

Toughness and Strength Improvement of Diglycidyl Ether of Bisphenol-A by Low Viscosity Liquid Hyperbranched Epoxy Resin

Daohong Zhang, Demin Jia

College of Materials Science and Engineering, South China University of Technology, Guangzhou 510641, China

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ABSTRACT: This article reports on the use of low viscosity liquid thermosetting hyperbranched poly(trimellitic anhydride-diethylene glycol) ester epoxy resin (HTDE) as an additive to an epoxy amine resin system. Four kinds of variety molecular weight and epoxy equivalent weight HTDE as modifiers in the diglycidyl ether of bisphenol-A (DGEBA) amine systems are discussed in detail. It has been shown that the content and molecular weight of HTDE have important effect on the performance of the cured system, and the performance of the HTDE/DGEBA blends has been maximum with the increase of content and molecular weight or generation of HTDE. The impact strength and fracture toughness of the cured systems with 9 wt % second generation of HTDE are 58.2 kJ/m² and 3.20 MPa m^{1/2}, which are almost three and two times, respectively, of

DGEBA performance. Furthermore, the tensile and flexural strength can be enhanced about 20%. The glass transition temperature and Vicat temperature, however, are found to decrease to some extent. The fracture surfaces are evaluated by using scanning electron microscopy, which showed that the homogeneous phase structure of the HTDE blends facilitates an enhanced interaction with the polymer matrix to achieve excellent toughness and strength enhancement of the cured systems, and the "protonema" phenomenon in SEM has been explained by *in situ* reinforcing and toughening mechanism and molecular simulation. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2504–2511, 2006

Key words: hyperbranched epoxy resin; toughness; reinforcement; molecular simulation

INTRODUCTION

Hyperbranched polymers are of interest for many applications because they are easier to synthesize than dendrimers and yet possess a high architecture, having their properties similar to dendrimers. In particular, hyperbranched polymers are often more soluble and possess a lower viscosity than linear polymers with similar molar mass and repeat unit structure, and so these materials have potential as thermoplastic tougheners for thermosets.^{1–4}

Epoxy resins are a class of versatile thermosetting polymers because of their high strength, low creep, very low cure shrinkage, excellent resistance to corrosion, good adhesion to many substrates, and appropriate electrical properties.^{5,6} However, they are brittle materials that inhibit further proliferation of the epoxy resins into various industrial applications. Hence,

modification of epoxy resins to impart fracture toughness has been the subject of intense investigation throughout the world. Epoxy resins are successfully toughened by blending them with carboxyl-terminated copolymer of butadiene and acrylonitrile (CTBN),⁷ core shell particles,⁸ rubber,⁹ PEI, and HBP.^{10–13} All these methods can availably increase toughness of epoxy resins, but the strength, including tensile strength and flexural strength, will decrease to different extend.

The aim of the present work is to investigate a novel modifier low viscosity liquid thermosetting aromatic polyester hyperbranched epoxy resin (HTDE), which could not only toughen epoxy resins diglycidyl ether of bisphenol-A (DGEBA), but also improve their tensile strength and flexural strength. To achieve this, a range of characterization techniques (including mechanical, SEM, DMA, and thermal) have been used in evaluating the effectiveness of HTDE polymer additives on the properties of the cured resin system.

Correspondence to: D. Jia (psdmjia@scut.edu.cn).

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EXPERIMENTAL

Materials

The epoxy resin used was liquid diglycidyl ether of bisphenol-A (DGEBA) (E 51 Dongfeng Chemical

TABLE I
Properties of the HTDE

HTDE	Molecular weight (g/mol)	Epoxy equivalent weight (g/mol)	Viscosity (cp)	Molecular weight distribution (M_w/M_n)
HTDE-1 (G1)	1,400	312.5	550	1.11
HTDE-2 (G2)	3,400	400.0	700	2.06
HTDE-3 (G3)	7,400	454.5	500	1.88
HTDE-4 (G4)	15,500	526.3	350	1.83

Corp., China) containing 5.1 mmol epoxy group per gram of resin. The curing agent was DETA-AN, which was produced by the addition reaction of equal molar of acrylonitrile (AN) and diethylene triamine (DETA).

