

Synthesis and Evaluation of Liquid Amine-Terminated Polybutadiene Rubber and Its Role in Epoxy Toughening

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ABSTRACT: Epoxy resin is widely used for coatings, adhesives, castings, electrical insulation materials, and other applications. However, unsolved problems still remain in its applications. The main problem is low toughness: cured epoxy resin is rather brittle, with poor resistance to the propagation of cracks derived from the internal stress generated by shrinkage in the cooling process from cure temperature to room temperature. The objective of this study was to improve the flexibility and toughness of diglycidyl ether of bisphenol A based epoxy resin with a liquid rubber. For this purpose, amine-terminated polybutadiene (ATPB) was synthesized. The product was characterized by Fourier

transform infrared and NMR spectroscopy and elemental analysis. ATPB-modified epoxy networks were made by curing with an ambient-temperature curing agent, triethylene tetramine. We varied the epoxy/liquid rubber compositions to study the effect of toughener concentration on the impact and thermal properties. Higher mechanical properties were obtained for epoxy resins toughened with 1 phr ATPB. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 2446–2453, 2005

Key words: polybutadiene; resins; thermal properties; toughness

INTRODUCTION

Epoxy resins were first offered commercially in 1946 and are now used in a wide variety of industries. They are used as protective coatings; in structural applications such as laminates and composites; and in tooling, molding, casting, construction, bonding, and adhesives. Epoxy resins are used as matrix materials for composites in the manufacturing of aircraft parts, rocket cases, pipes, rods, tennis rackets, ski poles, golf club shafts, and more.

Epoxy resins are also used as matrix materials for fishing poles and high-jumping rods, for which a high flexibility is required. Currently, epoxy resins constitute over 90% of the matrix resin material used in advanced composites. The most widely used epoxy resins are epichlorohydrin and bisphenol A derived resins. The raw materials for the synthesis of diglycidyl ether of bisphenol A (DGEBA) type epoxy resins are hard, rigid, and brittle and have rather low impact strengths and low elongations when they are cured. A greater elongation, a higher impact resistance, and a degree of flexibility are often desirable in many applications.¹

One can achieve the toughening of epoxy resins, especially by changing the network density, such as by modification with long-chain molecules. However,

network density can also be changed by a variety of low-molecular-weight materials and by the variation of the distance between the reactive groups in the resins and the hardener and the number of reactive groups in the monomers and the addition of monomers with lower or higher functionalities.

The most widely used method is to introduce long-chain molecules. There are basically two approaches in this method. The first is the introduction of long-chain molecules into the structures that remain unreacted after curing. These molecules can be inert plasticizers or natural and synthetic rubbers. In the second method, long-chain molecules are introduced into the epoxy, which reacts during curing. For this purpose, monofunctional or polyfunctional flexibilizers are used.^{2–5} Tong et al.⁶ used polysiloxanes to improve the flexibility of the epoxy resin. In that study, polysiloxanes were capped with bisphenol A, decanedioic acid, hexanedioic acid, and polyarylester oligomers. Tong et al. mixed the modified polysiloxanes, epoxy resin, accelerator, and phenolic resin (hardener) in a dual rolling machine. They indicated that the flexibility of the system increased when the molecular weight and dispersed particle concentration of polysiloxane was increased, and the particle size of polysiloxane decreased.

In a study by Ratna et al.,⁷ amine-terminated polysulfone (ATPS) was used as polyfunctional flexibilizer. The synthesized liquid polysulfone was mixed with a DGEBA-type epoxy resin and a triethylene tetramine (TETA) type hardener. They reported that as the ATPS

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concentration increased, the glass-transition temperature (T_g) and storage modulus (E') of the system decreased. They concluded that due to the presence of the flexible ether and sulfone linkages, ATPS increased the flexibility of the epoxy matrix. Nigam et al.⁸ reported that when epoxy cresol novolac resin (ECN) and diaminodiphenyl methane were mixed with carboxyl-terminated acrylonitrile-butadiene liquid polymer (CTBN), it caused chemical interactions between the oxirane ring of ECN and the carboxyl function of CTBN, which led to higher tensile, flexural, and impact strengths, but there was no improvement in the flexibility. Shih et al.⁹ used a synthesized poly(dimethyl siloxane) containing isocyanate groups to toughen *o*-cresol formaldehyde novolac epoxy resin cured with 4,4'-methylene dianiline. Kaynak et al.¹⁰ investigated the effect of the order of mixing of the constituents of hydroxyl-terminated polybutadiene (HTPB) with epoxy on flexibility improvement.

