

## EPOXY RESINS TOUGHENED WITH CARBOXYL TERMINATED POLYETHERS

YU Yunchao (余云照) and LI Yiming (李已明)

(*Institute of Chemistry, Academia Sinica, Beijing*)

### ABSTRACT

Carboxyl terminated polyethers, the adducts of hydroxyl terminated polytetrahydrofuran and maleic anhydride, were used as toughener for epoxy resins. The morphology of the toughened resins was investigated by means of turbidity measurement, dynamic mechanical testing and scanning electron microscope observation. It turned out that the molecular weight and the carboxyl content of the polyether and the cure conditions are important factors, which affect the particle size of the polyether-rich domains and, in turn, the mechanical properties of the cured resin. Carboxyl terminated polytetrahydrofurans have a low glass transition temperature, and in appropriate amount they do not affect the thermal resistance of the resin. These advantages make them preferable as toughener for epoxy resins.

It is well demonstrated since the last fifteen years that the fracture toughness, impact strength and thermal shock resistance of thermosetting resins can be greatly improved by incorporating a suitable amount of elastomeric particles without remarkable loss in their thermal resistance<sup>[1]</sup>. Intensive studies on the carboxyl terminated butadiene-acrylonitrile copolymer (CTBN)-epoxy resin system have resulted in the development of a new generation of toughened thermosetting resins, which can be used in coatings<sup>[2]</sup>, electrical encapsulants<sup>[3]</sup>, structural adhesives<sup>[4]</sup> and fiber-reinforced composites<sup>[5]</sup>. To better understand the toughening mechanism and with the hope of obtaining further improvements in mechanical performance, a series of liquid rubbers other than liquid nitriles have been evaluated as toughener for epoxy resins, including hydroxyl terminated polypropylene oxide and polycaprolactone<sup>[6]</sup>, carboxyl terminated polybutylacrylate<sup>[7]</sup> and amino terminated polysiloxanes<sup>[8]</sup>. This article is to describe the preparation, morphology and mechanical properties of epoxy resins toughened with carboxyl terminated polytetrahydrofuran. Polytetrahydrofuran has excellent low temperature flexibility and moderate thermal resistance, and is widely used as soft segment in polyurethanes and polyether-polyester block copolymers. However, as toughener for epoxy resins, no systematic research was found in the literature.

### EXPERIMENTAL

#### 1. Preparation of specimens

**Materials** The carboxyl terminated polyethers, the adducts of hydroxyl terminated polytetrahydrofuran of molecular weight 700 to 12000 and maleic anhydride, were prepared

in our laboratory with carboxyl functionality 1.7 to 1.8, and designated as CTPE<sub>700-12000</sub>, where the index indicates the molecular weight of the polytetrahydrofuran used. Epoxy resin 616 from the Wuxi Resin Factory was diglycidyl ether of bisphenol A (DGEBA), epoxy number 5.4 meq/g. 2-Ethyl-4-methylimidazole (EMI) was a special reagent from the Tianjin Second Chemicals Factory.

|             |                 |                 |
|-------------|-----------------|-----------------|
| Formulation | Epoxy resin 616 | 100 parts (wt.) |
|             | EMI             | 10 phr          |
|             | CTPE            | 0-30 phr        |

**Procedure** The ingredients were mixed thoroughly and the mixture was cast on a glass plate into a sheet of 0.6 mm in thickness. After precure at 60 to 120°C, the sheet was released in boiling water, then cured at 150°C for an additional hour.

## 2. Morphology studies

Turbidity was measured with a 721 type photometer (the Third Analytical Instruments Factory, Shanghai). The wave length of incident light was 665 nm and the thickness of the cuvette was 1.5 mm.

Dynamic mechanical spectra were obtained using a viscoelastometer (Kukusui Electron Corp.) at 3.3 Hz over a temperature range of -196°C to 180°C at 2 °C / min.

Morphology of the toughened resins was studied by using a DX-3A type scanning electron microscope (the Factory of Science Instruments, Academia Sinica). Specimens were sputtered with a thin layer of gold before observation.

