

CTBN-TOUGHENED EPOXY RESINS — EFFECT OF CURING MECHANISM ON NETWORK STRUCTURE OF THE RUBBER PHASE

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ABSTRACT

Epoxy resins toughened with carboxyl-terminated butadieneacrylonitrile copolymers (CTBN) are two-phase thermosets. The network of the in situ formed rubber particles depends upon the curing mechanism of the resin. When a primary polyamine such as triethylene tetramine was used as curing agent, the network of the rubber phase was quite incomplete, whereas a perfect rubber network was formed with 2-ethyl-4-methyl imidazole as the curing agent.

INTRODUCTION

Highly crosslinked brittle epoxy resins can be toughened by incorporation of rubber particles. Liquid carboxyl-terminated butadiene-acrylonitrile copolymers (CTBN) are usually used as toughener^[1,2]. The rubber domain forms during the curing of the resin. More energy is dissipated when a crack propagates through the resin in the presence of rubber particles. Possible mechanisms of the energy dissipation are cavitation around the rubber particles, localized shear yielding of the matrix, as well as microvoiding and tearing of the rubber particles. Complete network structure of the rubber particles and well bonding at the interface are essential for any of the above mentioned mechanism to operate^[3]. On account of the experimental difficulties little information can be found concerning the effect of network structure of the rubber phase on the properties of rubber-modified thermosets. Sayre et al.^[4] have attempted to change the crosslink density of the rubber phase through γ -irradiation of amine-cured epoxy resins. However, no direct measurement on network structure of the rubber phase was made. The present paper is to demonstrate how far the network structure of the dispersed rubber phase depends upon the curing mechanism of the resin.

EXPERIMENTAL

1. Materials

Epoxy resin used in this study was diglycidyl ether of bisphenol A (DGEBA) from Wuxi Resins Factory, epoxy value 5.1 meq/g. CTBN was supplied by Lanzhou Research Institute of Chemical Industry, $\overline{M}_n$ 3840, acrylonitrile 26%. Triethylene tetramine (TETA) was chemical reagent from Beijing Chemicals Factory. 2-Ethyl-4-methyl imidazole (EMI) was chemical reagent from Tianjin Second Chemicals Factory.

2. Preparation of CTBN-modified epoxy resin

The formulations for the preparation of CTBN-modified epoxy resins are given in Tab. 1. The liquid rubber was dissolved in epoxy resin, and the blend treated at 170 °C for 1 hr to effect the reaction between carboxyl and oxirane groups. After the content was cooled to room temperature, the curing agent was introduced. The mixture was cast into a PTFE container and cured at 120 °C for 3 hr.

Table 1 Formulations (weight parts)

Sample No.	1	2	3
EGEBA	100	100	100
CTBN	0	20	20
TETA	12.4	11.2	
EMI			6

3. Characterization

The cured resin was pulverized. 10 g powder was put in a conical flask, 20 ml solvent (toluene-acetone, 9:1 by vol.) was introduced. After 3 days at room temperature, the extract was filtered. The solvent was removed in vacuo. IR spectra of the extractives were taken on a Simadzu IR Spectrometer. For GPC analysis, a Du Pont HPLC with RI detector was used, solvent THF, elution rate 0.5 ml/min.

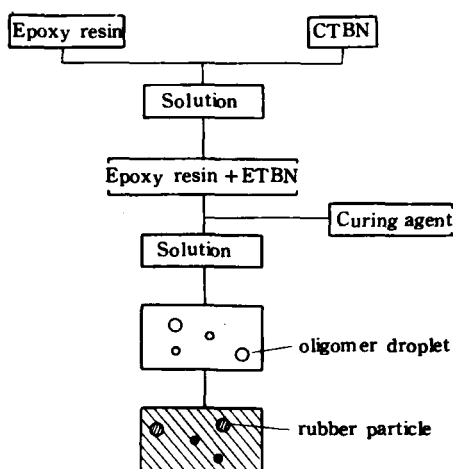


Fig. 1 Preparation of CTBN-toughened epoxy resin

RESULTS AND DISCUSSION

The preparation of CTBN-modified epoxy resins is described in Fig. 1. The liquid rubber was dissolved in DGEBA at the beginning. After a heat treatment CTBN converted into epoxy capped liquid rubber, ETBN (Fig. 5, Reaction 1). In the course of curing phase separation took place. The precipitated oligomer droplets were ETBN with some epoxy resin dissolved. Now, the question is whether the ETBN droplet can convert into perfect rubber particles while the cure of the resin matrix is accomplished.

