Synthesis and properties of novel trifunctional epoxy triglycidyl of 4-(4-aminophenoxy)phenol with high toughness

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ABSTRACT: A trifunctional epoxy containing oxyphenylene unit, triglycidyl of 4-(4-aminophenoxy)phenol (TGAPP) was synthesized and characterized. The chemical structure of TGAPP was confirmed with FTIR and ^{1}H-NMR. DSC analysis revealed that the reactivity of TGAPP with curing agent 4, 4′-diaminodiphenylsulfone (DDS) was significantly lower than that of triglycidyl para-aminophenol (TGPAP). Rheological analysis showed that the processing window of TGAPP/DDS was 20°C wider compared with that of TGPAP/DDS. The thermal and mechanical properties of cured TGAPP/DDS were investigated and compared with those of the cured TGPAP/DDS. Experimental results showed that, due to the introduction of oxyphenylene unit, the heat resistance and flexural strength were slightly reduced, while the tensile strength and impact strength were enhanced. SEM also confirmed that the introduction of oxyphenylene unit could enhance the toughness of the TGAPP/DDS as evident from ridge formation. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41878.

INTRODUCTION

Epoxy resins are one of the most important classes of thermosetting polymers. Due to their good thermal and chemical resistance, high tensile strength and modulus, good dimensional stability and processability, they are widely used as matrices for fiber-reinforced composite materials, structural adhesives, coatings, and electronic packaging. In the composites industry, the glycidyl ether epoxy resin and glycidyl amine epoxy resin are the two largest consumption kinds of epoxy resins. As an important representative of glycidyl amine type epoxy resin, triglycidyl para-aminophenol (TGPAP), has been increasingly used in the applications for advanced composite materials in the aerospace and aircraft industries due to its excellent thermal stability, adhesion strength, and low viscosity.[1–5]

However, due to the intrinsic brittleness of the network structure of cured TGPAP, their applications were limited in circumstances where higher toughness is required. Consequently, several approaches have been made to improve the toughness of the highly crosslinked epoxy resins. Although the incorporation of rubbers can effectively toughen the relatively low crosslinked epoxy resins, more highly crosslinked epoxy resins are difficult to toughen in this way.[6,7] The incorporation of rubbers tends to decrease the

modulus of elasticity and the heat resistance of the modified resins. Hence, thermoplastic resins, such as polyether sulphone, polyetherimides and poly(ether ketone) have been researched to achieve both toughness and thermal resistance in highly crosslinked epoxy polymer systems, but the resulting toughened systems possess an increased viscosity and require elevated temperature to be processed.[8–11] Inorganic particles have also been employed as toughening agents to the epoxy matrix,[12–15] but improving the distribution and adhesion between the inorganic particles and the polymer matrix is still a challenging task.[16,17]

This problem can be overcome by introducing the flexible spacer into the epoxy backbone. Taka Iijima *et al.* introduced flexible oxyethylene units into the backbone of the novolac epoxy resins, the resulting resins exhibited improved toughness, moreover, the strength and modulus were not affected compared to the pristine sample.[18,19] Yang *et al.* introduced different amount of oxyethylene units into the backbone of diglycidyl ether of bisphenol-A (DGEBA) (Scheme 1), and blended DGEBA with the ethoxylated DGEBA. It proved that the viscosities of the blends decreased and impact strength of the cured blends increased with the increase content of the ethoxylated DGEBA.[20] Zhang *et al.* introduced bisphenol containing flexible
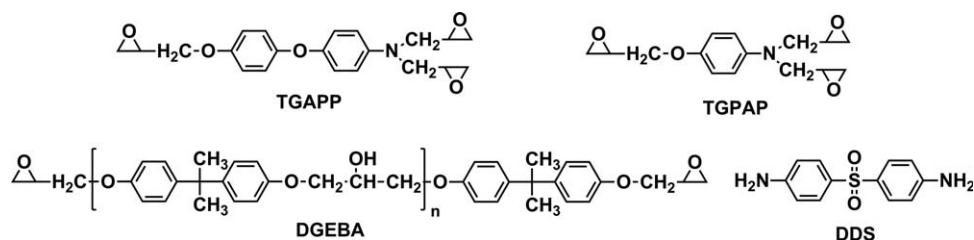
Scheme 1. Chemical structures of epoxy resins and curing agent.

aromatic ether linkage into the curing system of DGEBA and diamine to improve the toughness of the resultant thermosets.[21]

In this study, a novel trifunctional epoxy, triglycidyl of 4-(4-aminophenoxy)phenol (TGAPP), containing flexible oxyphenylene unit in the backbone, was synthesized and characterized. The reactivity of TGAPP with the curing agent 4,4′-diamino diphenylsulfone (DDS), and the properties of the cured resins were investigated with those of TGPAP for comparison.