## 3. Mechanical testings

The sheet of thickness 0.5 mm was cut into dumbbells with gauge length 35 mm and width of narrow section 5 mm. Stress-strain curves were measured at 25°C on an Instron testing machine at a crosshead moving rate of 2 mm / min.

# RESULTS AND DISCUSSION

## 1. Morphology of polyether-toughened epoxy resins

The carboxyl terminated polytetrahydrofuran of molecular weight up to 12000 is soluble in the mixture of epoxy resin 616 and curing agent EMI at room temperature, forming transparent solutions. Chemical reactions including the reaction between CTPE and DGEBA molecules and the crosslinking polymerization of the resin take place during the cure. As a result of the change in thermodynamic parameters the polyether may separate from the resin matrix. Sometimes phase separation can be observed directly through the development of turbidity. Turbidity curves of CTPE-modified epoxy resins at 80°C are shown in Fig. 1. For CTPE<sub>6000</sub>- and CTPE<sub>12000</sub>-modified epoxy resins (curves 1 and 2) there is a break on the curve, beyond which the sample became opaque. For CTPE<sub>2400</sub>- and CTPE<sub>1600</sub>-modified resins, however, the turbidity developed very slowly during precuring at a temperature under 80°C or 60°C, and the cured resins were practically transparent.

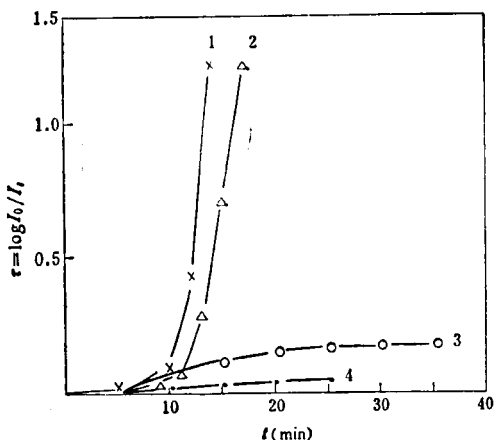


Fig. 1 Turbidity curves of CTPE (15 phr)-modified epoxy resin at 80°C

1—CTPE<sub>12000</sub>; 2—CTPE<sub>6000</sub>; 3—CTPE<sub>2400</sub>; 4—CTPE<sub>1600</sub>.

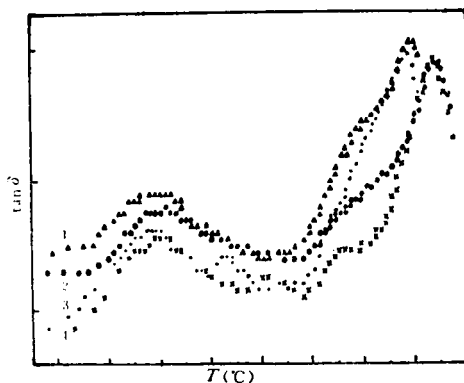


Fig. 2 Dynamic mechanical spectra of modified epoxy resins

1—CTPE<sub>700</sub> (20 phr); 2—CTPE<sub>1600</sub> (20 phr); 3—E-30 (20 phr); 4—unmodified.

Usually the appearance of a cloud point does indicate the occurrence of phase separation. However, the absence of a cloud point does not ensure the non-existence of microscopical phase separation, because the inclusion of microdomains with matched refractive index or with a diameter less than one tenth of the wave length of the observing light would not contribute much to the turbidity. For these transparent systems further investigations are needed.

Dynamic mechanical testing is a very sensitive method to study transitions in a polymer material. In Fig. 2 mechanical damping curves are shown. Curve 4 shows a glass transition temperature at 132.5°C and a  $\beta$ -transition at -84°C for the unmodified epoxy resin. Curve 2 indicates no shift in glass transition temperature of the epoxy resin by incorporating 20 phr CTPE<sub>1600</sub>, which illustrates that the resin was not plasticized by CTPE<sub>1600</sub>, thus the phase separation was perfect in this case. A much higher mechanical loss peak at -80°C resulted from the overlap of the glass transition of polytetrahydrofuran segment upon the  $\beta$ -transition of the epoxy resin.