The aim of this study was also to toughen and improve the flexibility of a DGEBA-type epoxy matrix resin with an amine-terminated polybutadiene (ATPB) polyfunctional flexibilizer with an ambient-temperature hardener. Most of the high-performance toughened epoxy resins modified by liquid rubber reported in the literature have suffered from the problem of heat cure. Heat curing is difficult and impractical in the repair and fabrication of many structures and requires a significant amount of energy. Curing at ambient temperature saves energy and is very advantageous for fabrication and repair in the aerospace and automotive transportation industries. This prompted us to undertake this study to develop an ambient-temperature-curing adhesive formulation with an HY 840-cured ATPB as modifier. In this article, we discuss the synthesis of ATPB and the evaluation of ATPB-modified epoxy networks with respect to their thermal properties and impact strength.

EXPERIMENTAL

Synthesis of the liquid rubbers

Liquid rubber ATPB was used as a toughening agent in this study. The monomer HTPB (molecular weight ≈ 4000) was obtained from VSSC (Trivandrum, India) as a gift sample. *p*-Amino benzoic acid was obtained from Fluka (Buchs, Switzerland). The epoxy resin was a liquid DGEBA type (Ciba Geigy, Mumbai, India, Araldite LY 556) with an equivalent weight per epoxide group of 195 ± 5 . TETA (Ciba Geigy, Mumbai, India, HY 951) was used as a curing agent.

ATPB was synthesized by solution polymerization with xylene (BDH, Mumbai, India) as a solvent, *p*-toluene sulfonic acid (BDH) as a catalyst, and hydroquinone (Aldrich, Milwaukee, WI) as an inhibitor. A typical recipe included 100 g of an inhibitor-free HTPB

and 13.7 g of *p*-amino benzoic acid in the stoichiometric ratio, 150 mL of xylene, 500 mg of *p*-toluene sulfonic acid, and 500 mg of hydroquinone. The materials were introduced into a three-necked reaction flask fitted with a reflux condenser, a nitrogen gas inlet, and a thermometer. Nitrogen was slowly bubbled to remove dissolved oxygen and to provide an inert atmosphere. The mixture was heated to reflux temperature (100°C) and allowed to reflux for 6 h. The flask was then allowed to cool to room temperature, and the solvent, inhibitor, and unreacted monomer, if any, were removed by distillation. After distillation, the yield of the rubber was 95%.

Characterization of the liquid rubbers

IR spectroscopic analysis

IR spectra of the samples were obtained with a Thermo Nicolet Fourier transform infrared spectrophotometer (Nexus 870) (Berkeley, CA). The spectra of liquid polymer samples were recorded as neat between KBr discs.

NMR spectroscopic analysis

¹H-NMR spectroscopy was carried out with a Bruker AC-200 spectrometer (Faellanden, Switzerland) at 200 MHz with CDCl₃ solvent.

Viscosity measurements

Viscosity measurements were carried out with a TA Instruments model AR-1000 instrument in a parallel-plate configuration (diameter = 40 mm, gap = 1 mm) at various shear rates at 25°C.

Elemental analysis

Elemental analysis of ATPB was done with a carbon, hydrogen, and nitrogen analyzer (2400 series II CHN analyzer, PerkinElmer, Ann Arbor, MI).

Modification of the epoxy resin by ATPB and curing

Liquid ATPB was mixed with epoxy resin with stirring at 200°C for 5 h. After the mixture was cooled to 25°C, the required amount of the hardener TETA in a stoichiometric amount [26 g/equiv of epoxy group (HY 951)] was subsequently added and mixed thoroughly. The samples were cured at 25°C for 24 h and postcured for 2 h at 50°C.

