

# Bisphenol-A epoxy resin reinforced and toughened by hyperbranched epoxy resin

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**Abstract** The study on toughening and reinforcing of bisphenol-A epoxy resin is one of important developmental direction in the field. This paper reports a one-pot synthesis of aromatic polyester hyperbranched epoxy resin HTDE-2, an effect of HTDE-2 content on the mechanical and thermal performance of the bisphenol-A (E51)/HTDE-2 hybrid resin in detail. Fourier transform infrared (FT-IR) spectrometer, scanning electronic microscopy (SEM), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dynamic mechanical thermal analysis (DMA) and molecular simulation technology are used to study the structure of HTDE-2, performance and toughening and reinforcing mechanism of the HTDE-2/E51 hybrid resin. It has been shown that the content of HTDE-2 has an important effect on the performance of the hybrid resin, and the performance of the HTDE-2/E51 blends has maximum with the increase in HTDE-2 content. The impact strength and fracture toughness of the hybrid resin with 9 wt-% HTDE-2 are almost 3.088 and 1.749 times of E51 performance respectively, furthermore, the tensile and flexural strength can also be enhanced about 20.7% and 14.2%, respectively. The glass transition temperature and thermal degradation temperature, however, are found to decrease to some extent.

**Keywords** hyperbranched epoxy resin, synthesis, toughness, mechanism, molecular simulation

## 1 Introduction

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. However, they are brittle materials that inhibit their further proliferation into various industrial applications [1]. Hence, the modification of epoxy resins to impart fracture toughness has been the subject of intense investigation throughout the world. Epoxy resins are successfully toughened [2–5] by blending them with plasticizer, low molecular weight toughening agent, thermoplastic resins, core shell particles, IPN, TLCP, rubber and nanometer particles. All these methods can availably increase the toughness of epoxy resins, but the strength including tensile and flexural strength will decrease to different extent.

Aliphatic hyperbranched polymers and hyperbranched epoxy resins can be used to enhance remarkably the toughness of epoxy resin [6–8], but the strength of the product will be reduced. That hyperbranched polymers both toughening and strengthening epoxy resins has been reported. The aim of the present work is to investigate a novel modified low viscosity liquid thermosetting aromatic polyester hyperbranched epoxy resin (HTDE-2), which could not only reduce the viscosity of the system, but also toughen epoxy resins E51, which was the base for no-solvent and function of epoxy resins. In addition, the toughness and improvement mechanism were discussed in detail.

## 2 Materials and methods

### 2.1 Experimental materials

Trimellitic anhydride (TMA) was purchased from Jiangsu Changzhou Global Chemical CO., LTD. Dihydroxy alcohol (DEG), epichlorohydrin (ECH), acrylonitrile (AN) and diethylene triamine (DETA) were purchased from Shanghai Chemical Reagent CO., LTD. Epoxy resin (E51) was purchased from Dongfeng Chemical Corp., China.

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## 2.2 Experimental apparatus

The experimental apparatuses include AG-1 omnipotent electron tensile tester (AG-1 Japan), DV-II + Pro Viscometer (Brookfield Engineering LABS), 1100 Series HPLC (Agilent); NETZSCH DSC204 F1 and NETZSCH TG209 (NETZSCH Gerätebau GmbH.), dynamic mechanical thermal analysis (DMA) (DMA242 NETZSCH Gerätebau GmbH.), Zwick-5113 (ZwickRoell, Germany) digital impact tester; Instron 5500R universal testing machine (USA) and low voltage scanning electron microscope (SEM) (XL-30FEG, Philip).

## 2.3 Synthesis of HTDE-2 and hybrid resin

### 2.3.1 Synthesis of HTDE-2

Carboxy-end hyperbranched polymer (HTD-2) was first prepared by the reaction between trimellitic anhydride (TMA) and dihydroxy alcohol with one-pot method [9]. The hyperbranched epoxy resin (HTDE-2) was synthesized from the reaction between HTD-2 and ECH [10]. The yield and epoxy equivalent weight of HTDE-2 are 70% and 400 g/mol, respectively.

### 2.3.2 Preparation of HTDE-2 / E51 blends and curing

The curing agent was DETA-AN which was prepared by the addition reaction of equal molar acrylonitrile (AN) with diethylene triamine (DETA). The HTDE-2, E51 and DETA-AN (formulation seen Table 1) were blended uniformly, and the mixtures were cured in a silicone rubber mold about 25°C for 4 h and post cured about 80°C for 2 h after having been degassed under vacuum for 10 min and become transparent. Afterwards, the mechanical performance of the cured system was measured after the samples were cooled gradually to room temperature and stood for 12 h.