The morphology of CTPE-modified epoxy resins was examined with SEM. Globular particles in the CTPE<sub>12000</sub>-DGEBA resins could be observed clearly in the fracture surfaces, which were believed to be polyether-rich domains (Fig. 3, a). In CTPE<sub>1600</sub>-modified resins precured at 80°C or 60°C, the particles of the separated phase were so small that they were not so distinct in the fracture surfaces (Fig. 3, b). Better pictures were obtained by a nitric acid-etching technique developed in this laboratory (Fig. 3, c-e). The particles in the CTPE<sub>1600</sub>-DGEBA resins precured at 80°C were believed to be mostly smaller than 0.1  $\mu\text{m}$ .

To be sure the differences between the turbidity curves shown in Fig. 1 did not answer the question whether the second phase existed or not, the feature of the curves depends on the domain size of the second phase.

The viscosity of the medium should be responsible for the domain size of the formed phase<sup>[9]</sup>. During the precuring of CTPE<sub>12000</sub>-DGEBA resin at 80°C, the cloud point

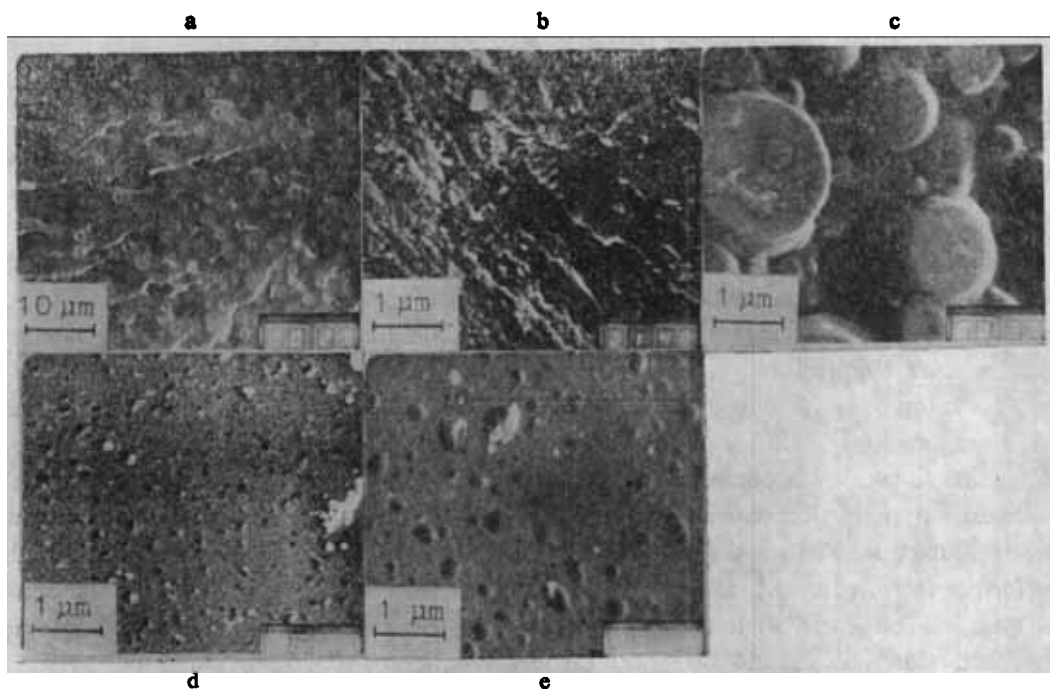


Fig. 3 Scanning electron micrograph of CTPE (20 phr)-modified epoxy resins

- a. CTPE<sub>12000</sub>, 120°C / 3h + 150°C / 1h, fracture surface;
- b. CTPE<sub>1600</sub>, 60°C / 15h + 150°C / 1h, fracture surface;
- c. CTPE<sub>12000</sub>, 120°C / 3h + 150°C / 1h, nitric acid-etched;
- d. CTPE<sub>1600</sub>, 80°C / 3h + 150°C / 1h, nitric acid-etched;
- e. CTPE<sub>1600</sub>, 120°C / 3h + 150°C / 1h, nitric acid-etched.

