of 80–100°C. Enough care was taken to avoid air bubbles getting trapped inside. Curing was affected at room temperature for 24 h and at 120°C for 2.5 h. Post-curing was done at 180°C for 1 h.

The physically blended specimen EP-PBR-5.0 was prepared by mixing 5 parts weight of HTBN directly with Araldite LY 556 (95 pbw) and then adding hardener HT 972 in powder form to the resin mixture after heating the latter to 120°C. The rest of the procedure was the same as explained before.

Techniques

Tensile testing of cast resin specimens were done in a J. J. tensile testing machine Model T22K according to the specification no. ISO R 527 at low values of crosshead movements. Flexural tests were performed in Hounsfield tensometer as per ASTM D790. TG-DTA thermograms were recorded in the Ulvac/Shinkuriko Model TA-500 at a heating rate of 15–20°C/min between temperatures 25 and 800°C, in both nitrogen atmosphere and air. Scanning electron micrographs (SEM) were obtained with a Cambridge stereoscan Model 150 at magnifications of the order of 3000. The resin specimens were sputtered with a layer of gold before subjecting to SEM.

RESULTS AND DISCUSSION

Mechanical Properties

Table II summarises the results of the mechanical testing. Ultimate tensile strength, tensile modulus, percentage elongation, flexural strength, and toughness (the average area under the stress-vs-strain curves) are tabulated. It is seen from the results that inclusion of HTBN in the epoxy matrix below 12% generally has increased the area under the stress-vs-strain curve, a measure of toughness. It can be inferred that rubber (HTBN) inclusion up to 6% by weight has toughened the system without much reduction in the tensile strength and tensile modulus. Those formulations having more than 6%

TABLE II
Mechanical Properties of HTBN-Toughened Epoxy Formulations

Sample no.	Formulation	Ultimate tensile strength [kg/mm ² (MPa)]	Tensile modulus [kg/mm ² (GPa)]	Percentage elongation	Flexural strength [kg/mm ² (MPa)]	Toughness ^a ($\times 10^3$ J)
1	EP-Neat	6.92(67.88)	276.10(2.71)	3.48	8.02(78.6)	1.40
2	EP-CRR-1.5	6.21(60.92)	304.25(2.98)	7.27	—	3.12
3	EP-CRR-3.0	6.08(59.61)	318.00(3.12)	9.10	10.97(107.6)	4.57
4	EP-CRR-6.0	5.19(50.91)	290.00(2.84)	8.62	8.34(81.8)	3.31
5	EP-CRR-9.0	4.75(46.60)	234.70(2.30)	7.90	7.35(72.1)	2.94
6	EP-CRR-12.0	4.10(40.22)	210.25(2.06)	10.00	3.82(37.4)	3.00
7	EP-PBR-5.0	4.68(45.91)	287.28(2.82)	4.50	6.6(64.74)	1.57

^aArea under the stress-vs.-strain curves expressed in joules.

rubber show significant drop in the strength and modulus values while toughening the system. Such systems act more like flexibilized ones where ductility improves with significant drop in the strength and modulus values.

The values for the physical blend of epoxy with 5% HTBN on comparison with a nearly similar composition in the case of chemically reacted rubber

