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Research paper

Investigation on fracture behavior and mechanisms of DGEBF toughened by CTBN

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ABSTRACT

Carboxyl-terminated butadiene-co-acrylonitrile (CTBN) was used as the toughener to improve the mechanical performance and fracture toughness of diglycidyl ether of bisphenol F (DGEBF) by prereacted approach. The results show that the chemical bonding interface was formed between DGEBF and CTBN particles in the prepolymerization reaction process, which remarkably enhances the fracture toughness of the composites. Based on the qualitative and quantitative analyses, it shows the main toughening mechanisms are the plastic shear banding effect resulted from the plastic deformation of the EP matrix and the plastic void expansion because of the debonding of CTBN particles from the EP matrix.

1. Introduction

Due to the advanced properties such as high modulus and strength, low density, high thermal resistance, and excellent chemical resistance, epoxy resins (EPs) are widely used as adhesives, coatings and matrix of composites [1–3]. However, because of their tight crosslinking network [4], EPs also exhibit undesirable shortcomings such as brittle fracture behavior and poor crack propagation resistance as well as poor impact-reistance *etc.* [5], which limits their further applications as matrix of high performance composites. For example, epoxy composites are widely applied to the explosion-proof and bullet-proof shelter for vehicles in the military and antiterrorism areas. The damage tolerance to impact epoxy composites is the key performance, which requires the EP matrix to have excellent fracture toughness. Therefore, it is important to improve the fracture toughness of the EP matrix.

There is a series of approaches for toughening brittle thermosets such as chemical modification of a given rigid thermoset backbone to a more flexible backbone structure, increasing thermoset molecular weight, lowering the crosslink density of the cured resin by means of low-functionality curing agents, and incorporating a dispersed toughener phase in the thermosetting matrix [6]. In these approaches, the toughening approach via incorporation of dispersed elastomeric phase in the resin was found to be the most effective method. Carboxyl-terminated butadiene-co-acrylonitrile (CTBN) has been widely employed since it is first reported by McGarry [7], for its good compatibility, mechanical properties and economy. The introduction of CTBN could enhance the toughness of EP through a change in material structure and stress state in the region around a rubber particle. One way to introduce CTBN rubber phase into the epoxy resins is to dissolving liquid CTBN in the EP matrix, in which the rubber phase separates from the EP matrix in the curing process and dispersed in the matrix. Sultan and McGarry [7] found that the inclusion of liquid CTBN in an epoxy gives a remarkable rise to the fracture energy. Similar study was also reported by Akbari [8], and it is found the maximum toughness was achieved at optimum content of CTBN. The other way is using preformed CTBN particles. Pearson et al [9], for instance, used preformed CTBN particles to toughen epoxy. However, in both of the above two ways, the CTBN particles are bonded to EP matrix by van der Waals forces. So the interfacial interaction between the rubber particles and the matrix is weak, which also causes undesirable reduction in strength and elastic modulus *etc.* [7–10]. Thus, it is necessary to enhance the fracture toughness without sacrifice of other mechanical properties.

In order to achieve the effective toughening results, the rubber particles are required to be chemically bonded to the EP matrix by covalent bonds [11]. This problem can be resolved by prereaction between the liquid rubber and the epoxy resin, and then curing [12–14]. Besides good fracture toughness, the prereacted composites show much higher modulus and yield stress than the mechanical blending ones. For example, Tripathi et al [14] used CTBN to toughen DGEBA by the prereaction method.

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The composites revealed the presence of two phase morphological feature, the CTBN particles were dispersed throughout the EP matrix. The toughness of the toughened composites was obviously enhanced with a slight decrease in the strength.

Prereaction method is frequently used to toughen EPs by CTBN, in which the researches are mainly focused on the epoxy resin of diglycidyl ether of bisphenol A (DGEBA). But by now, there has been rare report on the epoxy resin of diglycidyl ether of bisphenol F (DGEBF). Meanwhile, in the previous work, the toughening mechanisms are qualitatively discussed by the fracture surface analysis. Owing to DGEBF possesses lower viscosity and the better mechanical properties than DGEBA, it is widely applied in engineering fields and it is usually used as matrix in composite materials. Therefore, in this study, in order to enhance the fracture toughness without sacrifice of other mechanical properties, CTBN was used as toughener to fabricate epoxy composites (e-CTBN/EP) by prereaction approach. The influence of prereaction between CTBN and DGEBF on the mechanical performance and fracture toughness, microstructure and thermal properties of the e-CTBN/EP composites are studied. The toughening mechanisms of prereacted CTBN (e-CTBN) on DGEBF are investigated by both qualitative and quantitative analyses. The promising approach for fabricating high cost-effective epoxy composites with excellent mechanical performance and fracture toughness was proposed.