EXPERIMENTAL

Materials

Hydroquinone, p-fluoronitrobenzene were purchased from Aldrich and used as received. Triglycidyl of para-aminophenol (TGPAP) with a epoxy equivalent weight of 104.2 was obtained from Shanghai Research Institute of Synthetic Resins, 4,4′-diaminodiphenylsulfone (DDS) was supplied by Beijing Chemical Reagents Company (China) and used as received. Pd/C and hydrazine hydrate were purchased from Acros Organics Chemicals and used without further purification. Ethanol, N,N-dimethylformamide (DMF), epichlorohydrin (ECH), toluene, K_2CO_3, and NaOH were purchased from Beijing Chemical Reagents, China, and used as received.

Synthesis of 4-(4-Nitrophenoxy)phenol (NPP)

To a 1000 mL three-necked flask equipped with a mechanical stirrer, reflux condenser, a water separator and thermometer was added a mixture of 110 g (1 mol) hydroquinone, 168 g (1.21 mol) K_2CO_3, 500 mL DMF, and 200 mL toluene. The reaction solution was heated at 120°C for 6 h in nitrogen. During the reaction, the toluene−water azeotrope was distilled out of the solution. Then the reaction solution was cooled to 100°C, and p-fluoronitrobenzene (126.9 g, 0.9 mol) was dropped into the reaction solution at the rate of eight drops per second. The reaction mixture was heated at 100°C for 10 h. After it cooled to room temperature, the homogeneous solution was poured into an excess of water, a pale brown solid was washed with hot-water three times, then recrystallized with ethanol/water to yield the pale brown solid NPP. Yield: 140.0 g (61%). mp: 173°C (DSC). FTIR (KBr, cm^{-1}):

3439, 1607, 1587, 1506, 1343, 1243, 1111, 844, 813. ^{1}H-NMR (400 MHz, DMSO, ppm): 6.86(s, 2H), 7.0(m, 4H), 8.22 (d, 2H), 9.56(s, 1H).

Synthesis of 4-(4-Aminophenoxy)phenol (APP)

A mixture of 46.4 g (0.2 mol) NPP, 1.5 g 5% Pd/C and 500 mL ethanol was placed in a 1000-mL, three-necked, round-bottom flask fitted with a mechanical stirrer, thermometer, reflux condenser, and N_2 inlet. The reaction mixture was heated to reflux. Then 60 g (1.02 mol) 80% hydrazine monohydrate was added dropwise within 4 h, and the mixture was heated at 80°C for 8 h. The reaction solution was filtered hot to remove Pd/C, and the filtrate was distilled to remove the solvent. The obtained mixture was poured into an excess amount of distilled water to give a precipitate. After collected and recrystallized with ethanol/water, the product was dried in vacuum to give pale yellow solid. Yield: 36.2 g (90%). mp: 156°C (DSC). FTIR (KBr, cm^{-1}): 3368, 3306, 1615, 1510, 1449, 1372, 1223, 1092, 919, 849. ^{1}H-NMR (400 MHz, DMSO, ppm): 9.09(s, 1H), 6.7(m, 6H), 6.5(d, 2H), 4.85(s, 2H).

Synthesis of Triglycidyl of 4-(4-Aminophenoxy)phenol (TGAPP)