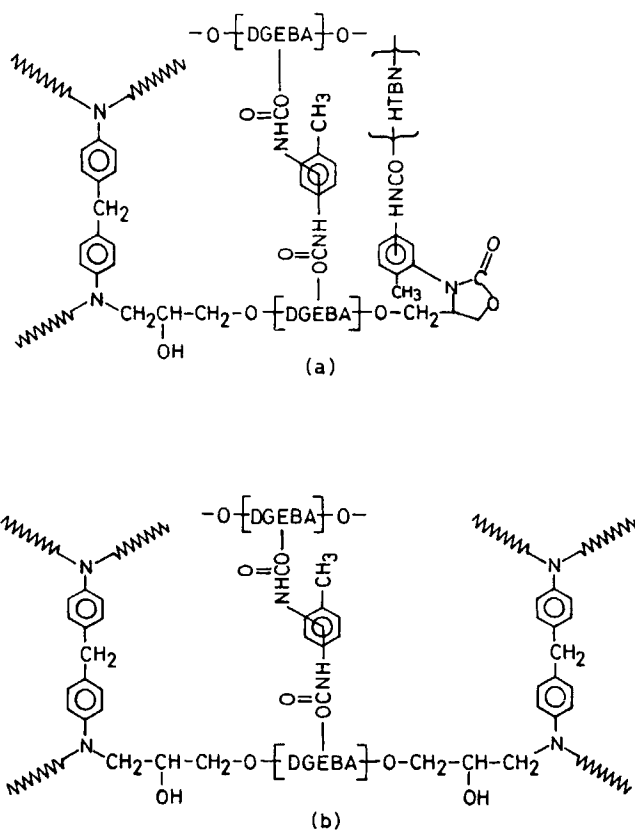


Fig. 1. Structure of different hard segments in the HTBN/TDI-modified epoxy.

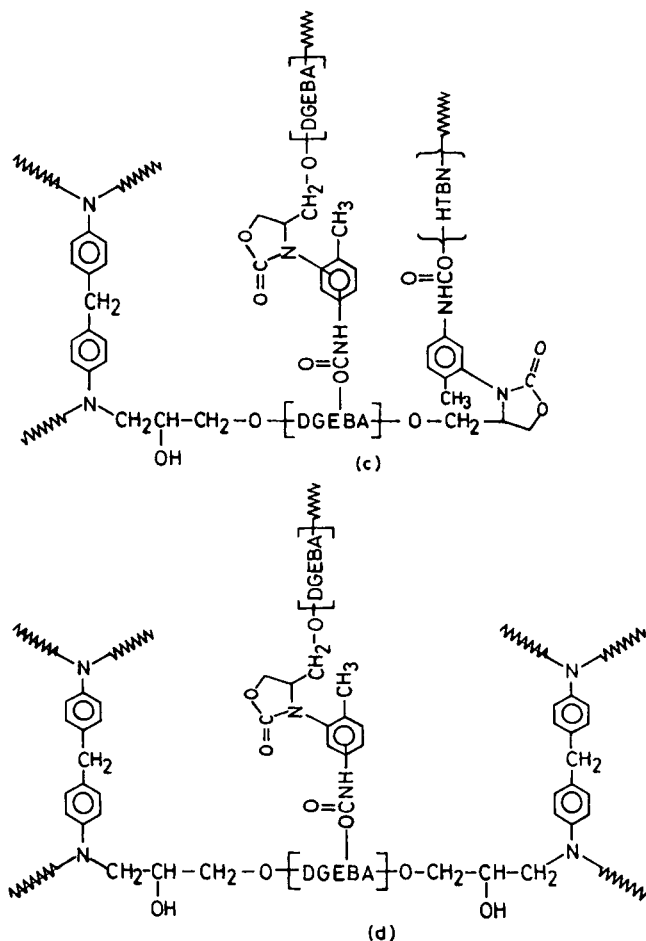


Fig. 1. (Continued from the previous page.)

shows that the latter toughens the epoxy matrix much better. The steep fall in the ultimate tensile strength will be a big disadvantage for such a physically blended system. It is interesting to note that the tensile modulus of the chemically reacted system increases slightly with increasing rubber inclusions in formulations of low rubber content (less than 6%). This may be due to an increase in the crosslink density resulting from the proposed side reaction in the modification procedure, of hydroxyl group of the epoxy resin with the isocyanate of TDI forming a urethane linkage. The other isocyanate group of the TDI molecule may have gotten linked to another epoxy molecule either through an oxazolidone formation (in case the epoxy has reacted with the $-\text{NCO}$) or through urethane linkage (in case the $-\text{OH}$ of the epoxy had reacted with the $-\text{NCO}$). The different hard segments resulting from such possible reactions are shown in Figures 1 (a)–(d), which explain the additional possibilities of forming crosslinks in the cured resin, thereby increasing slightly the crosslink density on the average per epoxy molecule.