For a given crosslinking polymerization system relation between the soluble fraction and the conversion of crosslink unit is existing^[5]. The soluble fraction can be taken as an index of the crosslinking polymerization. Although complete separation of the soluble part from dispersed rubber particles is experimentally impossible because the particles are surrounded by highly crosslinked matrix, a comparison of the soluble fraction has indicated how far the curing mechanism may affect the network of the rubber phase.

The soluble part of the unmodified resin cured with TETA (Table 1, No. 1) was less than 0.1%, which indicated the completion of the cure. For the CTBN-modified epoxy resin cured with EMI (Table 1, No. 3), the soluble fraction was also neglectable. The absence of 2250 cm^{-1} band in the IR spectrum of the extractive showed that no ETBN was removed from the cured resin. It was supposed that the rubber particles had a complete network.

From the CTBN-modified epoxy resin cured with TETA (Tab. 1, No. 2), a viscous substance was obtained by the extraction. GPC analysis showed that the extractive was roughly a mixture of DGEBA and liquid rubber (Fig. 3). The IR spectrum was consistent with the blend of ETBN and DGEBA (Fig. 2, b). Based on the extinction at 2250 cm^{-1} and 1610 cm^{-1} , the composition of the extractive was estimated, which corresponded to the blend of 82% ETBN and 18% DGEBA. All together 14% of the charged liquid rubber was collected in three repeated extractions.

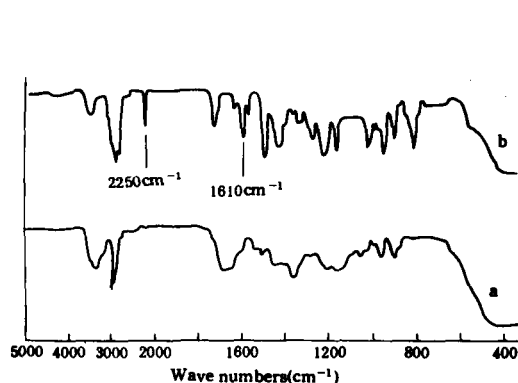


Fig. 2 IR spectra of extractives from CTBN-modified epoxy resin cured with (a) EMI, (b) TETA.

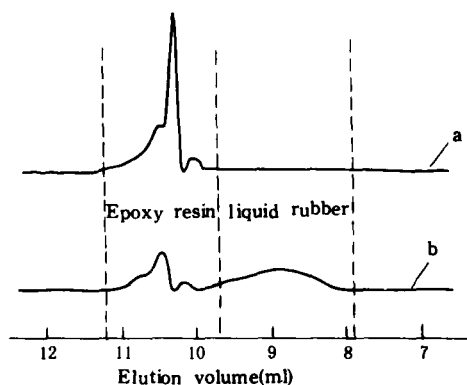


Fig. 3 GPC chromatogram of (a) epoxy resin and (b) extractive from CTBN-modified epoxy resin cured with TETA.

The surface of the resin powder after extraction was studied by using SEM. In the picture of the CTBN-modified resin cured with TETA holes of ca. $1\text{--}2\text{ }\mu\text{m}$ in diameter can be identified, while the surface of the unmodified resin is smooth (Fig. 4).

According to the above results it can be concluded that when TETA was used as curing agent, the network of the rubber phase was quite incomplete. This is understandable on account of the mechanism of the network formation.