To a 2000-mL, three-necked, round-bottom flask fitted with a mechanical stirrer, thermometer, reflux condenser, drop funnel and N_2 inlet, 925.2 g (10 mol) epichlorohydrin, 200 mL ethanol was added. The mixture was heated to 40°C, and 100.5 g (0.5 mol) APP was added in four batches in 3 h. Then the reaction solution was heated to 50°C for 4 h. 180 g (1.8 mol, 20% excess) 40% NaOH aqueous solution was dropped in three batches in 1.5 h, then the mixture was heated at 55°C for 5 h. The excess epichlorohydrin in the obtained solution was removed by vacuum distillation, then 800 mL toluene and 1000 mL distilled water was added with agitation. The aqueous phase was separated and the organic phase was washed successively with distilled water until the aqueous phase was neutral. The organic phase was dried with anhydrous $MgSO_4$ overnight and was filtered, followed by distilling under reduced pressure to get a clear brownish red liquid. Yield: 169.2 g (92%). FTIR (KBr, cm^{-1}): 3464, 2995, 2929, 2876, 1614, 1500, 1220, 1035,
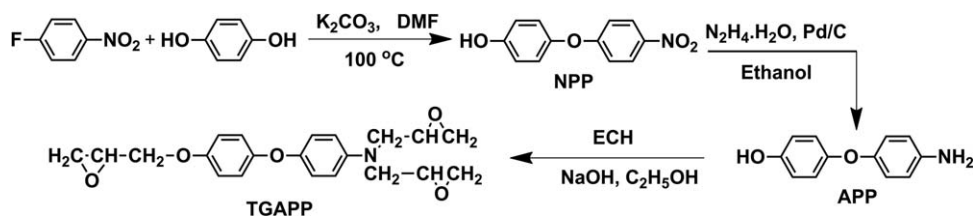
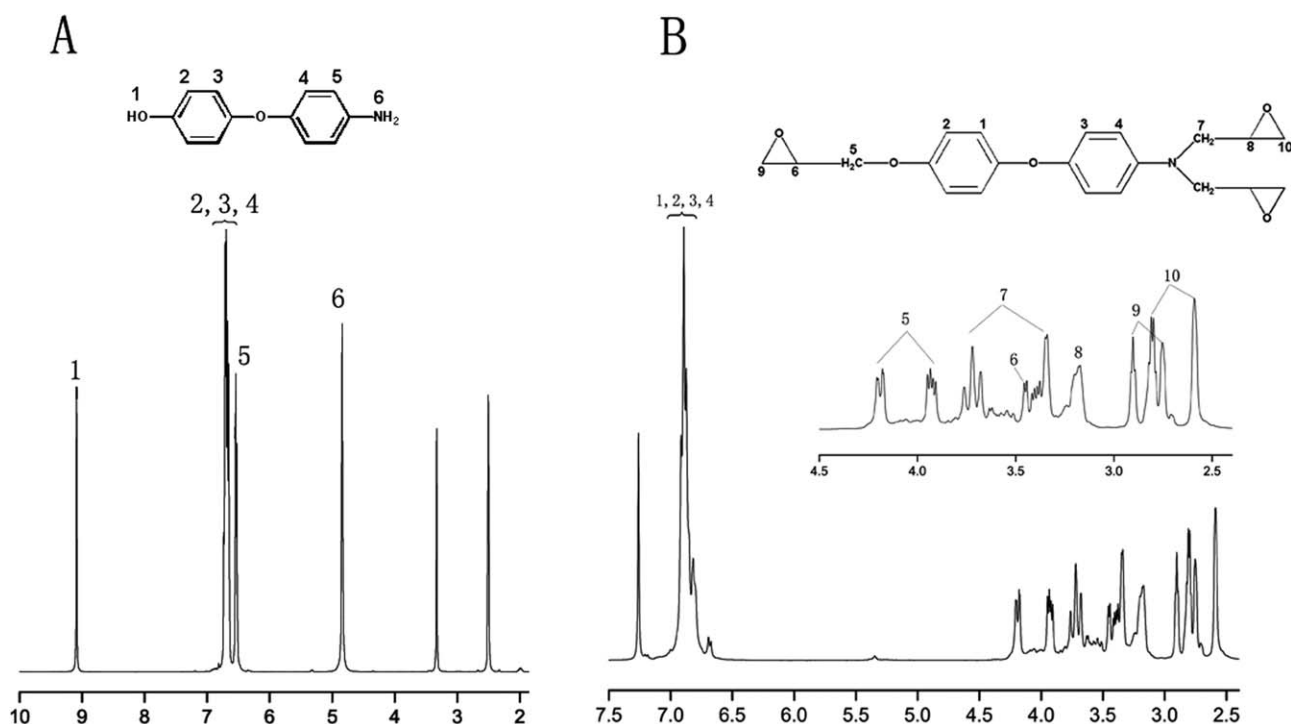**Scheme 2.** Synthesis of epoxy resin TGAPP.

Figure 1. ^{1}H-NMR spectra of APP (A) (400 MHz, DMSO-d_6) and TGAPP epoxy resin (B) (400 MHz, CDCl$_3$).