The presence of rubber domains (as evidenced by SEM in further discussions) imparts ductility, which in turn absorbs strain energy, leading to improved toughness, and improves the percentage elongation.

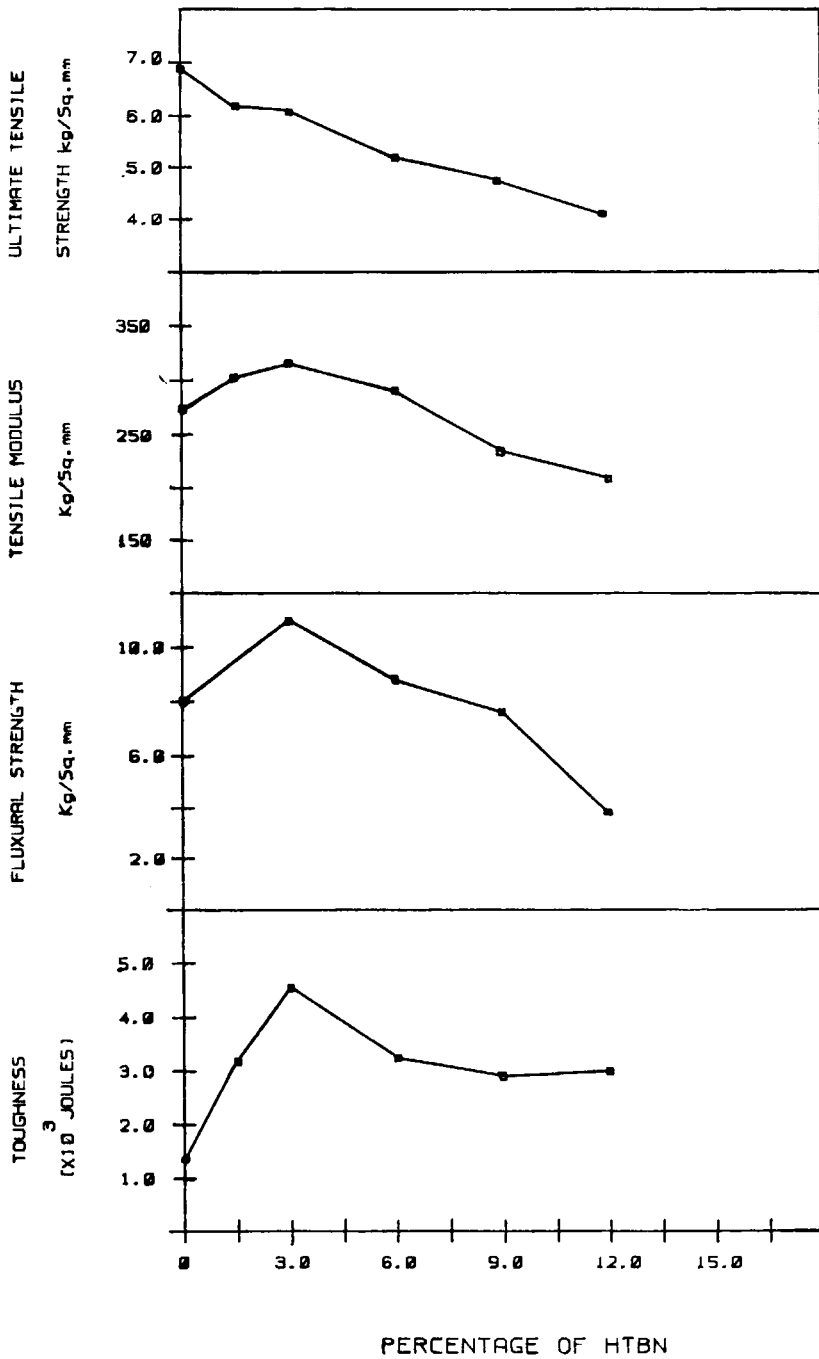


Fig. 2. Variation of (a) ultimate tensile strength, (b) tensile modulus; (c) flexural strength, and (d) toughness (area under the stress-vs.-strain curves) with rubber (HTBN) content in the cured epoxy formulations (EP-CRR series)