**Table 1** Formulation of curing samples

HTDE-2 content /%	E51 content /g	HTDE-2 content /g	DETA-AN content /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

## 2.4 Characterization of HTDE-2 and hybrid resin

### 2.4.1 Characterization of HTDE-2

The viscosity of HTDE-2 is measured by a Brookfield DV-II + Viscometer with RV-S06 spindle in 25°C and 20 r/min. The molecular weight distribution is measured by Agilent

1100 Series HPLC with the Agilent PL gel 5  $\mu\text{m}$  MIXED-C as GPC fixed phase and the tetrahydrofuran (THF) as flowing phase.

### 2.4.2 Mechanical performance of hybrid resin

Their tensile strength was measured by AG-1 omnipotent electron tensile tester (AG-1 Japan) according to ASTM D638-91a. Their flexural strength was determined according to ASTM D5045-91a by using an Instron 5500 universal testing machine. No-notch impact strength of the modified epoxy samples was determined by a Zwick-5113 (Zwick-Roell, Germany) digital impact tester. Fracture toughness testing was carried out by using the compact tension method according to ASTM D6110-96a using an Instron 5500 universal tester.

### 2.4.3 Thermal performance of hybrid resin

Differential scanning calorimeter (DSC) measurement was carried out on the cured samples for attaining their  $T_g$ . Thermal scans at constant heating rate of 10°C · min<sup>-1</sup> were performed in a temperature range 20°C–100°C for all the cured samples. Dynamic mechanical thermal analysis (DMA) was performed on the cured materials for attaining tan  $\delta$  traces with a DMA242 (NETZSCH Gerätebau GmbH) by ramping from –100°C to 150°C at the rate of 3°C · min<sup>-1</sup>. Thermal weight analysis of hybrid resin was performed at constant heating rate of 10°C · min<sup>-1</sup> under nitrogen.

### 2.4.4 SEM characterization

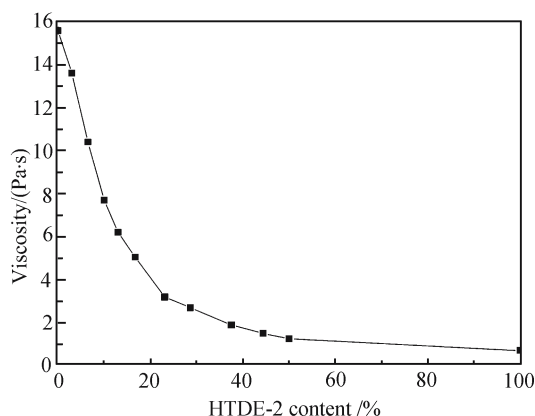
A thin section of the fracture surface was cut and mounted on an aluminum stub using a conductive (silver) paint and was sputter-coated with gold prior to fractographic examination. Images of scanning electron microscope were obtained under conventional secondary electron imaging conditions with an accelerating voltage of 15 kV.

## 3 Results and discussion

### 3.1 Viscosity characteristic of HTDE-2

Their viscosity of HTDE-2 and E51 are respectively 0.7 and 15.6 Pa · s by a Brookfield DV-II + Viscometer with RV-S06 spindle at 25°C and 20 r/min. The molecular weight of HTDE-2 and its distribution are respectively 2 637 (Theoretical molecular weight 3 404) and 2.06 by Agilent 1100 Series HPLC, but the molecular weight of E51 is only 392. The viscosity and molecular weight of HTDE-2 and E51 indicate that the HTDE-2 has lower viscosity with higher molecular weight, consistent with lower fluid mechanical volume, lower viscosity and easily flowing characteristics of hyperbranched polymers [9]. The effect of HTDE-2 content

on the viscosity of HTDE-2/E51 hybrid resin is shown in Fig. 1.

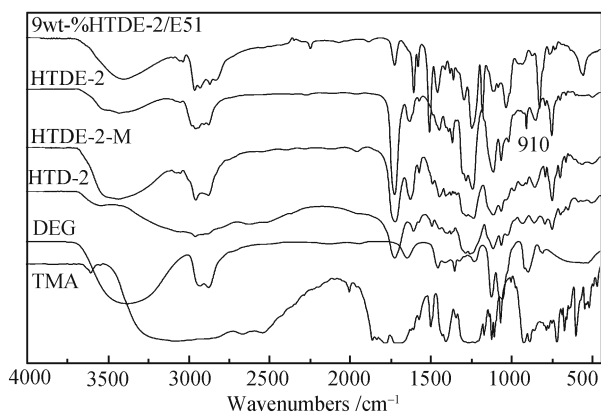


**Fig. 1** Effect of HTDE-2 content on the viscosity of HTDE-2/E51 hybrid resin

The viscosity of hybrid resin is reduced with the increase in the HTDE-2 content from Fig. 1, and the viscosity changes a little while the HTDE-2 content is above 20 wt-%.