913, 821. ^{1}H-NMR (400 MHz, CDCl$_3$, ppm): 6.83(m, 8H), 4.20(m, 2H), 3.75(m, 4H), 3.45(m, 1H), 3.18(m, 2H), 2.89(m, 2H), 2.76(m, 4H).

Preparation of Cured Epoxy Resins

One aromatic diamine (DDS) was used as curing agent to thermally cure the TGPAP and TGAPP epoxy resins. The chemical structures of the epoxy resins and curing agent are shown in Scheme 1. The reaction compositions were mixed homogeneously in a 1 : 1 molar ratio according to the EEW values. To prepare the samples for differential scanning calorimetry (DSC) measurement and rheology test, the DDS powder was mixed with epoxy resin by continuous mechanical stirring at 70°C for 10 min to get a homogeneous dispersion. To prepare the sam-

ples for mechanical properties, dynamic thermomehcanical analysis (DMA) and thermal gravimetric analysis (TGA), the epoxy/amine mixture was heated to 130°C to obtain a homogeneous solution. The mixtures were degassed in vacuum and cast into a preheated mold, then cured at 150°C for 4 h and 200°C for 6 h in a convection oven.

Characterization and Measurement

The structure of TGAPP was characterized by ^{1}H-NMR and fourier transform infrared (FTIR) analysis. The ^{1}H-NMR was recorder on a BRUKER AVANCE 400 MHz NMR spectrometer, using deuterated chloroform and deuterated DMSO as solvent and tetramethylsilane as internal reference. Epoxy equivalent
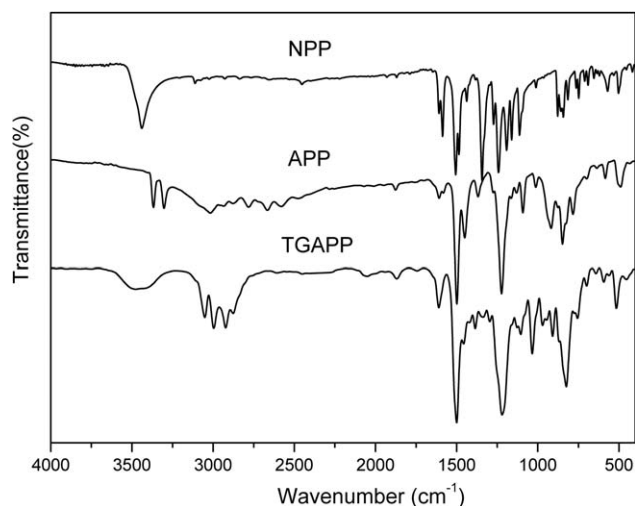

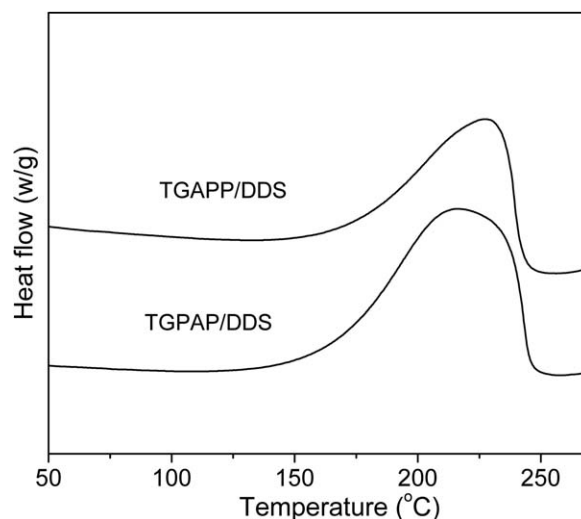
Figure 2. FTIR spectra of NPP, APP, and TGAPP.
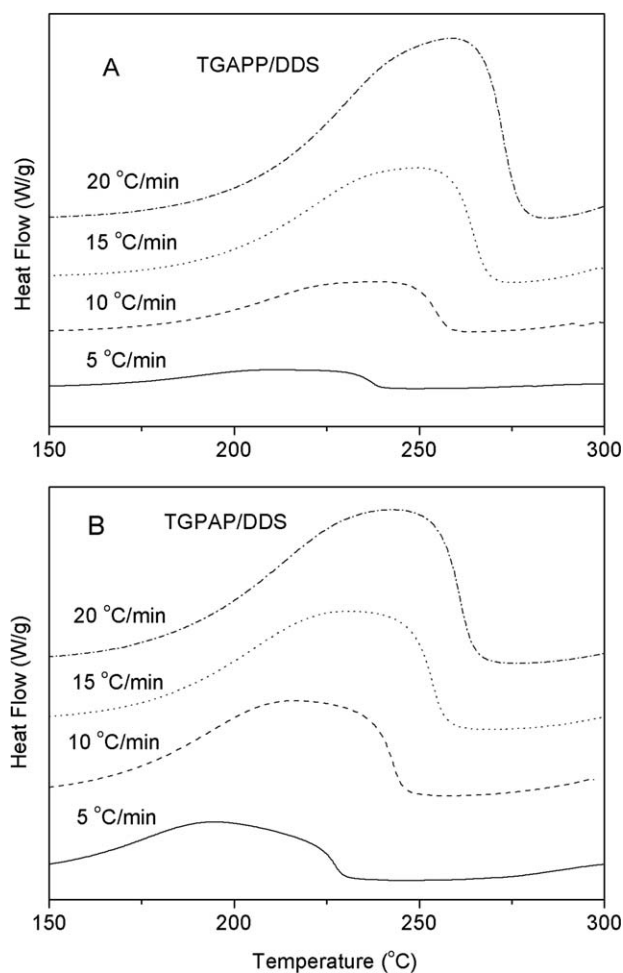