TABLE III
Comparison of Mechanical Properties of HTBN-Toughened Epoxy Formulations
with CTBN-Toughened Epoxies

	CTBN-toughened epoxy formulations					
	Riew et al. ³		Meeks ⁴		HTBN/epoxy formulation	
	A ^a	B ^b	A	B	A	B
Epoxy resin	100	100	100	100	100	97
CTBN	—	5	—	7.2	—	—
HTBN	—	—	—	—	—	3
Piperidine	5	5	—	—	—	—
Bisphenol-A	—	24	—	—	—	—
DDM	—	—	28.4	28.4	27	26
Tensile strength (MPa)	64.3	64.1	75.7	60.0	67.9	59.6
Tensile modulus (GPa)	2.7	2.6	2.67	2.3	2.71	3.1
Percentage elongation	4.8	9.0	6.12	5.0	3.48	9.1

^a Formulation A—without elastomeric toughener.

^b Formulation B—toughened with the elastomer (CTBN or HTBN).

Figures 2(a)–(d) illustrate how the mechanical parameters tensile strength, tensile modulus, flexural strength, and toughness (area under the stress-vs.-strain curves) vary with the weight percentages of rubber. It is seen that an optimum rubber content value of around 3% gives maximum gain in the tensile modulus, toughness, and flexural strength. Table III compares the mechanical properties of CTBN toughened epoxies reported by Meeks⁴ and Riew et al.³ with those of the HTBN-toughened epoxies of the present work. The comparison should be on the degree of improvement or deterioration of the parameters rather than the absolute values as the procedures followed for toughening, nature of the hardener, curing temperature, etc. vary widely.

Thermal Properties

The TG–DTA (thermogravimetric and differential thermal analysis) thermograms of the cured epoxy specimens, respectively, in nitrogen and air have the general shape and features shown in Figures 3 and 4.

The TG thermograms in nitrogen are characterized by a steep degradation peak. The process of degradation starts around 350°C and is almost complete around 480–500°C for all the specimens irrespective of any level of rubber inclusion (chemical or physical). In air, the TG thermograms have two broad features. The first oxidative degradation is between 350 and 450°C. The second degradation starts at a temperature of around 450°C and is so fast at the heating rates employed in the experiments that within 600°C the sample undergoes complete combustion. The corresponding DTA peak shows that it is a highly exothermic reaction.

Table IV shows the percentage weight loss of the samples during the thermal degradation in nitrogen and the first oxidative degradation in the