The hyperbranched epoxy resin (HTDE) consists of a highly branched aromatic polyester backbone. The characteristics of the HTDE are shown in Table I; the viscosity of the HTDE were measured using a Brookfield DV-II+ Viscometer with RV-S06 spindle at 25°C and at rotational speed of 20 rpm. The molecular weight distribution were measured by Agilent 1100 Series HPLC, the Agilent PLgel 5 μ m MIXED-C as GPC fixed phase, and the tetrahydrofuran (THF) as flowing phase. The structure of the HTDE-3 is shown

in Figure 1. The HTDE was prepared from the carboxy-terminated hyperbranched precursor.¹⁴

Preparation of HTDE/DGEBA blends and curing

The HTDE-filled samples were prepared by blending the HTDE in the DGEBA at about 25°C through stirring with glass stick. The modified resin was mixed with a stoichiometric amount (formulation given in Table II) of DETA-AN by continuously stirring the mixture for 5 min at about 25°C, and the mixtures were cured in a silicone rubber mold at about 25°C for 5 h and post cured at about 80°C for 2 h after being degassed under vacuum for 10 min and become trans-

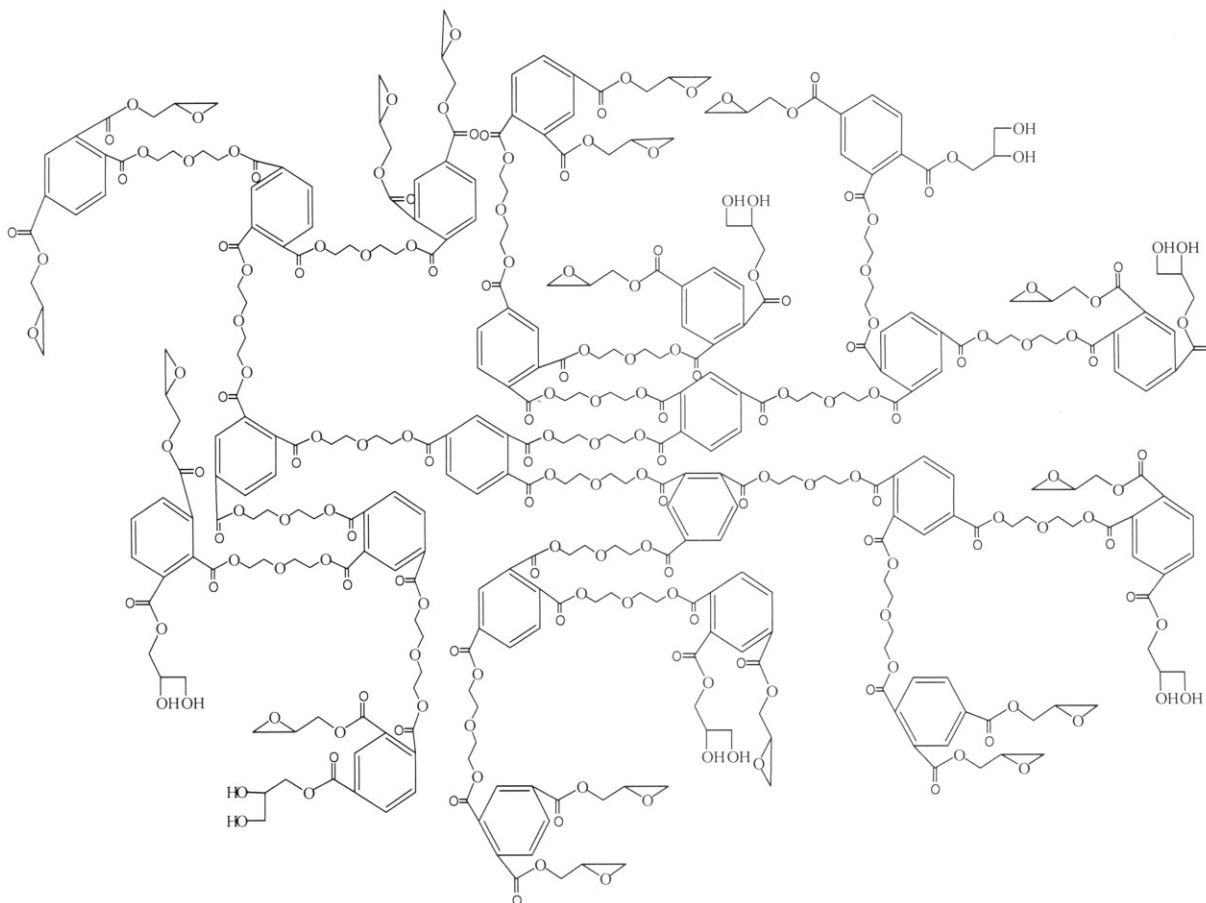


Figure 1 Idealized molecular structure of the third generation hyperbranched epoxy resin (HTDE-3).