appeared after 12 minutes, where the viscosity of the system was low (ca. 1000 cps), so that the primary particles could agglomerate into larger globules. During the precuring of CTPE<sub>1600</sub>-DGEBA resin, the phase separation must be much later, where the viscosity of the medium was higher, although we have not ascertained when the phase separation began. Moreover, for modifier of lower molecular weight there was more opportunity for DGEBA-CTPE-DGEBA block prepolymer, formed at the very beginning of the cure cycle, to further react with other matrix molecules. Chemical bonding of the resin molecules onto the CTPE molecule might have stabilized the primary particles from agglomeration. Consequently smaller particles were formed.

In segment block copolymers there should be a low molecular weight limit for CTPE, below which no domains of second phase would form, yet we have not found this value in the molecular weight range we studied. CTPE<sub>700</sub> was partially separated from epoxy resin as shown by the mechanical damping curve (Fig. 2, curve 1). A 20°C drop in glass transition temperature of epoxy resin was estimated for 20 phr CTPE incorporation, while a 57.5°C drop is expected for a plasticized material according to the Gordon-Taylor equation. The precure temperature is a very important factor controlling the morphology of CTPE-modified epoxy resins. The end product of CTPE<sub>1600</sub>-DGEBA resin precured at a temperature under 80°C was transparent, while it was opaque if the precure temperature was above 100°C. It could be noticed from the micrograph that the particle size of the dispersed phase increased

with the precure temperature. Thus it seems that the particle size of the dispersed phase is also responsible for the difference in the transparency of the cured products. It is likely that at higher precure temperature the dispersed phase was separated from a medium of lower viscosity.

## 2. Mechanical properties of CTPE-toughened epoxy resins

Mechanical properties of CTPE-toughened epoxy resins were controlled by the particle size and the volume fraction of the dispersed elastomeric phase, which were, in turn, regulated through the molecular weight of CTPE, the CTPE concentration in the formulation and the cure temperature.

The result of tensile tests demonstrated that the toughening effect of CTPE<sub>1600</sub> for epoxy resin was apparent. Stress-strain curves are shown in Fig. 4. A 50% increase in elongation to break was obtained by incorporating 10 phr CTPE<sub>1600</sub>, while the modulus and the tensile strength were not affected. At 20 phr CTPE level the ultimate elongation was nearly doubled with only a slight decrease in tensile strength. The ultimate elongation could be further increased at the cost of modulus and tensile strength by incorporating more CTPE<sub>1600</sub>. Toughness, in terms of the area under the stress-strain curve, was improved by a factor 186%, 248% and 313% with the incorporation of 10, 20 and 30 phr of CTPE<sub>1600</sub> respectively.

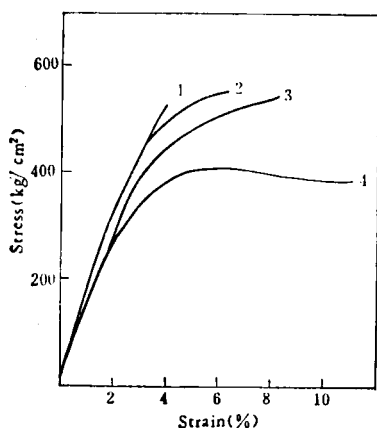


Fig. 4 Stress-strain curves of CTPE<sub>1600</sub>-toughened epoxy resin cured at 80°C/3 h and 150°C/1 h  
1—0 phr; 2—10 phr; 3—20 phr;  
4—30 phr.