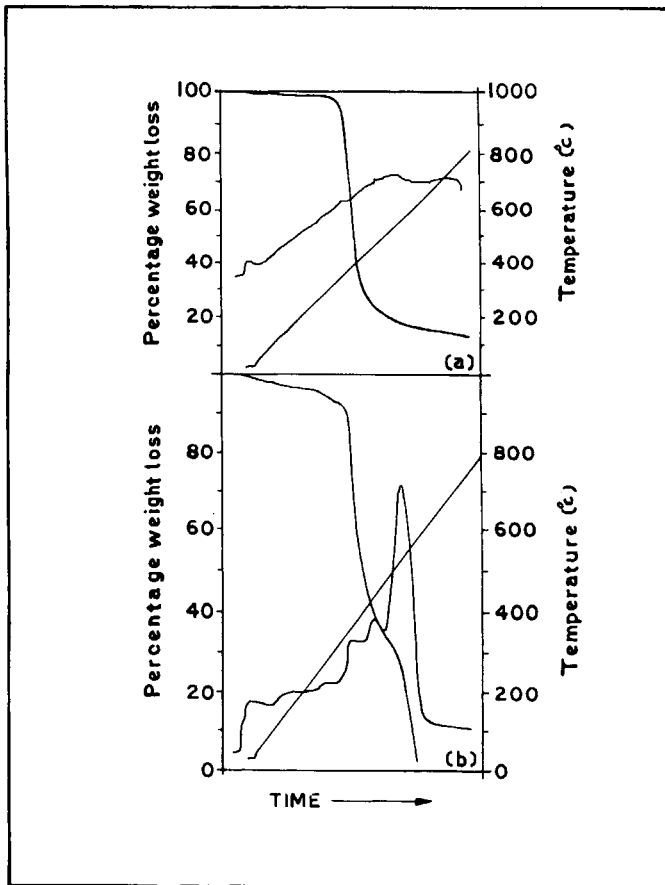


Fig. 3. General shape of the thermograms (TG-DTA) of cured epoxy formulations (a) in nitrogen at a heating rate of 15°C/min and (b) in air at a heating rate of 20°C/min.

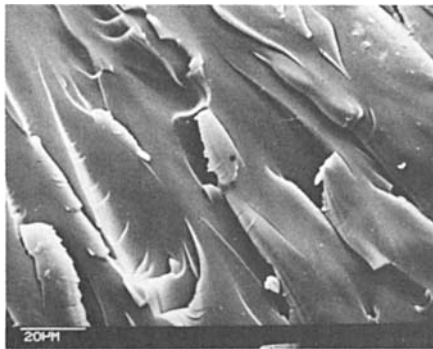


Fig. 4. Scanning electron micrograph of the fracture surface of unmodified epoxy (EP-Neat).

TABLE IV
Results of TG-DTA Experiments on the Toughened Epoxy Formulations

No.	Formulation	T_g (°C)	In nitrogen		In air	
			% Weight loss	T_L	% Weight loss	T_L
1	EP-NEAT	152	78	355	47.0	285
2	EP-CRR-1.5	152	—	—	60.5	305
3	EP-CRR-3.0	152	82-83	350	57.0	300
4	EP-CRR-6.0	152	84-85	350	52.0	285
5	EP-CRR-9.0	151	84-85	345	57.0	300
6	EP-CRR-12.0	152	84	350	71.0	290
7	EP-PBR-5.0	152	86	360	62.5	300

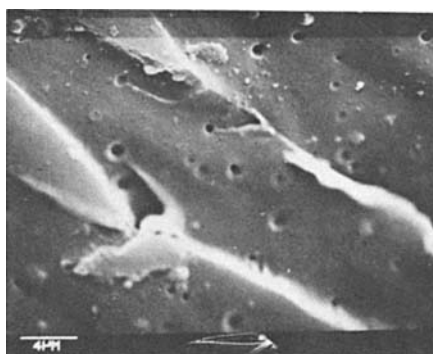
^a T_L = temperature at which 5% weight loss is noted.

case of air. In both cases the percentage weight loss is slightly more for the rubber-toughened epoxies compared to the neat resin. This may be due to the high susceptibility of the aliphatic chains of the rubber network in the molecular backbone for thermal and oxidative degradation. Nevertheless, there is no strict correlation found with the amount of rubber inclusions in tests conducted in nitrogen atmosphere. The weight losses seem to be increasing with rubber concentration in air. Similar correlation (in air) has been reported for CTBN toughened TGDDM/DDS systems.⁵

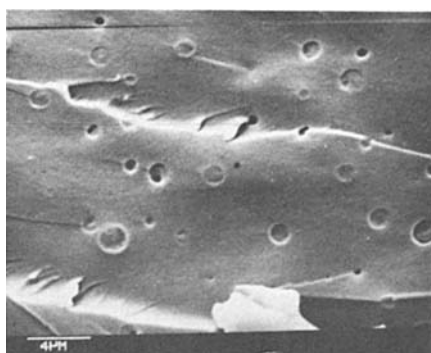
The comparable thermal performance of the toughened epoxies with the nontoughened ones can be seen from the glass transition temperatures of the cured resins (as shown by the slight baseline shift in the DTA thermograms) and the temperatures at which a 5% weight loss occurs in air and nitrogen which are also tabulated in Table IV. The glass transition temperature of the toughened compositions are almost the same as the neat resin (cured). But for slight variations in the temperatures at which a 5% weight loss occurs, the toughened ones behave similar to the unmodified epoxies under heating. This will be a big advantage for design involving such resins in FRP composites.