TABLE II
Formulation of Curing Samples

Content of HTDE (wt %)	DGEBA (g)	HTDE (g)	DETA-AN (g)
3	48.5	1.5	10.8
6	47.0	3.0	10.6
9	45.5	4.5	10.4
12	44.0	6.0	10.2
15	42.5	7.5	10.0
20	40.0	10.0	9.6

parent. Blends containing 0–20 wt % HTDE, including HTDE-1(G1), HTDE-2(G2), HTDE-3(G3) and HTDE-4(G4), were made. Afterwards, the mechanical performance of the cured system were measured after the samples were cooled gradually to room temperature and placed for 12 h.

Characterization of blends

Differential scanning calorimeter (DSC) measurement was carried out on the cured samples for attaining their T_g with a DSC204 F1, (NETZSCH Gerätebau GmbH) using 8–10 mg samples in aluminum pans. Thermal scans at constant heating rate of 10°C/min were performed in a temperature range of 20–100°C for all the cured samples.

Dynamic mechanical thermal analysis (DMTA) was performed on the cured materials for attaining $\tan \delta$ traces with a DMA242 (NETZSCH Gerätebau GmbH), by ramping from –100 to 150°C at the rate of 3°C/min at a frequency of 2 Hz, and the samples dimensions was 1 × 4 × 20 mm³.

The HDT3 VICAT (CEAST, Italy) was used to measure the Vicat temperature and study the heat-resistant performance of the cured samples. The constant heating rate and load were 120°C/h and 49.053N, respectively.

No-notch impact strength of the modified epoxy samples were determined by a Zwick-5113 (ZwickRoell, Germany) digital impact tester according to ASTM D256. The sample size used for the test was 80 × 10 × 4 mm³. The impact test was carried out at room temperature (25°C) and span was 60 mm, and impact strength σ_1 (calculated by $\sigma_1 = 1000A/(bh)$, A , b , and h , respectively, refer to impact energy, width, and thickness of the sample) was reported in kJ/m². Their tensile strength was measured by AG-1 omnipotent electron tensile tester (AG-1 Japan) according to ASTM D638. The dumbbell sample size was 75 × 5 × 5 mm³, and the tensile rate was 10 mm/min.

Fracture toughness testing was carried out by using the compact tension method according to ASTM D5045–96, using an Instron 5500 universal tester. Prior to testing, the specimens were “precracked” by inserting a thin razor blade into the machined notch and

pulling with strong force. The specimens were then placed into a jig and tested at a cross-head speed of 5 mm/min. After fracture, the exact crack length was measured from the fracture surfaces and the fracture toughness at crack initiation, in terms of the critical stress intensity factor, K_{IC} , was calculated by using the following equation:

$$K_{IC} = (SP/BW^{3/2})F(x) \quad (1)$$

where P is the maximum load in kN; B and W are the thickness and width of the specimen in cm, respectively; S is the span (64 mm); and $F(x)$ is expressed as follows:

$$F(x) = 3/2x^{1/2}[1.99 - x(1 - x)(2.15 - 3.93x + 2.7x^2)]/[(1 + 2x)(1 - x)^{1.5}] \quad (2)$$

where $x = a/W$ and a is the crack length. The size of the specimen was 80 × 10 × 4 mm³.

Their flexural properties were determined according to ASTM D790 by using an Instron 5500 universal testing machine. The strength was determined in a three-point bending mode by using samples of dimensions 80 × 10 × 4 mm³.

A low voltage scanning electron microscope (SEM) (XL-30FEG, Philip) was used to examine the fracture surface morphology of the samples. A thin section of the fracture surface was cut and mounted on an aluminum stub using a conductive (silver) paint and was sputter-coated with gold prior to fractographic examination. SEM photo micrographs were obtained under conventional secondary electron imaging conditions, with an accelerating voltage of 15 kV.

RESULTS AND DISCUSSION

Tensile strength

Effect of the content and molecular weight of HTDE on the tensile strength of the cured systems are shown in Figure 2. Tensile strength increases first and decreases afterwards with the increase of HTDE content, and so the tensile strength is maximum with the change of HTDE content. From Figure 2, the molecular weight or generation number of HTDE also has important effect on the tensile strength, and tensile strength is maximum with the increase of molecular weight or generation number of HTDE. The maximum tensile strength of the four kinds of modified cured systems HTDE-1/DGEBA, HTDE-2/DGEBA, HTDE-3/DGEBA, and HTDE-4/DGEBA are, respectively, 75.94, 78.24, 77.71, and 74.81 MPa. So the optimum modifier in all the cured systems should be HTDE-2, and tensile strength of cured system increases from 64.74 to 78.24 MPa, which has improved about 20.85%.