Figure 3. DSC curves of TGAPP and TGPAP cured with DDS.

Figure 4. DSC thermograms of TGAPP/DDS (A) and TGPAP/DDS (B) at 5, 10, 15, 20°C/min heating rates in N₂ atmosphere.

DSC was used to investigate the curing behavior of epoxy blends by scanning with a SII EXSTAR6000-DSC6220 from 50 to 300°C at a heating rate of 5, 10, 15, 20°C/min in nitrogen. The instrument was calibrated with a high-purity indium standard, and α-Al₂O₃ was used as the reference material. The average activation energy (E_a) for each epoxy system was determined using the Kissinger's [22,23] and Ozawa's [24,25] methods, as shown eqs. (1) and (2), respectively.

$$\ln\left\{\frac{\beta}{T_P^2}\right\} = \ln\left\{\frac{AR}{E_a}\right\} - \frac{E_a}{RT_P} \qquad (1)$$

$$\frac{d(\ln\beta)}{d(1/T_p)} = \frac{1.052E_a}{R}. \qquad (2)$$

where β is heating rate, A is preexponential factor, R is universal gas constant, E_a is activation energy of the reaction, and T_p is peak temperature at which the reaction rate is maximum. The plots of $-\ln(\beta/T_p^2)$ vs. $1/T_p$ and $\ln\beta$ vs. $1/T_p$ give straight lines. E_a values were calculated from the respective slopes of the straight line of the plots. The reaction order was determined using Crane equation shown in eq. (3)[26]

$$\frac{d(\ln\beta)}{d(1/T_p)} = \frac{E_a}{nR} \qquad (3)$$

where n is the reaction order, other parameters are the same as eq. (1).

TGA was carried out on a SII EXSTAR6000-TGA6300 in nitrogen at 10°C/min. The rheology test was carried out with an AR2000 rheometer of TA Instruments under air atmosphere at a heating rate of 5°C/min and a temperature range of 30−250°C. The measurements for the compacted resin discs were performed using a parallel-plate fixture (diameter: 25 mm, gap: 1.0 mm) in oscillation mode with a shear rate of 1.5 s⁻¹.

DMA was performed on a TA Q800 instrument (TA instruments) in the double-cantilever mode under nitrogen atmosphere at a frequency of 1 Hz and a heating rate of 5°C/min, and with a sample size of 60 mm × 12 mm × 2.5 mm. Tensile and flexural properties of cured epoxy resins were measured on an Instron Universal Tester Model 3365 according to GB/T 16421-1996 and GB/T 16419-1996, respectively. No-notch impact strength was measured at room temperature with a JC-25 impact tester (Chengde Precise Tester To., China) according to ASTM D-256. The reported mechanical properties were the average of at least five samples. The morphology of the impact-fractured surfaces was observed by a Hitachi S4800 scanning electron microscope

was tested by hydrochloric acid acetone method according to GB/T 2793.

The FTIR measurement was performed on a BRUKER TENSOR-27 FTIR spectrometer at room temperature in the range of 4000-400 cm⁻¹. The gel fraction of the cured samples was determined by Soxhlet extraction using acetone as solvent for 24 h. The insoluble materials were drying at 120°C under vacuum for 24 h and weighted to determine the gel fraction.