Morphology and Toughening Mechanism

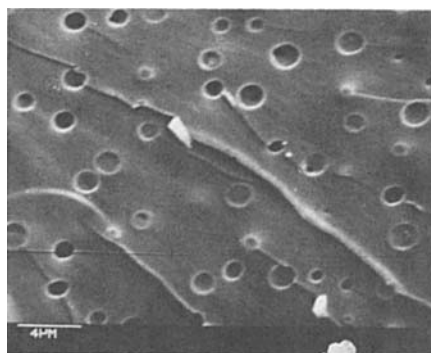
The scanning electron micrograph of the fractured surface of the neat epoxy and the rubber toughened compositions are presented in Figures 4 and 5(a)-(f), respectively. They reveal the presence of two-phase morphological feature in the latter, similar to CTBN-toughened epoxies. The soft elastomeric phase is phase-separated from the hard epoxy matrix during the early stage of cure. It is also evident from the micrographs that, within the CRR series, the size of the precipitated rubber particles increases with the increasing rubber content of the formulations. The average diameter of precipitated rubber domains, their distribution, and the related data are presented in Table V. The diameter of the particles are of the same magnitude obtained by Kunz-Douglass et al.² for a similar epoxy/hardener system toughened with CTBN, but for very minor variations arising probably due to slight variations in the molecular weight and acrylonitrile content of the rubber employed. It can be inferred from the tabulated values that the particle sizes vary between 0.3 and



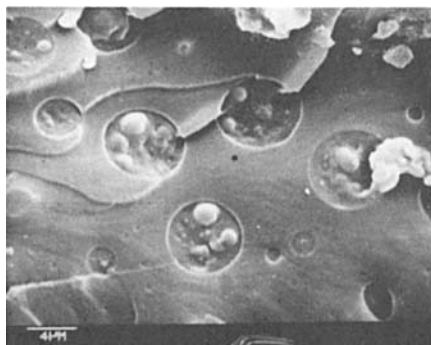
(a)



(b)

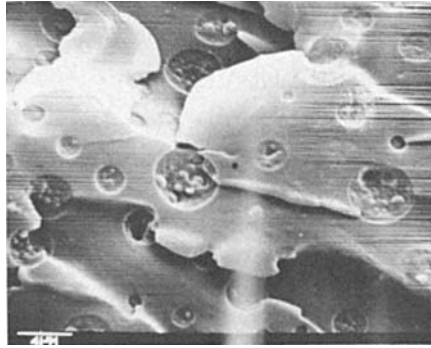


(c)

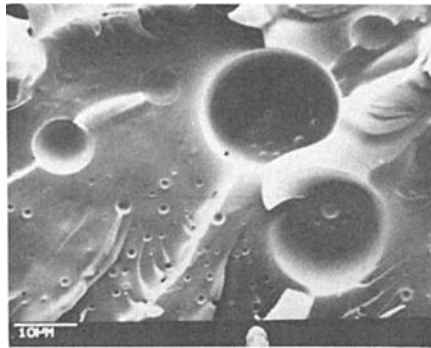


(d)

Fig. 5. Scanning electron micrographs of the fracture surface of modified epoxy specimens: (a) EP-CRR-1.5; (b) EP-CRR-3.0; (c) Ep-CRR-6.0; (d) EP-CRR-9.0; (e) EP-CRR-12.0; (f) EP-PBR-5.0.



(e)



(f)

Fig. 5. (Continued from the previous page.)

6.3 μm (even up to a concentration of 12%) for chemically reacted rubber, which is a small range compared to the values of 0.66 and 21.3 μm (for a concentration of 5%) for the physically blended ones, which represents a much broader range. Also the number of particles in the latter is much less compared to the former type.