Mechanical property evaluation of the liquid-rubber-modified epoxy resin

An Izod unnotched impact bulk test was carried out according to ASTM D 4812-93 specifications with an

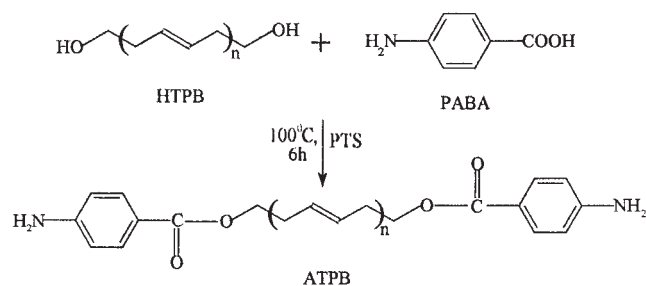


Figure 1 Reaction scheme of the synthesis of ATPB. PTS, para-toluene sulphonic acid; PABA, para-amino benzoic acid.

impact tester with a striking velocity of 3.35 ms^{-1} . Impact test specimens in all cases were $125 \times 10 \times 10 \text{ mm}^3$. The impact test was carried out at 25°C , and the impact energy was reported in J/m . Five test samples were used for each formulation.

Thermal analysis

Dynamic mechanical analysis was carried out for the cured epoxy samples with a dynamic mechanical an-