Table I. DSC Data, Rheological Data, and Gel Fraction for TGPAP/DDS and TGAPP/DDS

Samples	Exothermic peak temperature (°C) at different heating rate (°C/min)				Ozawa E_a (kJ/mol)	Kissinger E_a (kJ/mol)	Reaction order	T_{gel}[a] (°C)	α[b] (%)
	5	10	15	20					
TGPAP/DDS	195.1	215.9	231.1	242.8	55.56	50.26	0.91	192	99.7
TGAPP/DDS	210.1	237.8	249.4	258.7	57.39	51.93	0.91	205	98.9

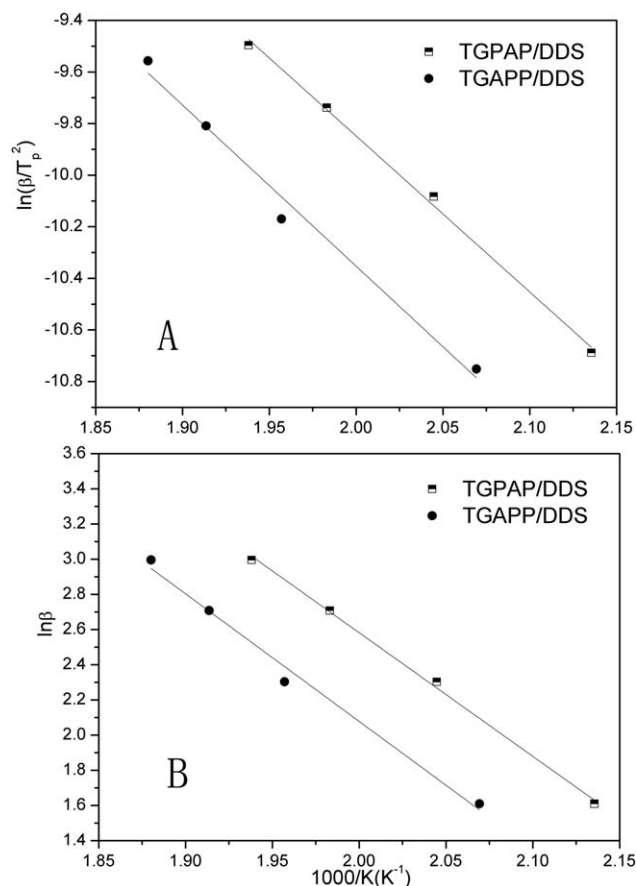[a] T_{gel}, gel temperature.
[b] α: gel fraction.

Figure 5. The plots of Kissinger (A) and Ozawa (B) of TGAPP/DDS and TGPAP/DDS.

(Hitachi, Japan) at an activation voltage of 10 kV. The fracture surfaces were coated with thin layers of gold of about 100 Å.

RESULTS AND DISCUSSION

Synthesis and Characterization of TGAPP

The epoxy resin TGAPP was synthesized through a three-step procedure as shown in Scheme 2. First, hydroquinone was reacted with p-fluoronitrobenzene by aromatic nucleophilic substitution reaction to yield NPP. Then NPP was reduced with
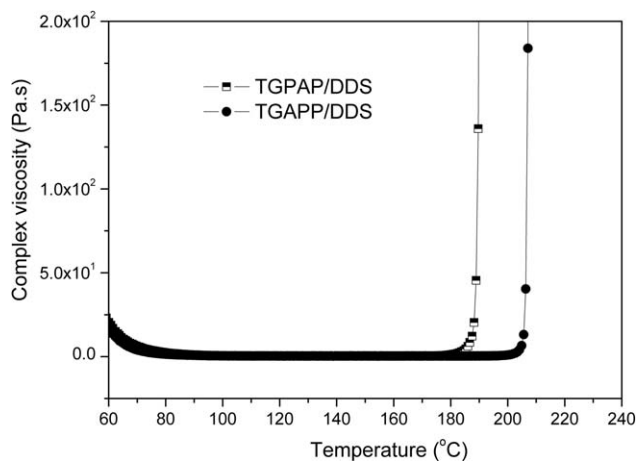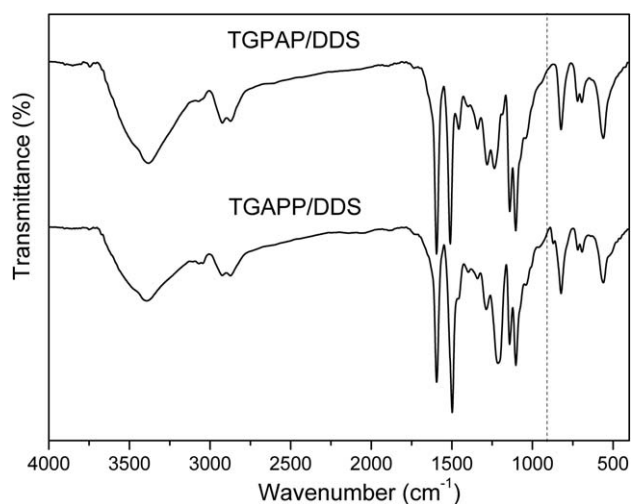