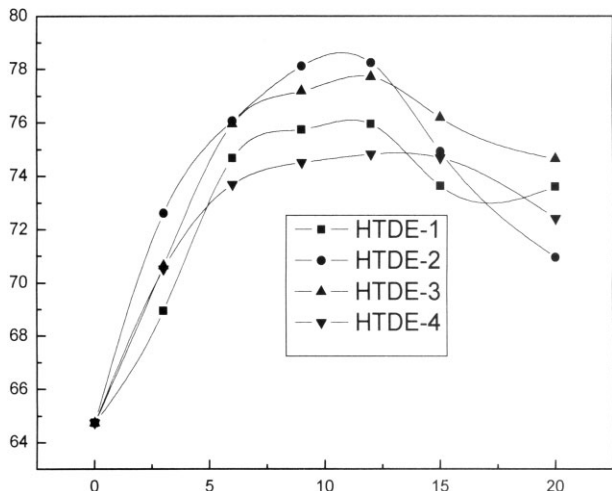


Figure 2 Effect of the content and molecular weight of HTDE on the tensile strength.

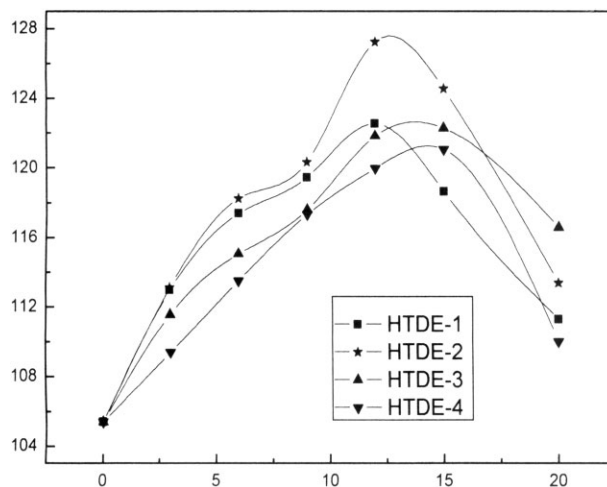


Figure 3 Effect of the content and molecular weight of HTDE on the flexural strength.

The tensile strength of the cured system is determined by the rigidity of hyperbranched polymer chain, intramolecular defect of HTDE, and the crosslinking density. The chain rigid and crosslinking density have positive effect on the tensile strength, but the intramolecular defect has negative effect.¹ The increase of the content of HTDE containing much rigid benzene ring makes the tensile strength to increase, at the same time, the decrease of the crosslinking density makes the tensile strength to decrease, and so the two reverse effects should result in the appearance of their maximum. With the increase of molecular weight or generation of HTDE, the increase of rigid benzene ring and the increase of the intramolecular defect of HTDE also result in appearance of their maximum.

Flexural strength

Effect of the content and molecular weight of HTDE on the flexural strength of the cured resins are shown in Figure 3. With the increase of the content and molecular weight of HTDE, the flexural strength increases first and decreases afterwards, and so they have maximum. The flexural strength of all cured systems containing about 12 wt % HTDE come to a head and the maximum flexural strength of HDTE-1/DGEBA, HTDE-2/DGEBA, HTDE-3/DGEBA, and HTDE-4/DGEBA cured systems are, respectively, 122.54, 127.23, 121.81, and 121.06 MPa, and their flexural strength have improved, respectively, 16.28, 20.73, 15.59, and 14.88%. So the optimum modifier in the cured system should also be HTDE-2. The effect factors of flexural strength of the cured system also attribute to the integrated effect of hyperbranched polymer chain rigid, intramolecular defect of HTDE, and the crosslinking density.

Impact strength and fracture toughness

Effect of the content and molecular weight of HTDE on the impact strength of the cured resins is shown in Figure 4. It is clear from the figure that impact strength increases with an increase in HTDE concentration or their molecular weight, attain a maximum, and then decrease. The maximum impact strength is achieved at 9–12 wt % HTDE concentration and HTDE-2 as modifier, and the maximum impact strength of HDTE-1/DGEBA, HTDE-2/DGEBA, HTDE-3/DGEBA, and HTDE-4/DGEBA cured systems are, respectively, 57.2, 58.2, 53.2, and 45.1 kJ/m²; however, the impact strength of unmodified DGEBA is only 17.4 kJ/m². The optimum impact strength is about three times higher than the value observed for unmodified DGEBA. The impact strength improvement of the HTDE/DGEBA blends should be attributed to the

