

# Chemical Toughening of Epoxies. I. Structural Modification of Epoxy Resins by Reaction with Hydroxy-Terminated Poly(Butadiene-co-Acrylonitrile)

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## Synopsis

In an attempt to toughen the epoxy resin matrix for fiber-reinforced composite applications, a chemical modification procedure of a commercially available bisphenol-A-based epoxy resin using reactive liquid rubber HTBN [hydroxy-terminated poly(butadiene-co-acrylonitrile)] and TDI (tolylene diisocyanate) is described. The progress of the reaction and the structural changes during modification process are studied using IR spectroscopy, viscosity data, and chemical analysis (epoxy value determination). The studies support the proposition that TDI acts as a coupling agent between the epoxy and HTBN, forming a urethane linkage with the former and an oxazolidone ring with the latter. The chemical reactions that possibly take place during the modification are discussed.

## INTRODUCTION

Toughening of thermoset matrix materials like epoxies has received much attention in the area of FRP composites, since the toughened resins improve the fracture toughness, impact strength, and delamination resistance of the composites. Reactive liquid rubber (CTBN) carboxy-terminated poly-(butadiene-co-acrylonitrile) is reported to improve the toughness of cured laminating epoxy resins.<sup>1-3</sup> The variation in the extent of toughening with concentration and acrylonitrile content of CTBN,<sup>1</sup> nature of different hardeners,<sup>4</sup> conditions of curing,<sup>5,6</sup> etc. has been the main subject of study of a number of publications. Invariably CTBN has been the liquid rubber of choice in all these studies, although liquid rubbers of other end groups are also commercially available. To a lesser extent, studies using amine-terminated liquid rubbers (ATBN)<sup>7</sup> are also available.

Since chemically linking the elastomer to the epoxy matrix results in maximum gain in toughness,<sup>3</sup> the choice of CTBN is advantageous, owing to the ready reaction under milder conditions of the carboxyl function of CTBN with the epoxy group to establish a chemical bond forming hydroxyester functions. Attempts to toughen the epoxy matrix using HTBN in a similar manner suffer from two disadvantages: The first one is the poor selectivity of HTBN towards generating a hydroxylate anion under mild conditions compared to the carboxyl of CTBN. The second is the self-polymerization of epoxy resin on employing moderately high temperatures with a Lewis base or



## Procedure for Chemical Modification of Epoxy with HTBN

### *Stage I*

A suitable quantity of the epoxy resin and HTBN, the amount of latter chosen judiciously to have the viscosity in workable range, was taken in a resin kettle. This mixture was degassed at a higher temperature to eliminate any moisture and volatiles. A few drops of *o*-chloro benzoyl chloride was added to the contents and then an appropriate quantity of TDI was added in drops while stirring. The contents were heated to 100–110°C with stirring under an inert atmosphere of nitrogen.

### *Stage II*

The tetra-*n*-butylammonium iodide catalyst was added (approximately 1% by weight of the mixture) at this stage and the reaction mixture was heated to 145–150°C. It was maintained at this temperature for nearly 1.5 h, during which time a substantial increase in viscosity was noted. The mixture was cooled to room temperature and stored in a desiccator.

### Material Characterization

Viscosity measurements were done using a Brookfield viscometer. Infrared spectra were taken as neat using Perkin-Elmer Model 577. Qualitative information on DSC were obtained with DuPont thermal analyzer 990. The heating rate was 5°C/min. Epoxy equivalent weights were determined by the HCl/dioxan method.<sup>8</sup>

## RESULTS AND DISCUSSION

The chemical modification was done in two stages in the same reaction mixture using LY 556 itself as the reaction medium. In the first stage hydroxyl group of HTBN was reacted with the isocyanate group of TDI (using excess of TDI) to form isocyanate-terminated poly(butadiene-co-acrylonitrile) elastomer dissolved in the reaction medium (Fig. 1). In the second stage the end isocyanate groups of the elastomer chain were reacted with the epoxy groups of LY 556 by adding tetra-*n*-butylammonium iodide (the catalyst) to the reaction mixture after the first stage was over (Fig. 2).