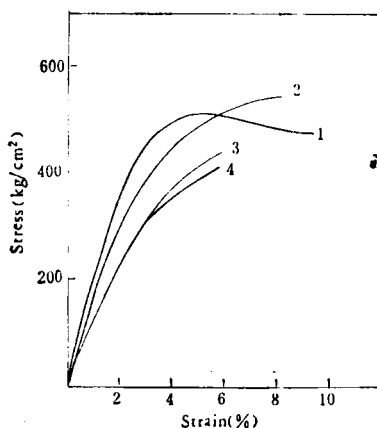


Fig. 5 Stress-strain curves of CTPE<sub>1600</sub> (20 phr)-modified epoxy resin cured at  
1—60°C/15 h + 150°C/1 h;  
2—80°C/3 h + 150°C/1 h;  
3—100°C/3 h + 150°C/1 h;  
4—120°C/3 h + 150°C/1 h.

Fig. 5 illustrates the influence of the precure temperature. The specimens were precured at 60, 80, 100 and 120°C respectively, all of them were postcured at 150°C for 1 hr. The difference in stress-strain performance was evident. The situation was more complicated in this case, because the particle size of dispersed phase was affected by the precure temperature as indicated above and, on the other hand, the precure temperature had a significant

influence on the network structure of the epoxy matrix: the end product of the epoxy resin 616 with 10 phr EMI had a higher modulus and a higher tensile strength if it was precured at a lower temperature. If the moduli of the specimens in Fig. 5 were affected by the network structure of the matrix, the ultimate elongation depended mainly on the particle size of the dispersed phase. Epoxy resins with smaller rubber particles have a higher ultimate elongation, they are tougher under tensile test.

### 3. Comparison between CTPE and CTBN

CTPE<sub>1600</sub> is a better toughener in comparison with the liquid carboxyl terminated butadiene-acrylonitrile copolymer E-30 prepared in this laboratory for toughening epoxy adhesives<sup>[10]</sup>. Both of them can be used to improve the toughness of epoxy resins (Table 1). CTPE<sub>1600</sub> has a lower glass transition temperature ( $-79^{\circ}\text{C}$ ) compared to E-30 ( $-30^{\circ}\text{C}$ ); and the  $T_g$  of modified epoxy resin was less affected by CTPE<sub>1600</sub>, while a  $20^{\circ}\text{C}$  depression has been found with an incorporation of 20 phr E-30 (see Fig. 2, curve 3). However, strict cure conditions should be observed since the morphology and mechanical properties of CTPE-modified epoxy resins are very sensitive to the cure conditions.

Table 1 Comparison between CTPE<sub>1600</sub> and E-30

| Modifier<br>(level)                                   | CTPE <sub>1600</sub><br>(20 phr) | —                 | CTPE <sub>1600</sub><br>(20 phr) | —                  | E-30*<br>(20 phr)  |
|-------------------------------------------------------|----------------------------------|-------------------|----------------------------------|--------------------|--------------------|
| Cure cycle ( $^{\circ}\text{C}$ / hrs)                | 80 / 3<br>150 / 1                | 80 / 3<br>150 / 1 | 60 / 15<br>150 / 1               | 60 / 15<br>150 / 1 | 60 / 15<br>150 / 1 |
| Particle size of rubber phase ( $\mu\text{m}$ )       | $<0.1$                           | —                 | $<0.1$                           | —                  | $\sim 0.3$         |
| $T_g$ of rubber phase ( $^{\circ}\text{C}$ )          | $-79$                            | —                 | $-79$                            | —                  | $-30$              |
| $T_g$ of resin phase ( $^{\circ}\text{C}$ )           | 130                              | 135               | 132.5                            | 132.5              | 110                |
| Tensile strength ( $\text{kg} / \text{cm}^2$ )        | 516                              | 492               | 470                              | 543                | 506                |
| Elongation to break (%)                               | 8.1                              | 4.2               | 9.5                              | 4.3                | 7.9                |
| Toughness ( $\text{kg}\cdot\text{cm} / \text{cm}^2$ ) | 29                               | 11.8              | 34                               | 16.8               | 28                 |

\* acrylonitrile content 30%,  $\bar{M}_n$  2500.

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