One can draw a conclusion that a large number of smaller particles toughen the matrix better than a small number of larger particles within the CR/R

TABLE V
Average Particle Sizes and Distribution of Rubber Particles in the Toughened Epoxies

No.	Formulation	Range of particle size (μm)	Average size of particles (μm)	Number of particles (per mm^2)
1	EP-NEAT	—	—	—
2	EP-CRR-1.5	0.33-1.00	0.66	49×10^3
3	EP-CRR-3.0	0.36-1.10	0.92	59.4×10^3
4	EP-CRR-6.0	0.50-1.25	0.98	67.2×10^3
5	EP-CRR-9.0	0.77-6.30	1.63	25.4×10^3
6	EP-CRR-12.0	1.10-4.90	2.89	31.3×10^3
7	EP-PBR-5.0	0.66-21.3	2.30	10.8×10^3

series. The much smaller sizes of the particles of CRR series specimens compared to physically blended ones can be explained by the better compatibility of the chemically reacted rubber with epoxy, resulting in much smaller particle sizes, as is the case with the CTBN toughened epoxies. The poor toughening effect observed in the physical blending can also be explained by the relative easiness with which debonding can occur between the two phases during fracture. In the absence of chemical reaction, the two phases are held together by weak secondary forces of the van der Waals/hydrogen bonding type whereas, in CRR series the interphase is strong due to the establishment of covalent bonds which have to be ruptured during fracture.

No detailed studies have been made in this paper to interpret the toughening mechanisms in the HTBN-toughened epoxies which are similar to those in CTBN, for the subject is far from settled as observed by Yee and Pearson,^{6,7} even though every possible mechanism is proposed in the available literature,⁸⁻¹⁰ giving some experimental evidence supporting their mechanisms. Determination of volume fraction of the precipitated rubber has also not been attempted and hence the amount of dissolved rubber in the matrices is not known. But a few observations made with the SEM experiments are worth mentioning. There are no reasons to believe that a certain amount of reacted rubber has flexibilized the hard epoxy matrix, since from thermal data one finds that there is no reduction in the T_g of toughened formulations, even up to a concentration of 12% rubber. This observation is also supported by the fact that there is no reduction in the tensile modulus values of the formulations toughened with optimum rubber concentration (up to 6%). Had the rubber flexibilized the hard epoxy matrix, one would expect a decrease in crosslink density resulting in lowering of the modulus. On the other hand, an increase in the tensile modulus values has already been explained in a previous section.

In the scanning electron micrographs of the CRR series, one observes debonding and cavitation associated with the rubber particles of lower diameter ($< 2 \mu\text{m}$) and tearing of rubber particles as one of the features in particles of larger diameter ($> 3 \mu\text{m}$). In the optimum range of rubber concentrations (up to 6%) where the particles are invariably of sizes $< 2 \mu\text{m}$, hardly any torn rubber particles are visible. In the EP-PBR-5.0 system the situation is quite different, where even in larger particles (up to $20 \mu\text{m}$) no tearing of rubber particles is observed. This can be explained on the basis of poor interphase bonding, which arises due to secondary forces of attraction.

CONCLUSIONS

Chemical modification of commercially available epoxies with HTBN (hydroxyl-terminated copolymer of butadiene and acrylonitrile) using tolylene diisocyanate as a coupling agent has resulted in toughening the system, the extent of which is maximum around an optimum elastomer concentration of 3%. Around the same elastomer concentration the flexural strength shows a maximum before falling, with further increase in the rubber concentration. There is a continuous fall in the ultimate tensile strength with increasing rubber content in the formulations, though not significant at the optimum concentrations. There is no deterioration in the thermal properties as shown

by the T_g values and the weight loss data at higher temperatures of the neat and toughened formulations. The micrographs of the toughened formulations reveal the presence of dual phase morphology in the system with the rubber particles precipitated out from the hard epoxy matrix. Physical blending of the elastomer HTBN with epoxy results in poor toughening effects compared to a chemically modified epoxy.

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Received March 31, 1989

Accepted April 3, 1989