Figure 7. FTIR spectra of cured TGAPP/DDS and TGPAP/DDS.

hydrazine and Pd/C catalyst in reluxing ethanol to yield APP, which was epoxidated with ECH to give the trifunctional epoxy TGAPP. In the aromatic nucleophilic substitution reaction, it was important to control the rate of addition of p-fluoronitrobenzene to ensure mono-substituted product. If the rate of addition was too fast, both the phenoxide ion of hydroquinone reacted with p-fluoronitrobenzene to yield bis-substituted product, which decreased the yield and increased the difficulty of purification. The obtained TGAPP is a clear brownish red liquid. The epoxy equivalent tested by hydrochloric acid acetone method was 135, which was higher than the theoretical value of 123, indicating that the product contained a small amount of oligomers.

Figure 1(A) shows the ^{1}H-NMR spectrum of APP, the absorptions at 9.09 ppm and 4.85 ppm were attributed to the hydroxyl and amino groups, respectively. After epoxidation, the resonance signals of hydroxyl and amino groups in APP disappeared, and the absorptions at 3.47-3.42, 3.22-3.12, 2.93-2.86, 2.84-2.68, and 2.67-2.59 ppm were assigned to the protons in oxirane ring [Figure 1(B)]. The FTIR spectrum of TGAPP is given in Figure 2. It can be seen that the nitro group appearing at 1506 cm^{-1} and 1343 cm^{-1} in NPP disappeared in APP, and the amino
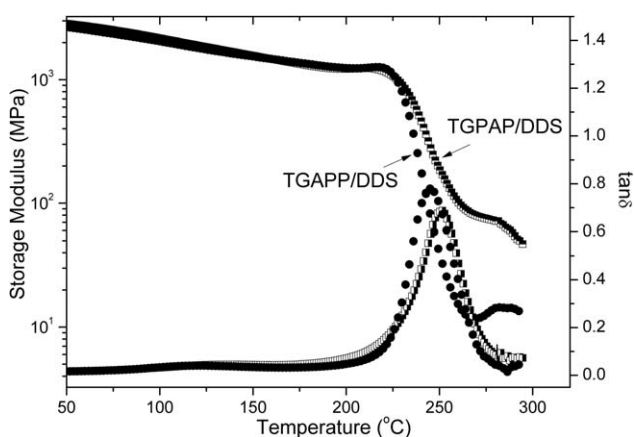

Figure 6. The rheological curves of TGAPP and TGPAP cured with DDS.

Figure 8. DMA curves of cured TGAPP/DDS and TGPAP/DDS.

Table II. Thermal Properties of the Cured Epoxy Resins

Samples	T_g[a] (°C)	E_{50}'[b] (GPa)	T_d[c] °C	T_5[d] (°C)	W_{800}[e] (%)
TGPAP/DDS	250.2	2.8	369.7	333.8	27.0
TGAPP/DDS	242.1	2.7	367.8	331.4	26.0

[a] Peak temperature of tan δ.
[b] Storage modulus at 50°C.
[c] Onset decomposition temperature.
[d] Temperatures at 5% weight loss.
[e] Char at 800°C.
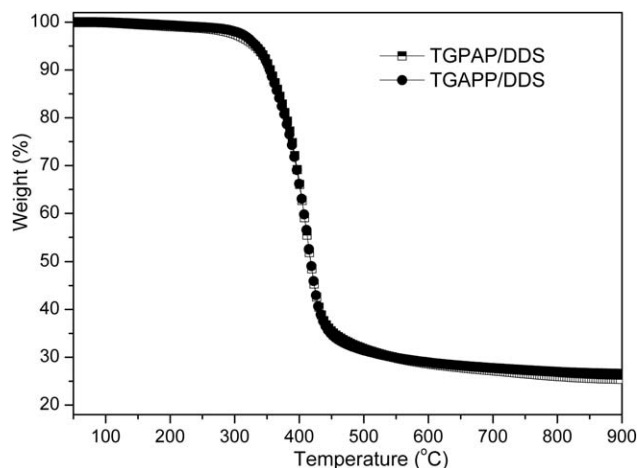
Figure 9. TGA curves of cured epoxy resins.