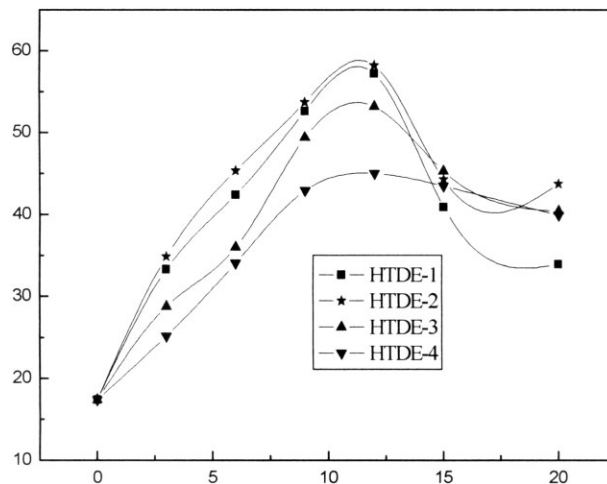


Figure 4 Effect of the content and molecular weight of HTDE on the impact strength.

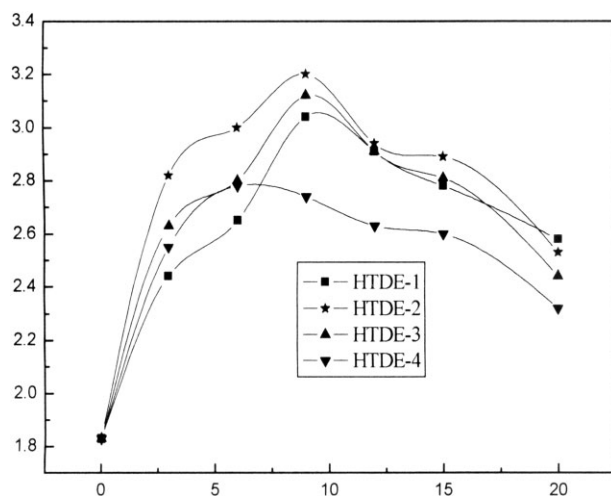


Figure 5 Effect of HTDE content and molecular weight of the fracture toughness of the cured systems.

intramolecular defect of hyperbranched polymers, which can absorb much more energy while impacting. However, the chain rigid also can reduce the impact strength of the blends, and so the impact strength has peak with increase of HTDE content and their molecular weight or generation.

Figure 5 shows the substantial improvement in fracture toughness (in terms of the critical stress intensity factor (K_{IC})) with increase in HTDE addition, but the fracture toughness is also maximum and the results are in accord with the impact strength improvement. As can be seen, with a 9 wt % content of HTDE-2 in the epoxy there is a 75% increase in fracture toughness, and the K_{IC} of the cured system containing 9 wt % HTDE-2 is more than $3.0 \text{ MPa m}^{1/2}$, which is higher than the value reported^{10–13} before.

Thermal performance

Table III shows the Vicat temperature of all the cured systems. The Vicat temperature decreases with the increase of HTDE content and the results indicate that

TABLE III
Vicat Temperature of all the Cured Systems

Content of HTDE (wt %)	HTDE-1 cured system (°C)	HTDE-2 cured system (°C)	HTDE-3 cured system (°C)	HTDE-4 cured system (°C)
Pure DGEBA	89.2	89.2	89.2	89.2
3	84.4	80.3	80.2	82.5
6	76.0	78.7	79.0	73.8
9	74.1	70.8	77.6	72.1
12	71.3	69.9	70.8	70.1
15	67.0	65.7	65.8	65.2
20	59.3	59.3	59.7	59.3

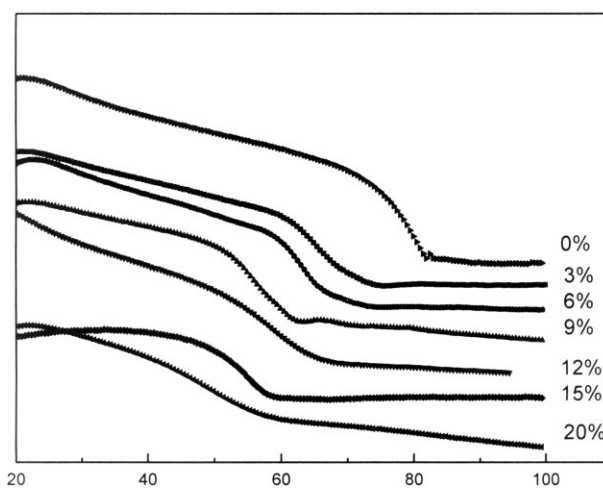


Figure 6 The effect of HTDE-2 content on T_g of the cured systems.

the heat-resistant properties of the blends become bad with the addition of HTDE. The Vicat temperature reduction should be attributed to decrease of crosslinking density from the epoxy equivalent weight increase of the cured systems and the intramolecular defect of hyperbranched polymers.