### 3.2 Structure characterization of HTDE-2

Fourier transform infrared spectra of HTDE-2 and relative materials are shown in Fig. 2.

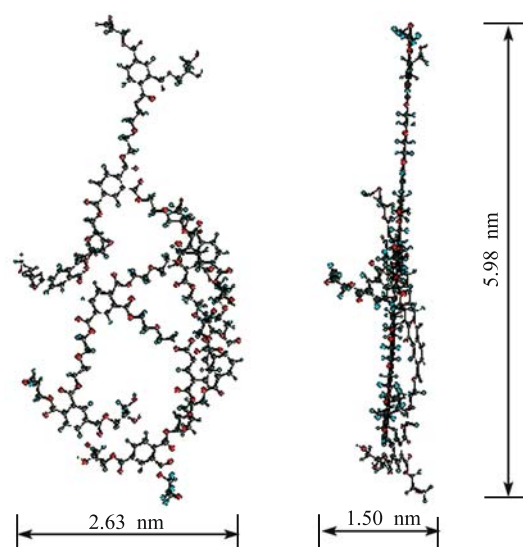


**Fig. 2** FT-IR spectra of HTDE-2 and its raw materials

The appearance of the strong absorption peak at  $1720\text{ cm}^{-1}$  and the disappearance of a broad and strong absorption peak at  $1860\text{ cm}^{-1}$  from the FT-IR spectrum of HTD-2 confirmed that the reaction between TMA and DEG took place. The absorption peaks at  $3440\text{ cm}^{-1}$  become more broad and stronger from the FT-IR spectrum of HTD-2-M indicated the formation of the reaction product between HTD-2 and ECH. The FT-IR spectrum of HTDE-2 shows the hydroxyl group at  $3350\text{ cm}^{-1}$ , and the epoxy group at  $910\text{ cm}^{-1}$ . After curing reaction, the characteristic peak of epoxy resin at  $910\text{ cm}^{-1}$  disappeared, and the  $940\text{ cm}^{-1}$  peak is attributed to outside bending vibration of hydroxyl group [11].

### 3.3 Molecular structure simulation of HTDE-2

Figure 3 shows that molecular simulation size of HTDE-2 belongs to nanometer scope and the thickness of some section is not more than 1 nm by molecular simulation technology, and its simulation size is  $2.63\text{ nm} \times 1.5\text{ nm} \times 5.98\text{ nm}$ . Moreover, there is much molecular level cavity in the HTDE-2 structure and the stick shape results in excellent flowing and low viscosity.



**Fig. 3** Molecular shape simulation of HTDE-2

### 3.4 Effect of HTDE-2 content on mechanical performance of the hybrid resin

Material performance is one of important factors for their application, and the study on mechanical performance of epoxy resin, which is widely used thermosetting resin, is great important. The bisphenol-A epoxy resin (E51) was used as main resin for its excellent flowing and low viscosity, and the curing agent DETA-AN selected had longer curing induction period. The effect of HTDE-2 content on mechanical performance of the hybrid resin was shown in Table 2, including tensile strength, flexural strength, impact strength and fracture toughness.

**Table 2** Effect of HTDE-2 content on mechanical performance of the hybrid resin

HTDE-2 content /wt-%	0	3	6	9	12	15	20
Tensile strength /MPa	64.74	72.61	76.06	78.11	78.24	74.91	70.95
Flexural strength /MPa	105.38	113.09	118.23	120.33	127.23	124.55	113.35
Impact strength /(KJ·m <sup>-2</sup> )	17.40	34.85	45.34	53.73	58.20	44.31	43.73
Fracture toughness /(KPa·m <sup>1/2</sup> )	1.83	2.82	3.00	3.20	2.94	2.89	2.53

From Table 2, the HTDE-2 content has an important effect on the mechanical performance of the hybrid resin. Mechanical performance of the hybrid resin increases first and decreases afterwards with the increase in HTDE-2 content, and it reached maximum at about 9 wt-% to 12 wt-% HTDE-2 content. The impact strength of 9 wt-% HTDE-2/E51 cured systems is 58.2 KJ/m<sup>2</sup>, whereas that of unmodified E51 is only 17.4 KJ/m<sup>2</sup>. Moreover, tensile strength and flexural strength of the 9 wt-% HTDE-2/E51 cured systems are more 20% than those of unmodified E51, so the functional thermosetting epoxy resin can be used as toughening and enhancing materials for E51 epoxy resin.