Of these two reactions the first stage reaction, i.e., the reaction of HTBN with excess difunctional isocyanates occurs very readily to yield a stable prepolymer with isocyanate end groups. Such a reaction with the polybutadiene diol has been successfully used in polyurethane elastomers. The second reaction between the isocyanate and the epoxy is also a known reaction in the chemistry of polyoxazolidones. It is reported that the reaction between epoxy and isocyanate takes place at high temperatures with<sup>10</sup> and without<sup>11</sup> catalysts to form oxazolidones. Quarternary ammonium halides are the common catalysts employed and temperatures of the order of 160°C are used. In fact, such

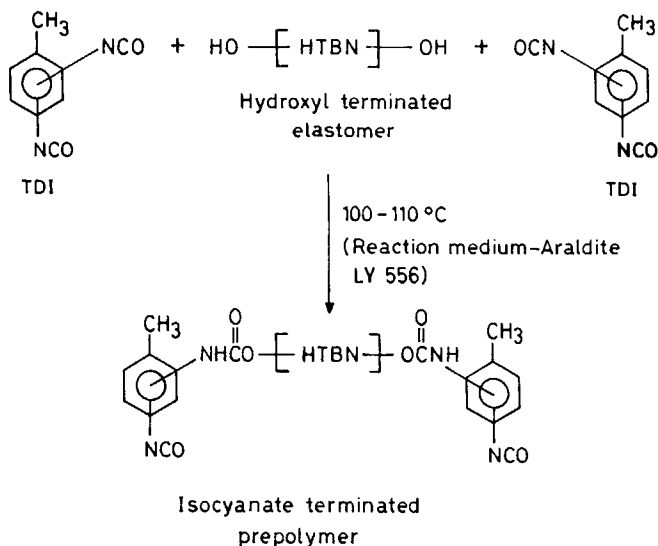


Fig. 1. Formation of isocyanate-terminated prepolymer in stage I of the chemical modification of epoxy resin with HTBN/TDI.

a reaction is used to cure diisocyanate prepolymers as an alternate to the diamines.

In the present synthetic procedure, a temperature of 150°C was employed and tetra-*n*-butylammonium iodide was used as the catalyst. The selection of the catalyst and reaction temperature is supported by the DSC thermograms of a mixture of equimolar epoxy (LY 556) and isocyanate (TDI) without and with the catalyst, tetra-*n*-butylammonium iodide [Figs. 3(a) and (b), respectively]. The presence of a reaction exotherm centered around 150°C in Figure 3(b) is due to the reaction of epoxy and isocyanate groups in the presence of the catalyst. This exotherm is missing from Figure 3(a) obtained without catalyst.

Figures 4(a) and (b) are the infrared spectra of pure LY 556 and HTBN, respectively. Figure 4(c) is the IR spectra of the reaction mixture (containing HTBN, TDI, and LY 556) after the first stage of the reaction was over. Figure 4(d) is the IR spectra of the same reaction mixture after the second stage of the reaction was completed. The following conclusions regarding the chemical linkages that were established during the modification reaction can be drawn by a comparison of these spectra.

(i) The presence of very strong absorption peaks at 3500  $\text{cm}^{-1}$  in Figures 4(a) and (b) are due to the —OH stretching vibrations of LY 556 and HTBN. The conspicuous reduction in the intensity of this peak in Figure 4(c) is due to the conversion of the hydroxyl to urethane by reaction with the isocyanate of TDI. The formation of urethane linkage is also confirmed by the appearance of a new peak in the region 3310  $\text{cm}^{-1}$  (—NH stretching).

(ii) The presence of a strong peak at 2215–2220  $\text{cm}^{-1}$  in Figure 4(b) is a characteristic one for the —C≡N group. In Figure 4(c) this same peak