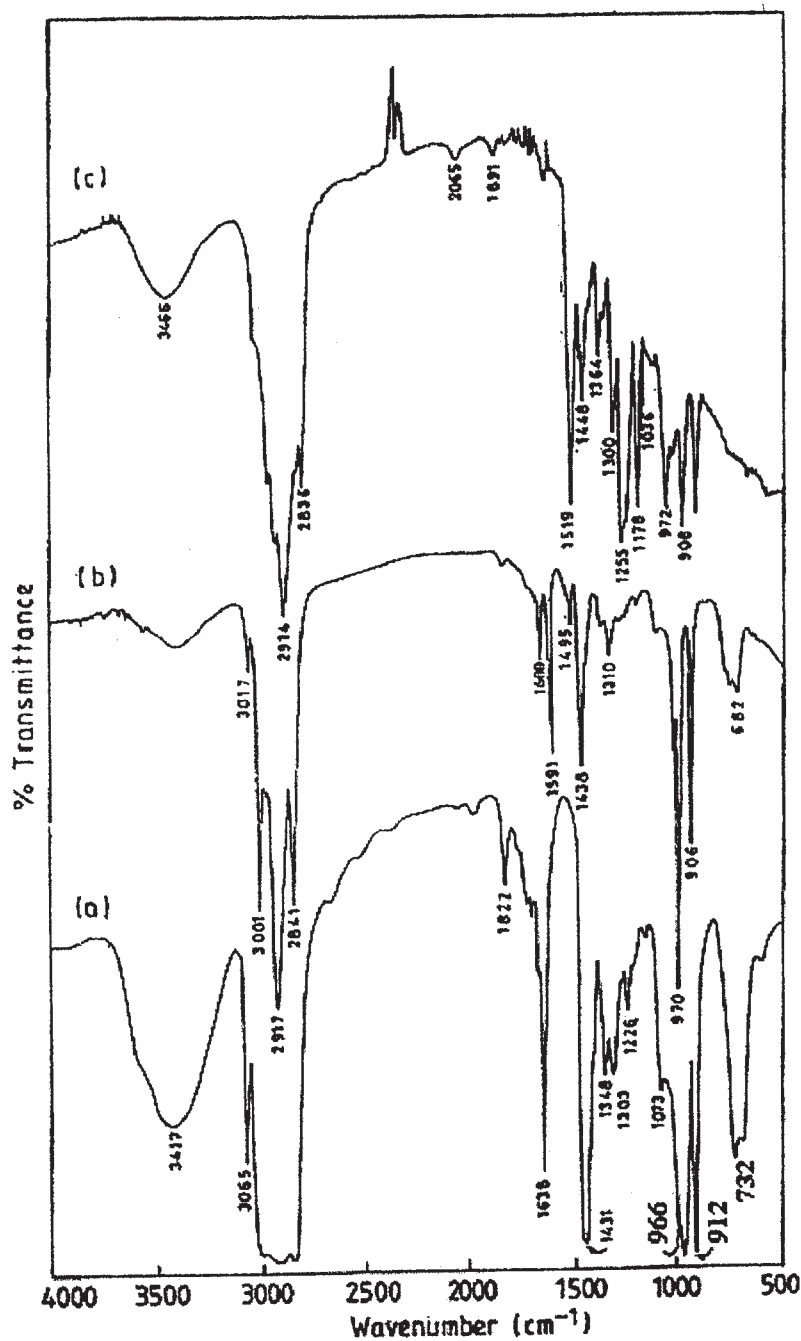


Figure 2 IR spectra of (a) HTPB, (b) ATPB, and (c) the ATPB-modified epoxy resin.

TABLE I
Cis, Vinyl, and Trans Ratio Determination of HTPB

A_C	A_V	A_T	C	V	T	Cis (%)	Vinyl (%)	Trans (%)
10.2434	24.09	77.089	17.5161	8.9524	32.3108	29.79	15.23	55.49

alyzer (DMTA MK III, Rheometric Scientific, Piscataway, NJ) at a fixed frequency of 1 Hz with a 3°C/min heating rate and with liquid nitrogen as the subambi-

ent region. Dynamic moduli and loss factors ($\tan \delta$'s) were obtained in a dual-cantilever mode for a sample $14 \times 10 \times 2$ mm in size.