2. Experimental

2.1. Materials

The epoxy resin in this study was diglycidyl ether of bisphenol F EP (NP170) with an epoxy equivalent of 184–190 g/eq from NAN YA, China. The curing agent was polyether amine (Baxxodur^{TM} EC301) from BASF, Germany. The CTBN (1300 × 13) was provided by CVC, USA, and its main parameters are listed in Table 1.

2.2. Preparation of specimens

In amine curing system, the ideal reaction procedure is that the curing agents react firstly with the epoxy group, which suppresses the reaction between the epoxy and liquid rubber to prevent from the deteriorating of distribution of rubbery phases and ensure the chemically bonding between rubbery phases and matrix of epoxy group. So, the prereaction was conducted prior to curing to insure strong interface and properties. In general, there are two approaches for prereaction, one is catalytic prereaction, and the other one is noncatalytic prereaction. The catalytic prereaction can be operated at room temperature, but it is sensitive to the catalyst content and temperature, in which the slight fluctuations may lead to explosive polymerization. So the catalytic prereaction cannot be controlled easily. Therefore, in this study, the noncatalytic prereaction method was adopted. The concrete preparation procedures are as follows:

Firstly, the CTBN with different contents were mixed with DGEBF by a high-speed motor stirrer at the speed of 2000 rpm in ultrasonic bath, and under the protection of nitrogen environment to prepare the blends. The CTBN content of 5 phr was mixed with DGEBF for 60 min. On this basis, the stirring time for the increasing content of CTBN will prolong 20 min in turn as the content of CTBN increases by every 5 phr to get a clear homogeneous mixture. Secondly, the blends were heated to 150 °C for 30 min under the state of vacuum to ensure the prepolymerization reaction process completely. Finally, the curing agent of EC301 was mixed with the blends according to the content shown in Table 2, in which the composite mixtures were cured in a PTEF mould to fabricate the final composites. The whole schematic description of the fabrication of e-CTBN/EP composites was shown in Fig. 1.

In addition, in order to investigate the toughening effects of prereacted CTBN (e-CTBN) on epoxy resin, the unprereacted CTBN blends were also prepared as the contrast specimens.

2.3. Characterization

FTIR spectroscopy was used to monitor the reaction in the cure system of DGEBF/CTBN/EC301 and the reaction result between CTBN and DGEBF. The measurements were recorded by Thermo Scientific NicoletiS10.

The morphologies of the fracture surfaces were observed by the scanning electron microscope (SEM, Hitachi S4800, Japan). All the fracture surfaces were previously coated with gold. In addition, the dispersion of the CTBN particles in the EP matrix was also observed by the transmission electron microscope (TEM, JEM-200CX, Japan). The dimension of specimens is 0.5 mm × 0.5 mm × 100 nm, which were cut by an ultra microtome. They were collected in a trough filled with water and placed on a 200 mesh copper grids.

The glass transition temperature (T_g) of the composites was measured by the differential scanning calorimetry (DSC, Mettler-Toledo DSC823e, Switzerland). All the measurements were carried on under nitrogen atmosphere with the specimen mass of 15 mg. The specimens were tested under the temperature from 50 °C to 300 °C at the scanning rate of 10 °C/min.

The tensile properties were conducted on the SANS CMT5105 universal testing machine at the temperature of 23 °C. The measurements were carried out at the speed of 10 mm/min according to the ASTM D638-2010 standard. The dumbbell shaped test specimens dimensions were 120 mm × 10 mm × 4 mm with a measurement gauge length of 50.0 mm. At least five specimens were tested for each category.

The fracture toughness of the composites was determined by the single edge notched bend (SENB) specimens in accordance with ASTM D5045-99 as illustrated in Fig. 2. The rectangular coupons were cured in a PTEF mold with dimensions of 60 mm × 10 mm

Table 2
Compositions of materials studied.

Series	Material codes	Matrix (phr)	CTBN (phr)	e-CTBN (phr)
Neat epoxy	EP	100	–	–
CTBN/EP composites	5 CTBN	100	5	–
	10 CTBN	100	10	–
	15 CTBN	100	15	–
	20 CTBN	100	20	
e-CTBN/EP composites	5 e-CTBN	100	–	5
	10 e-CTBN	100	–	10
	15 e-CTBN	100	–	15
	20 e-CTBN	100	–	20

Phr: parts per hundreds of resin.

Table 1
Typical properties of CTBN 1300 × 13.

Acrylonitrile (%)	Carboxyl Content (phr)	Viscosity (cps @ 27 °C)	Solubility Parameter($(cal/cm^3)^{1/2}$)	Polymer Functionality	Molecular Weight
26	0.057	500,000	9.15	1.9	3150