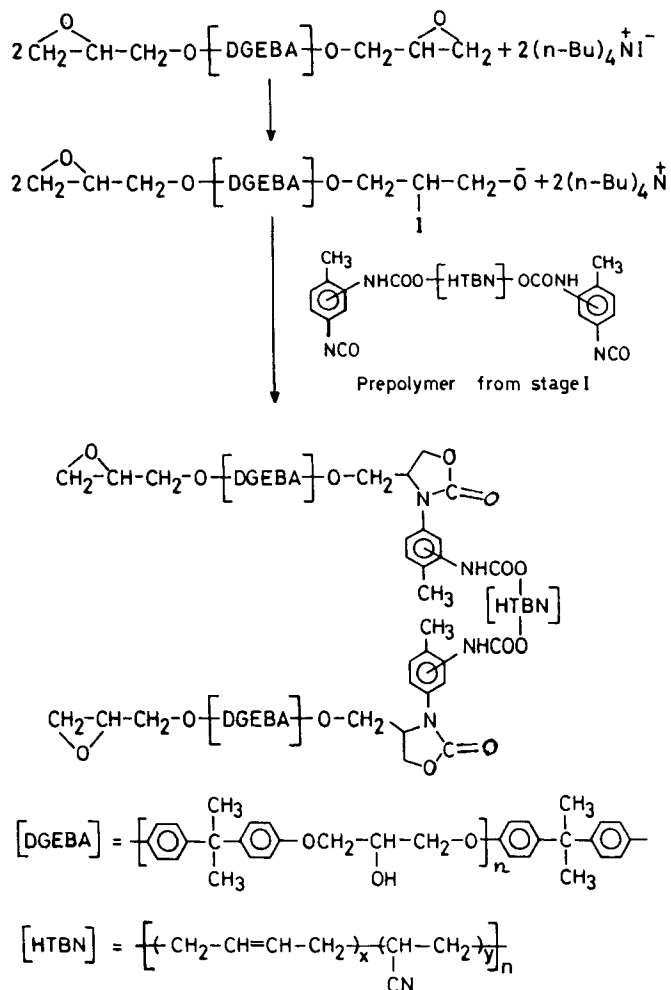


Fig. 2. Stage II in the chemical modification of epoxy resin with HTBN/TDI.

appears broad centering around  $2260 \text{ cm}^{-1}$ . This is due to the merger of  $\text{---N=C=O}$  vibration from the isocyanate-terminated elastomer with that of  $\text{---C}\equiv\text{N}$ . The  $\text{---N=C=O}$  normally appears around  $2270 \text{ cm}^{-1}$ .

(iii) The above observation is confirmed by the reappearance of the peak at  $2215 \text{ cm}^{-1}$  in Figure 4(d) with the same shape and sharpness of  $\text{---C}\equiv\text{N}$  of HTBN. Since all the isocyanates are consumed in forming oxazolidone ring, the merger of  $\text{---N=C=O}$  peak with that of  $\text{---C}\equiv\text{N}$  is not observed.

(iv) The formation of oxazolidone can also be indirectly inferred from the change in the shape and intensity of the peak at  $1730 \text{ cm}^{-1}$  in Figure 4(d) compared to Figure 4(c).

Combined with these observations, the increase in viscosity of the reaction mixture after chemical modification and also the epoxy equivalent weight of the reaction mixture before and after modification (Table I) give evidence for

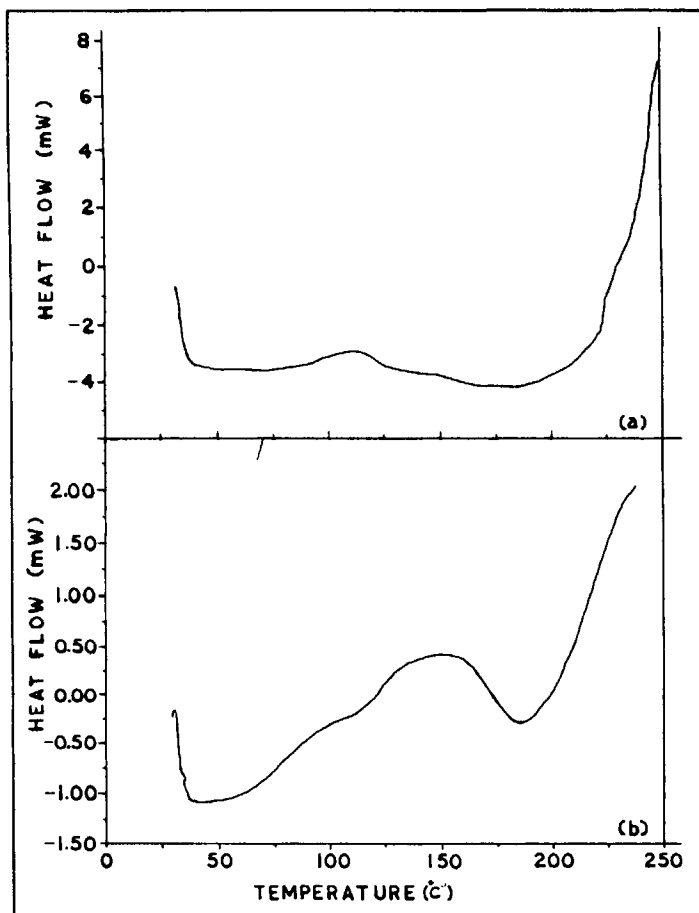


Fig. 3. (a) DSC scan of mixture (equimolar) of LY 556 and TDI at a heating rate of  $5^{\circ}\text{C}/\text{min}$  (without catalyst); (b) DSC scan of mixture of LY 556 and TDI (equimolar) with the catalyst tetra-*n*-butylammoniumiodide, at a heating rate of  $5^{\circ}\text{C}/\text{min}$ .