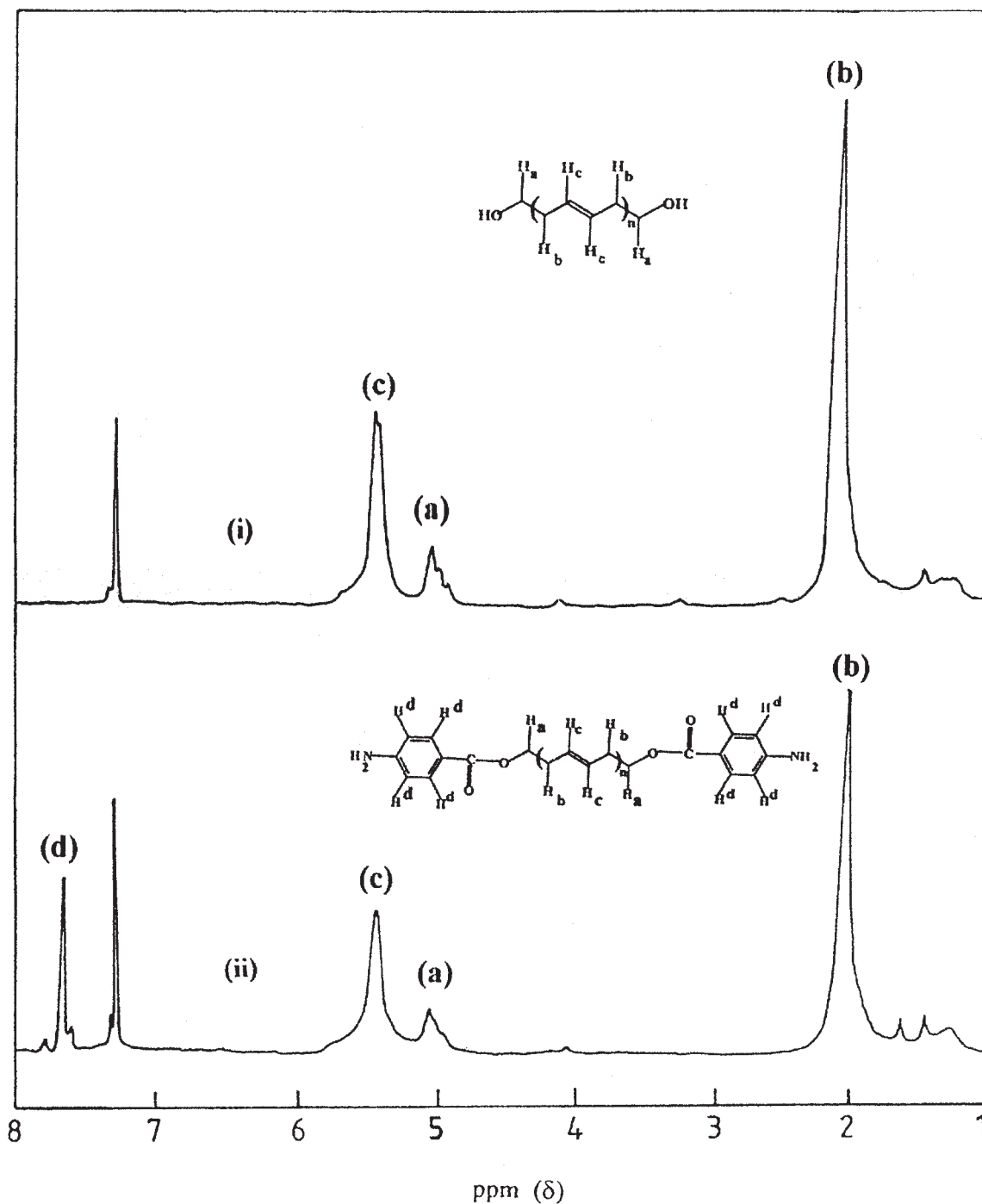


Figure 3 NMR spectra of (a) HTPB and (b) ATPB.

TABLE II
Elemental Analysis

	C (%)	H (%)	N (%)
Theoretical	86.4	10.55	0.7
Experimental	85.10	9.75	Traces not found

RESULTS AND DISCUSSION

Synthesis of the liquid rubber

The reaction scheme of the synthesis of ATPB from HTPB is shown in Figure 1.

Characterization of the liquid rubbers

IR spectroscopic analysis

To characterize the structures of HTPB and ATPB, both samples were subjected to IR analysis, and the spectra are presented in Figure 2(a,b), and prominent peaks are identified. In the IR spectra of HTPB, the peak at 3417 cm^{-1} was due to O—H stretching, and the peaks at 1636 and 3064 cm^{-1} were due to —C=C and —C—H stretching vibrations, respectively, indicating the presence of —CH=CH— groups. The peaks at 734 , 912 , and 966.3 cm^{-1} were due to the cis, vinyl, and trans conformations of the —CH=CH— group.

In ATPB, the additional peaks were at 3000 cm^{-1} , due to —C—H stretching of an aromatic ring. Unlike in the spectrum of HTPB, there was a sharp peak at 1600 cm^{-1} due to —N—H deformation and at 1309 cm^{-1} due to —C—N stretching, indicating the presence of Ar—NH_2 . This indicated the formation of ATPB.

After the epoxy resin was reacted with ATPB, the product was subjected to IR analysis, and the spectra are presented in Figure 2(c). In this spectra, the characteristics peaks of the —NH_2 group and the epoxy group were absent. This indicated epoxy ring opening by the amine groups of ATPB.

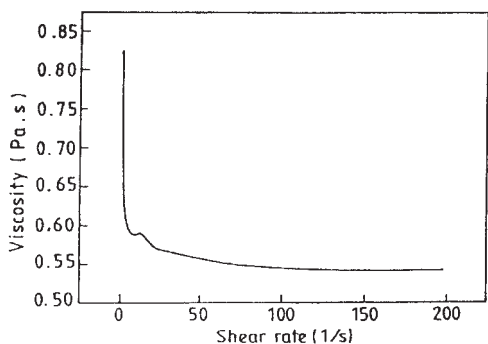


Figure 4 Viscosity measurements of HTPB.