The glass transition temperature (T_g) of the cured systems with HTDE-2 are determined by differential scanning calorimetry (DSC) in Figure 6 and Table IV. The DSC traces of the cured systems showed the decrease in T_g with increase in HTDE-2 content. The result of T_g decrease is in accord with the Vicat temperature decrease. Low glass transition temperature and Vicat temperature of the HTDE-2/DGEBA blends have been attributed to the reduction of crosslinking density, because epoxy equivalent weight of HTDE-2 is more than that of DGEBA.

Toughness mechanism

The impact behavior of the HTDE/DGEBA blends can be explained in terms of morphology observed by SEM. Scanning electron micrographs of the fracture

TABLE IV
 T_g of the HTDE-2 Modified Systems According to Figure 6

HTDE-2 content (wt %)	T_g (°C)
0	80.6
3	65.3
6	63.5
9	56.2
12	55.9
15	55.8
20	53.0

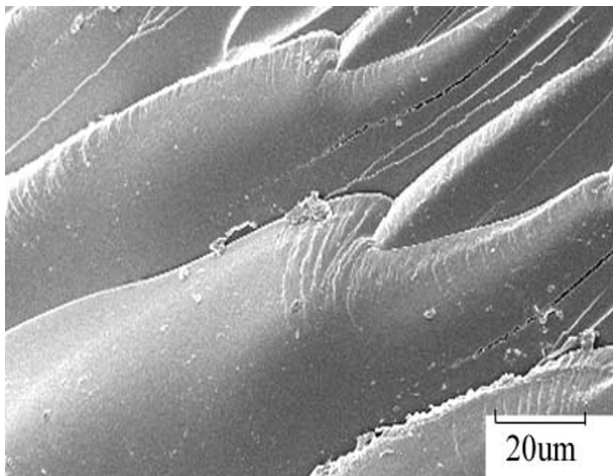


Figure 7 SEM of DGEBA fracture surface.

surfaces are presented in Figure 7 and 8. The clear surface and some creak in Figure 7 are substantial evidence of brittle materials. Figure 8 show the appearance of a lot of “protonema” (which refers to filar shape) of about 5 μm in diameter for all the four cured systems after the cured samples has impacted. Figure

9 shows that molecular simulation size of all four kinds of hyperbranched epoxy resins from chemoffice Ultra 2002 soft belongs to nanometer scope and the thickness of some section is not more than 1 nm by molecular simulation technology¹⁵; moreover, there are much molecular level cavity in the HTDE structure. In the HTDE/DGEBA blends system, the structure of HTDE resembles the structure of DGEBA and nanometer molecular size of HTDE result in excellent miscibility. So there is no phase separation on the fracture surfaces. Therefore, the mechanism of toughness improvement can not be explained by phase separate mechanism¹² but can be explained by *in situ* homogeneous reinforcing and toughening mechanism.¹⁶ Small molecular size of HTDE and similar structure make HTDE *in situ*-disperse homogeneously in the DGEBA matrix. The epoxy groups of HTDE and DGEBA react with amine group, while curing and external crosslinking structure of HTDE make the movement of end-groups of HTDE limited, but the intramolecular cavity of HTDE can not react with any group. Therefore, a lot of intramolecular cavity will distort while impacting and form protonema. So the shape of the protonema is similar to the morphological