The strength and toughness of the hybrid resin depend on the rigid of hyperbranched polymer chain, intramolecular defect of HTDE-2 and the crosslinking density. The chain rigid and crosslinking density have a positive effect on strength, but the intramolecular defect has a negative effect. The increase in the content of HTDE-2 containing much rigid benzene ring makes the strength increase, and the decrease in the crosslinking density makes the strength decrease, so the two reverse effects should result in the appearance of the maximum strength. The toughness improvement of the HTDE-2/E51 hybrid resin should be attributed to the 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, so the impact strength has peak with the increase in HTDE-2 content [8,12].

### 3.5 Toughness and enhancement mechanism

The impact behavior of the HTDE-2/E51 hybrid resin and E51 can be explained in terms of morphology observed by SEM. Scanning electron micrographs of the fracture surfaces are presented in Fig. 4.

The clear surface and some creak in Fig. 4(a) are substantial evidence of brittle materials. Figure 4(b) shows the appearance of a lot of “protonema” (which refers to filar shape) of about 5 micron in diameter for the cured system

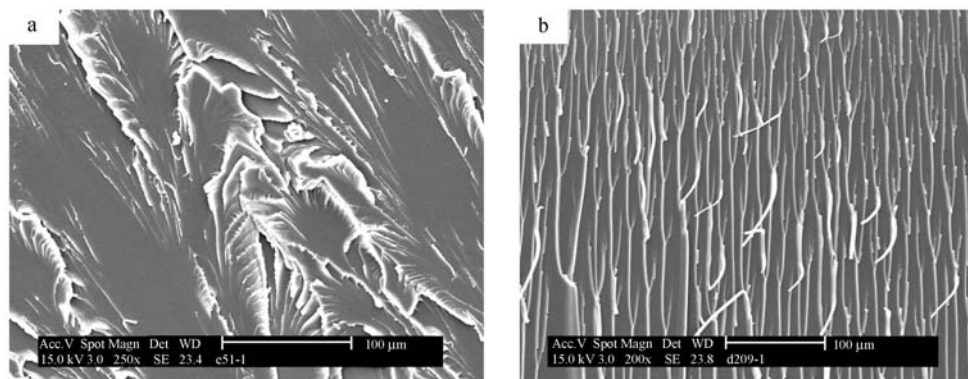
after the cured sample has impacted which indicates the toughness fracture characteristics. The surface shape is not the same as cavity toughness mechanism [8,12,13]. There is not phase separate obviously on the fracture surfaces. Therefore, instead of a phase separate mechanism [12], toughness improvement can be explained by a situ reinforcing and toughening mechanism [14]. Small molecular size of HTDE-2 and similar structure of E51 make HTDE-2 situ-disperse in the E51 matrix. The epoxy groups of HTDE-2 and E51 react with amine group while curing and external crosslinking structure of HTDE-2 make the movement of end-groups of HTDE-2 limit, but the intramolecular cavity of HTDE-2 cannot react with any group. Therefore, a lot of intramolecular cavity will distort while impacting and form “protonema”. Therefore, the shape of the “protonema” is similar to the morphological structure of molecular simulation. The shape with some molecular level cavity can absorb energy while impacting and the much rigid phenyl groups have a positive effect on their strength. Therefore, the cured HTDE-2/E51 not only has outstanding toughness and but also has excellent tensile and flexural strength because of the synergetic effect of much rigid benzene and the intramolecular structure of the HTDE-2.

The  $\tan \delta$ -T spectra of the cured systems are shown in Fig. 5. The only  $\tan \delta$  peak or  $\alpha$ -relaxation peak also is fundamental evidence of no phase separation in the cured system. The  $\beta$ -relaxation peak is very prominent for the cured systems, in addition, it shifts toward low temperature with increasing HTDE-2 content. The magnitude and area of the  $\beta$ -relaxation are often quoted to reflect the toughness [15,16]: the higher the  $\beta$ -relaxation is, the greater the toughness is.