the chemical linkages established during the modification procedure. The substantial increase in viscosity can be explained by the increase in molecular length and hence the molecular weight of the rubber chain at the end of chemical modification, since the two ends of HTBN chain are connected to two epoxy molecules separately through reactions with the coupling agent, TDI. The decrease in epoxy equivalent weight is due to the disappearance of epoxy groups in the formation of oxazolidone linkages. However, a closer look at the epoxy equivalent weight of the reaction mixture after modification reveals that the measured value is higher than the calculated value based on the stoichiometry of the reactants. This can be explained if one considers the possible side reaction of the hydroxyl functions from LY 556 with isocyanate groups during the first stage of the reaction. Even though a primary hydroxyl function is three times as reactive as a secondary one,<sup>12</sup> this side reaction cannot be overlooked. This side reaction leaves fewer isocyanate groups than

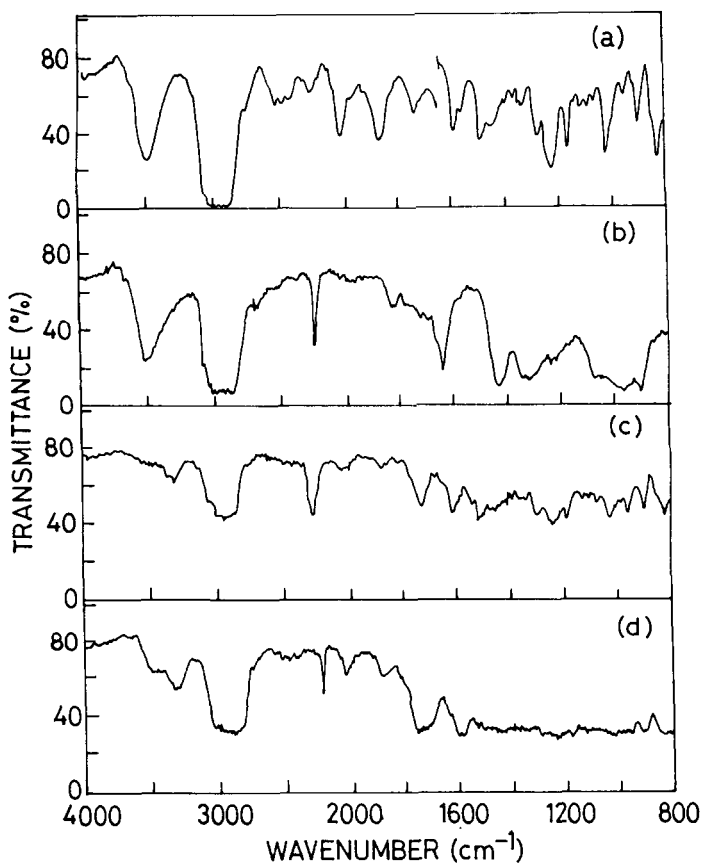


Fig. 4. Infrared absorption spectrum of: (a) LY 556 (neat, KBr disc); (b) hydroxy-terminated poly(butadiene-co-acrylonitrile) (neat, KBr disc); (c) reaction mixture (LY 556, TDI, and HTBN) after the first stage of the reaction; (d) reaction mixture (LY 556, TDI, and HTBN) after the second stage of the reaction (completion of chemical modification).

TABLE I  
Viscosity and Epoxy Equivalent Weight of the Reaction Mixture before and after Chemical Modification<sup>a</sup>

No.	Property evaluated	Before modification	After modification
1	Viscosity <sup>b</sup> (Brookfield) (cP) at 21°C	13,800	1, 10, 000
2	Epoxy equivalent weight	303.4	330.2 305.7 <sup>c</sup>

<sup>a</sup> Composition of the reaction mixture (parts by weight): Araldite LY 556, 100.0; HTBN, 51.7; tolylene diisocyanate, 6.9.

<sup>b</sup> Measured after diluting the reaction mixture with fresh LY 556 to have 12% by weight of HTBN.

<sup>c</sup> Theoretically calculated value assuming no reaction of the —NCO with the secondary —OH of LY 556.

expected at the end of the first stage for reaction with epoxy groups in the presence of tetra-*n*-butylammonium iodide in the subsequent stage.

### CONCLUSIONS

Commercial laminating epoxy resin was structurally modified with hydroxy-terminated poly(butadiene-co-acrylonitrile) using tolylene diisocyanate as coupling agent between the epoxy resin and the elastomer. TDI established urethane linkages with the hydroxyl of HTBN and an oxazolidone ring with the oxirane of the epoxy resin. The secondary hydroxyl group of the epoxy resin had entered into a secondary chemical reaction with the isocyanate during modification using this procedure.

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