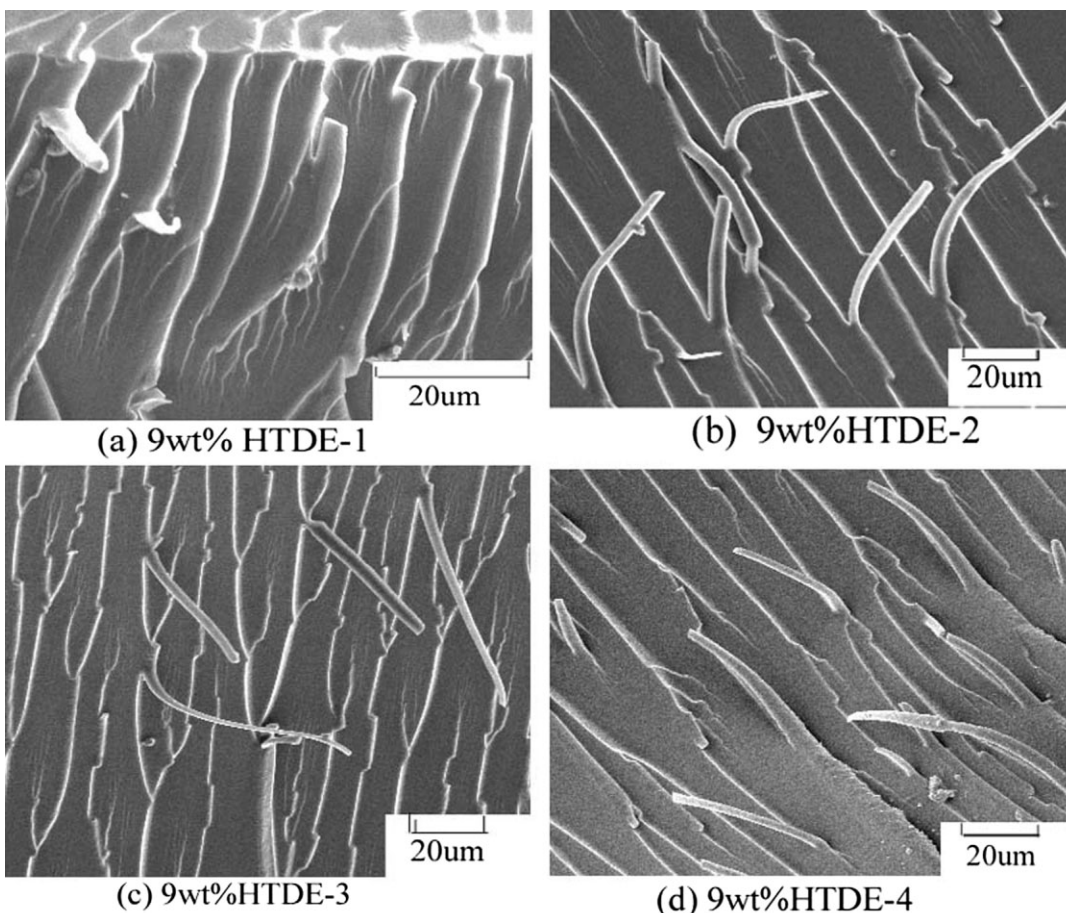


Figure 8 SEM of the fracture surfaces of the cured systems.

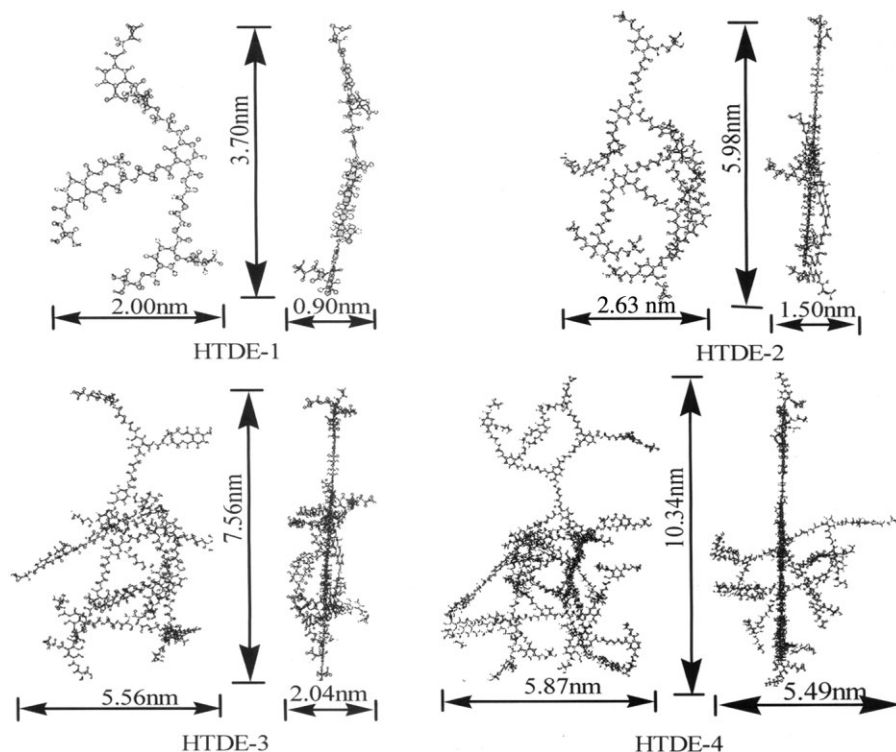


Figure 9 Simulation structure of HTDE- n ($n = 1,2,3,4$).

structure of molecular simulation. The shape with some molecular level cavity can absorb energy while impacting and the much rigid phenyl groups have positive effect on their strength. So the cured HTDE/DGEBA not only have outstanding toughness but also have excellent tensile and flexural strength for the synergetic effect of much rigid benzene and the intramolecular structure of the HTDE.