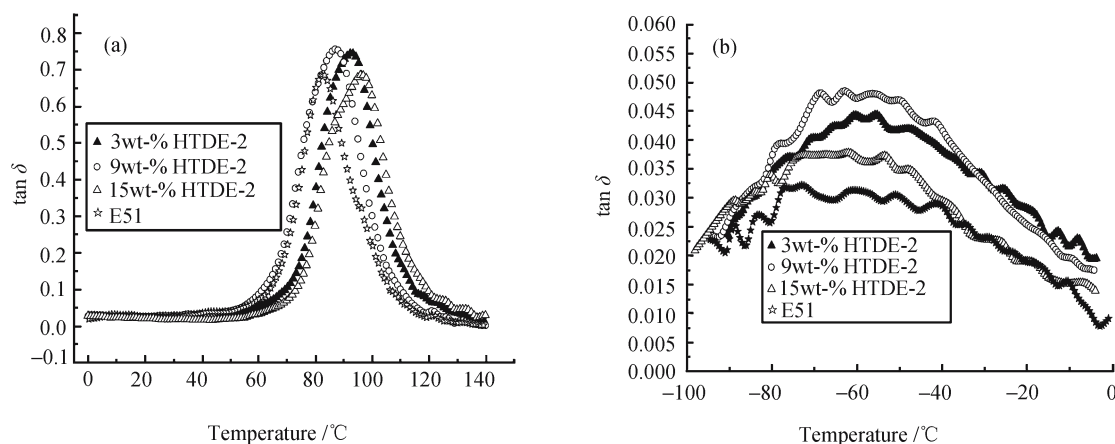
Therefore, the reinforcement and toughness mechanism of the HTDE-2/E51 should be accord to situ reinforcing and toughening mechanism. The “protonema” phenomenon can be explained by the molecular simulation shape of HTDE-2.

### 3.6 Thermal performance of hybrid resin

The effect of HTDE-2 content on glass transition temperature ( $T_g$ ) and thermal degradation temperature are shown in Figs. 6

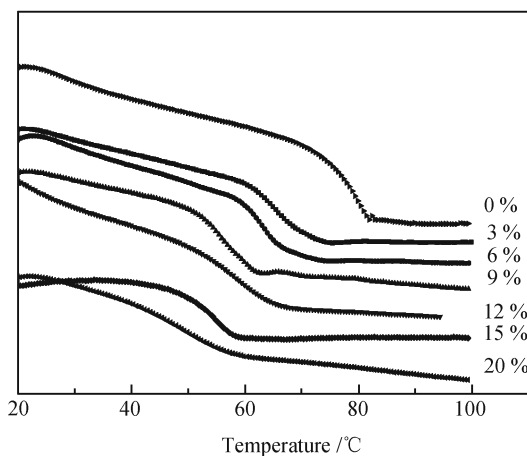


**Fig. 4** SEM graphs of fracture surface of E51 and hybrid resin (a) Pure E51; (b) 9 wt-% HTDE-2/E51



**Fig. 5** DMA curves of HTDE-2/E51 hybrid resins and E51 epoxy resin (a)  $\alpha$ -relaxation; (b)  $\beta$ -relaxation

and 7, respectively. The DSC and TGA traces of the hybrid resin showed the decrease in  $T_g$  and thermal degradation temperature with increasing HTDE-2 content. The results are related to the intramolecular cavity density of the HTDE-2, and the intramolecular cavity density increases and heat-resisting performance with the increase in HTDE-2 content [8].

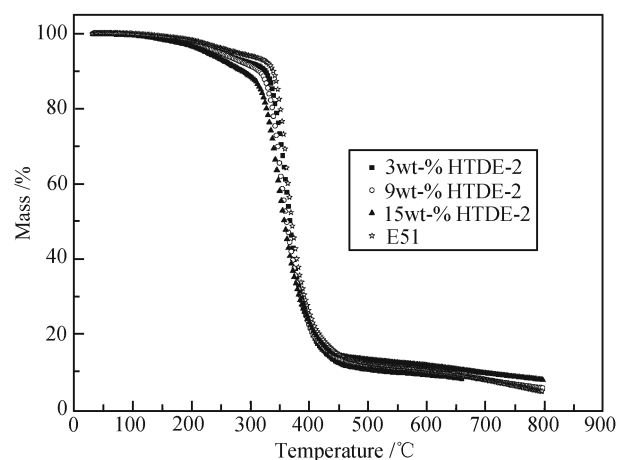


**Fig. 6** DSC curves of HTDE-2/E51 hybrid resin and E51 epoxy resin

## 4 Conclusions

1) This paper 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 hybrid resin, and the performance of the HTDE-2/E51 blends has maximum with the increase in HTDE-2 content.

2) The toughness and strength improvement mechanism is discussed by SEM technology and accords to situ reinforcing and toughening mechanism. A lot of “protonemas” (which



**Fig. 7** TGA curves of HTDE-2/E51 hybrid resins and E51 epoxy resin

refers to filar shape) appear in the impact surface of hybrid resin.

3)  $\beta$ -relaxation peak is very important evidence of toughness of hybrid resin by DMA analysis, and the glass transition temperature and thermal degradation temperature, however, are found to decrease to some extent.

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