Reactions responsible to the formation of rubber network are given in Fig. 5. When EMI was used as curing agent, the network forms through anionic

polymerization of ETBN (reaction 2) where no stoichiometry of the curative is required . When TETA was used as curing agent , the network forms through addition of N-H to oxirane groups (reaction 3) . In this case equivalence of the reactant is critical to the network structure . Analysis of the extractive of the CTBN-modified epoxy resin cured with TETA has indicated that there is insufficient TETA curative in the rubber phase

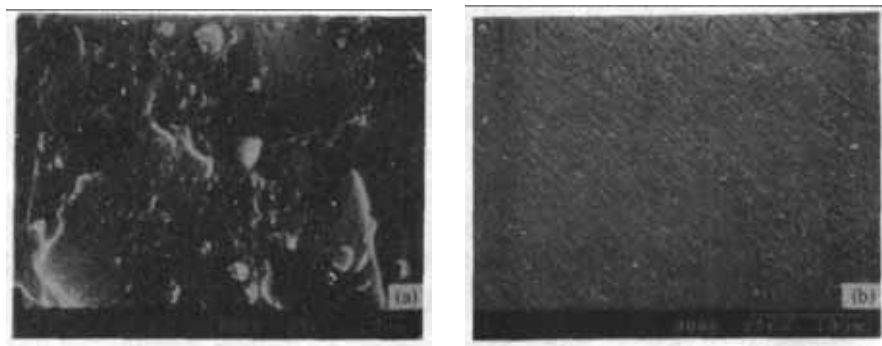
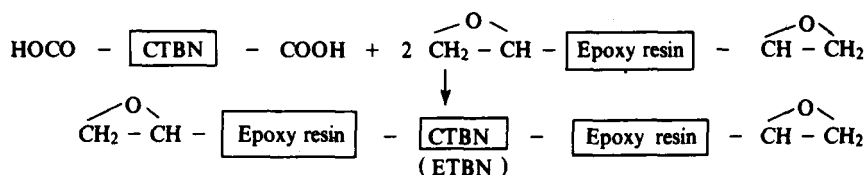
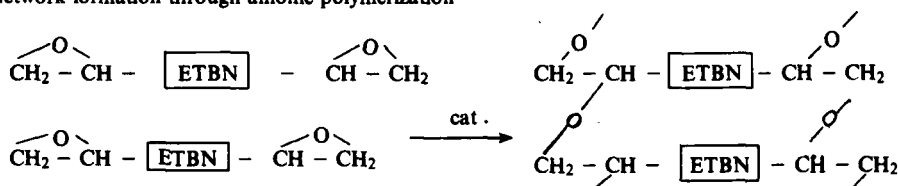


Fig . 4 SEM micrograph of the surface after extraction .
(a) CTBN-modified epoxy resin cured with TETA .
(b) unmodified epoxy resin cured with TETA .

1 . Formation of ETBN



2 . Network formation through anionic polymerization



3 . Network formation through polyaddition

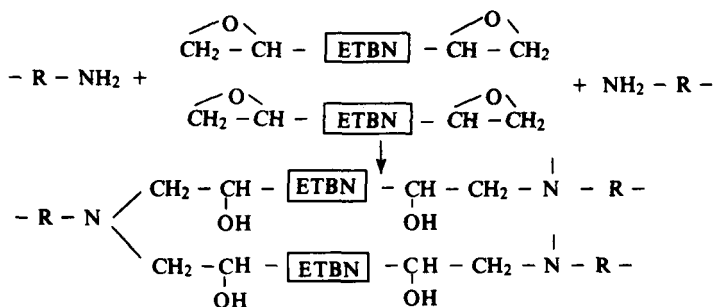


Fig . 5 Reactions responsible to network formation of the rubber phase

Primary polyamines are an important class of curing agent for epoxy resins. Many published works have been devoted to CTBN- modified epoxy resins cured with a primary polyamine. For these two-phase systems the distribution of the curing agent between the phases always might be a problem, therefore a review on the network structure of the dispersed rubber phase is necessary.

Keywords :

Epoxy resin , toughening , liquid rubber .

REFERENCES

- [1] McGarry , F . J . , *Proc . Roy . Soc .* , 1970 , A 319 , 59 .
- [2] Riew , C . K . ; Rowe , E . H . and Siebert , A . R . , *ACS Adv . Chem . Ser .* , 1976 , Vol . 154 .
- [3] Lindgren , I . F . , 29 the Nat . SAMPE Symp . , 1395 . 1984 .
- [4] Sayre , J . A . ; Kunz , S . and Assink , R . H . , *Polym . Mater . Sci . Eng .* , 1983 , 49 , 442 .
- [5] Tang Aoqing , " Statistical Theory of Polymer Reactions " (in Chinese) , Science Press , Beijing 1985 .