The $\tan \delta$ - T spectra of the cured systems are shown in Figure 10 and 11. The only $\tan \delta$ peak or α -relax-

ation peak also is a fundamental evidence of homogeneous structure in the cured system. It can be seen that there is a constant decrease in T_g with increase in HTDE-2 content, from Figure 10. A similar result is found for the DSC traces of the cured material, as shown in Figure 6. The appearance of a narrow T_g (α -relaxation peak) conforms the good compatibility between the resins. The β -relaxation peak are very prominent for the cured systems, in addition, it shifts toward low temperature with increase in HTDE-2 con-

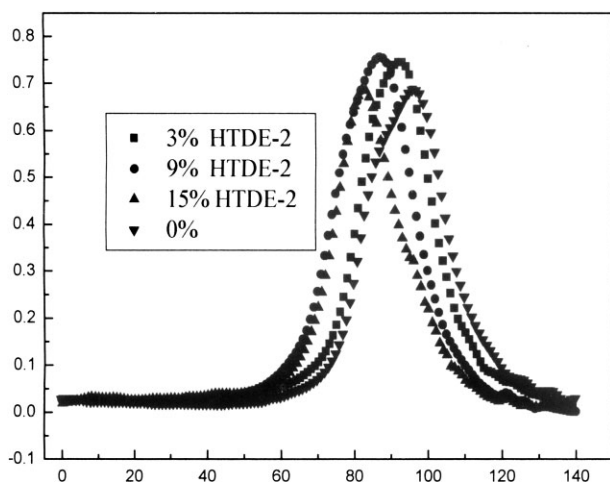


Figure 10 Traces of $\tan \delta$ versus T for the α -relaxation of the cured systems.

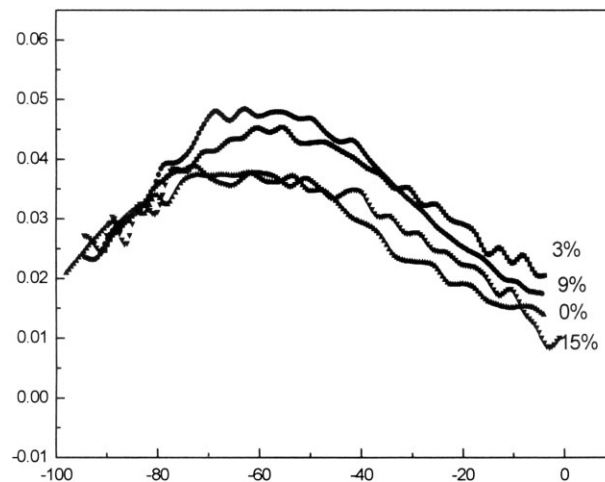


Figure 11 Traces of $\tan \delta$ versus T for the β -relaxation of the cured systems.

tent. The pronounced β -relaxation peak may be traced to the chair-boat conformation transition of the benzene unit in the cured systems,¹⁷ and so the HTDE-2 with much benzene unit can increase the intensity of the chair-boat conformation transition and the magnitude of the β -relaxation. The magnitude and area of the β -relaxation are often quoted to reflect the toughness¹⁸: the higher the β -relaxation is, the greater is the toughness.

Therefore the reinforcement and toughness mechanism of the HTDE/DGEBA should be in accord to *in situ* reinforcing and toughening mechanism. The protonema phenomenon can be explained by the molecular simulation shape of HTDE.

CONCLUSIONS

In conclusion, this article has shown that a low viscosity liquid aromatic polyester hyperbranched epoxy resin is an excellent candidate material for improving the toughness, flexural strength, and tensile strength of the epoxy amine resin system. The low viscosity liquid nature of the HTDE indicates that they will have positive effect upon the processing viscosity. Importantly, the HTDE has been shown to impart excellent improvements in toughness and strength, although there has been some compromise to the glass transition temperature having little decrease. Moreover, the content and molecular weight or generations of the HTDE have effect upon the performance of the cured systems, and optimum modifier of the cured system is modest content and molecular weight

HTDE-2. The toughness and strength improvement mechanism is discussed and is in accord to *in situ* reinforcing and toughening mechanism. The protonema phenomenon can be explained by the molecular simulation shape of HTDE.

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