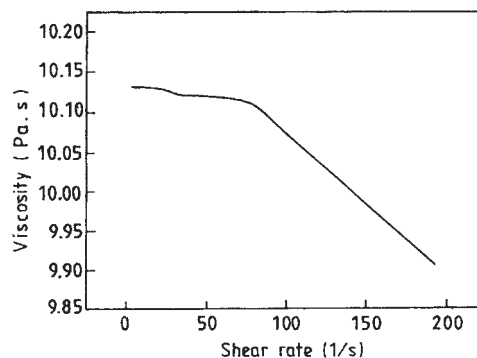


Figure 5 Viscosity measurements of ATPB.

The Morero method with IR spectra was used to determine the proportions of cis, vinyl, and trans conformations in HTPB. The peak area values for the cis (A_T), vinyl (A_V), and trans (A_T) conformations were measured from the spectra. The relative concentrations were calculated from A_T , A_V , and A_T values with the following expressions:

$$C = (1.7455 - 0.0151A_V) \quad (1)$$

$$V = (0.3746A_V - 0.0070A_C) \quad (2)$$

$$T = (0.4292A_T - 0.0129A_V - 0.0454A_C) \quad (3)$$

where C is the relative concentration of the Cis conformation in ATPB, V is the concentration of the vinyl conformation in ATPB, and T is the relative concentration of the transconformation in ATPB.

The proportions of cis, vinyl, and trans conformations are shown in Table I.

NMR spectroscopic analysis

HTPB and ATPB were subjected to analysis, and the spectra are presented in Figure 3(a,b), and prominent peaks are identified. In the spectra in Figure 3(a), the

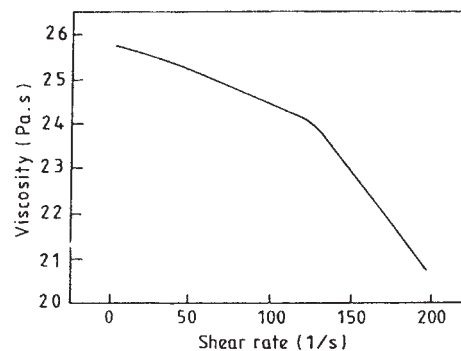


Figure 6 Viscosity measurements of the ATPB-modified epoxy resin.

TABLE III
Solubility Parameters of the Liquid Rubbers
and Epoxy Resin

Sample	Solubility parameter (J/cc) ^{0.5}
LY 556	22.30
HTPB	17.50
ATPB	21.50

peaks at 2, 5, and 5.4 ppm were due to the protons in Figures 3(a), 3(b), and 3(c), respectively. In the spectra shown by Figure 3(b), one additional peak at 7.8 ppm was found, which was attributed to the presence of an aromatic ring. This supported the formation of ATPB.

Elemental analysis

The carbon, hydrogen, and nitrogen contents of ATPB are shown on Table II. The percentages of the elements present in ATPB found experimentally were close to the theoretical values.

Viscosity measurements

From the viscosity results, it was evident that HTPB (Fig. 4) showed almost Newtonian behavior with an average viscosity of 0.60678 Pa s. However, both ATPB (Fig. 5) and the ATPB-modified epoxy (Fig. 6) showed pseudoplastic behavior, as shear thinning was evident in these two cases. The ATPB-modified epoxy had a higher viscosity than ATPB itself. This was attributed to the enhancement of the chain entanglements of longer polymeric chains. The pseudoplastic behavior of these modified liquid rubbers helped with the better dispersion of rubber into the matrix and the subsequently better morphology after curing. To evaluate its compatibility with epoxy, the solubility parameter of the liquid rubber was determined theoretically by Small's method (Table III). The close proximity of the solubility parameters ($\Delta\delta = 0.80$) indicated a high level of compatibility of ATPB with the epoxy. This viscous liquid ATPB seemed to have very good potential for use as a flexibilizer for epoxies.

TABLE IV
Compositions of Networks of Rubber-Modified
Epoxy Resins

Sample	Composition
A-0	LY 556 + HY 951 + ATPB (0 phr)
A-1	LY 556 + HY 951 + ATPB (5 phr)
A-2	LY 556 + HY 951 + ATPB (7.5 phr)
A-3	LY 556 + HY 951 + ATPB (10 phr)
A-4	LY 556 + HY 951 + ATPB (15 phr)
A-5	LY 556 + HY 951 + ATPB (20 phr)

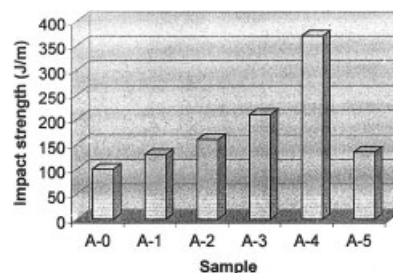


Figure 7 Impact strength of the ATPB-modified epoxy resin.

Impact properties of the modified networks

To study the effect of liquid rubber modification on the impact strength of the epoxy, various formulations were made by the incorporation of different concentrations of liquid rubbers. Various compositions of ATPB-toughened epoxy resins are illustrated in Table IV. All of the formulations were evaluated with respect to their impact properties. The evaluation was carried out for each sample after postcuring according to the test method A described in the Experimental section.

The toughening effect of the ATPB was reflected in the results of the impact resistance test, as a result of the incorporation of liquid rubber in the adhesive formulation; these results are presented in Figure 7. The toughening agent ATPB reacted with the epoxy group at 200°C and led to the chain extension of the epoxy resin. The probable mechanism is shown in Figure 8. This viscous liquid seemed to have very good potential for use as a flexibilizer for epoxies. The curing agent (HY 951) used in this study was an aliphatic amine. For the HTPB-modified epoxy resin, because the phase separation was arrested after gelling,^{11,12} the HTPB-rich phase could not undergo phase separation and thus imparted simply the plasticizing effect.¹³

A modified epoxy network with two separate phase was obtained with a chain-extended product of HTPB and an amine hardener. The higher molecular weight of the polymer decreased its compatibility with the

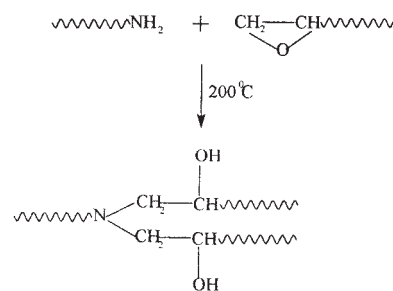


Figure 8 Mechanism of the reaction of ATPB with epoxy.

TABLE V
DMTA of the ATPB-Modified Networks

Sample	E' (GPa)	Tan δ peak temperature ($^{\circ}\text{C}$)	Tan δ_{max}
A-0	2.45	130	0.56
A-2	1.91	123	0.65
A-4	1.55	114	0.72
A-5	1.20	97	0.67

epoxy resin and initiated phase separation. The hardener at the interface was expected to react with both the epoxy group of the epoxy resin and the unreacted epoxy group of the ATPB and to form chemical bonds between the rigid matrix and rubber particles, which was necessary for effective toughening.¹⁴⁻¹⁶

Hence, both toughening and flexibility effects can be operative, resulting a maximum improvement in impact strength.¹⁷⁻²¹ The viscous liquid ATPB seemed to have very good potential for use as a flexibilizer for epoxies. It has been well established that rubber particles dispersed and bonded to epoxy matrix increase the fracture resistance by different mechanisms, namely, rubber cavitations and the formation of shear band.^{22,23} The partial miscibility of ATPB increased the ductility of the matrix and enhanced the effectiveness of the dispersed particles as toughening agents.^{22,24} The reduction in impact resistance at higher ATPB concentrations might have been due to the breakdown of the desired morphology.

Thermal analysis

To study the effect of the incorporation of liquid rubbers on the viscoelastic properties of the modified epoxy network, the pure epoxy and the modified epoxy network containing ATPB (1:1) were subjected to dynamic mechanical analysis from 30 to 150 $^{\circ}\text{C}$. All of the modified networks showed one transition peak. From the dynamic mechanical thermal analysis (DMTA) spectra, the values of E' at 35 $^{\circ}\text{C}$, tan δ_{max} , and the tan δ peak temperature were obtained and are reported in Table V. The effect of the liquid rubber concentration on the high-temperature relaxation peak is shown in Figure 9, which represent the tan δ plots against temperature for the pure and liquid-rubber-modified epoxy networks. The peak was attributed to the α relaxation of the unmodified epoxy. From the results, it was evident that E' at 35 $^{\circ}\text{C}$ and the tan δ peak temperature (indicative of T_g) gradually decreased with increasing ATPB concentration, and maximum depression was observed for the A-5 composition. E' was greatest for the A-2 system and smallest for the A-5 system (Fig. 10). A-2 and A-4 formed semicompatible blends and A-5 formed compatible blends with the epoxy. However, all of the blends exhibited a higher tan δ_{max} in

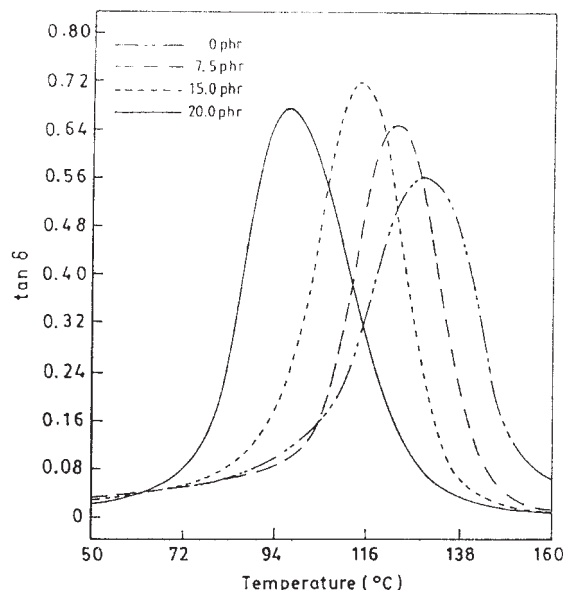


Figure 9 High-temperature relaxation of the unmodified epoxy, 7.5-phr ATPB-modified epoxy networks, 15-phr ATPB-modified networks, and 20-phr ATPB-modified networks.

comparison to the pure epoxy, indicating a better dissipation of mechanical energy and, hence, a higher impact strength. This can similarly be explained on the basis of the dual role of A-4 in imparting both flexibility and toughening characteristics to the resultant epoxy networks.

CONCLUSIONS

Liquid rubber ATPB was developed, which formed compatible blends with an epoxy resin. The developed

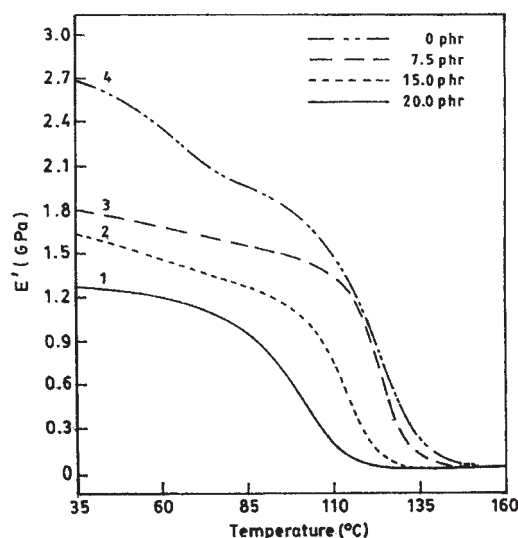


Figure 10 E' versus temperature plot of the unmodified epoxy, 7.5-phr ATPB-modified epoxy networks, 15-phr ATPB-modified networks, and 20-phr ATPB-modified networks.

ATPB, when used as a modifier for the epoxy resin and cured with a hardener (TETA), imparted toughening and flexibility.

The liquid rubber was evaluated as a toughening agent for the epoxy resin with respect to the impact strength of the modified networks. Our results show that an improvement in impact strength was achieved by the incorporation of ATPB into the epoxy matrix. The increase in the adhesive and impact strengths depended on the concentration of the modifier; the maximum increase was obtained at 5 wt % ATPB. An increase of about three- to four-fold in impact was achieved by this modification. The epoxy-ATPB formulation may be a potential ambient-temperature-cured toughened composite.

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