group at 3368 cm^{-1} and 3306 cm^{-1} in APP disappeared in TGAPP, the characteristic band of oxirane rings was detected at 913 cm^{-1}, indicating the successful preparation of TGAPP. The absorption in the range of 3313−3583 cm^{-1} was assigned to the hydroxyl groups which existed in the oligomers, the result is in agreement with the result of epoxy equivalent.

Curing of Epoxy Resins
Figure 3 compares the dynamic DSC curves of TGAPP/DDS and TGPAP/DDS and the results are shown in Table I. It can be seen that the exothermic temperature of the TGAPP/DDS was observed in the range of 163−245°C, while the exothermic temperature of the TGPAP/DDS was observed in the range of 152−246°C. The T_p of TGAPP/DDS is 12°C higher than that of TGPAP/DDS, indicating that TGAPP is difficult to react with DDS compared with TGPAP. DSC curves of TGPAP/DDS and TGAPP/DDS at the heating rates of 5, 10, 15, and 20°C /min are shown in Figure 4. Table I lists the exothermic peak temperatures (T_p), which increase with increasing heating rate.

Activation energies (E_a) of the epoxy-amine reactions were determined using Kissinger and Ozawa equation, the reaction orders were determined with Crane equation, the plots are shown in Figure 5 and the results are summarized in Table I. It can be seen that TGPAP/DDS and TGAPP/DDS show the same reaction order of 0.91, indicating that they share the same reaction mechanism, the curing reaction was approximately first order reaction. Comparing the E_a of TGPAP/DDS and TGAPP/DDS, the E_a of TGAPP/DDS was about 1.7 kJ/mol higher than that of TGPAP/DDS. The possible reason might be attributed to the introduction of oxyphenylene unit into the molecular structure, which attenutated the electron-withdrawing effect of benzene groups on the epoxy groups.

The rheological curves are shown in Figure 6 and the results are summarized in Table I. It can be found that the viscosity of TGAPP/DDS is slightly lower than that of TGPAP/DDS at the beginning. With the increase of temperature, the complex viscosity of the epoxy resins first decreased, then reached a plateau, at which the viscosity kept almost constant at 0.3 Pa s at the plateau. Then a very rapid increase of viscosity was observed, which was due to crosslinking reaction. Gelation occurred during this stage.[27,28] The gel temperature of TGAPP/DDS was 13°C higher than that of TGPAP/DDS, indicating the decreased reactivity of TGAPP, which was consistent with the results of DSC. It was interesting to find that TGAPP/DDS demonstrated a processing temperature window of 80−200°C, about 20°C wider compared to that of TGPAP/DDS, indicating the much improved processability of TGAPP/DDS.[29]

As the properties of the epoxy system are highly dependent on the extent of cure, the FTIR and gel fraction of the cured epoxy were measured. Figure 7 shows the FTIR spectra of the cured epoxy resins. It can be seen that the absorption at 3500 cm^{-1} increased after curing with DDS, which was due to the generation of secondary hydroxyl groups by the ring-opening reaction of epoxy groups. And the characteristic epoxy absorption at 913 cm^{-1} disappeared, indicating the complete cure of TGAPP. As can be seen from Table I, the gel fraction was ∼100%, revealing that a complete cure was reached under the program procedure.

Thermal Properties of Epoxy Resins
Figure 8 shows the DMA curves of TGAPP/DDS and TGPAP/DDS resins. The glass transition temperatures (T_g, the tanδ peak temperatures) and storage modulus at 50°C (E_{50}') are listed in Table II. It can be seen that E_{50}' of TGAPP/DDS was 3.6% lower than that of TGPAP/DDS, and the modulus of TGAPP/DDS decreased at the same rate with temperature compared to that of TGPAP/DDS. In addition, the peak position of

Table III. Mechanical Properties of the Cured Epoxy Resins

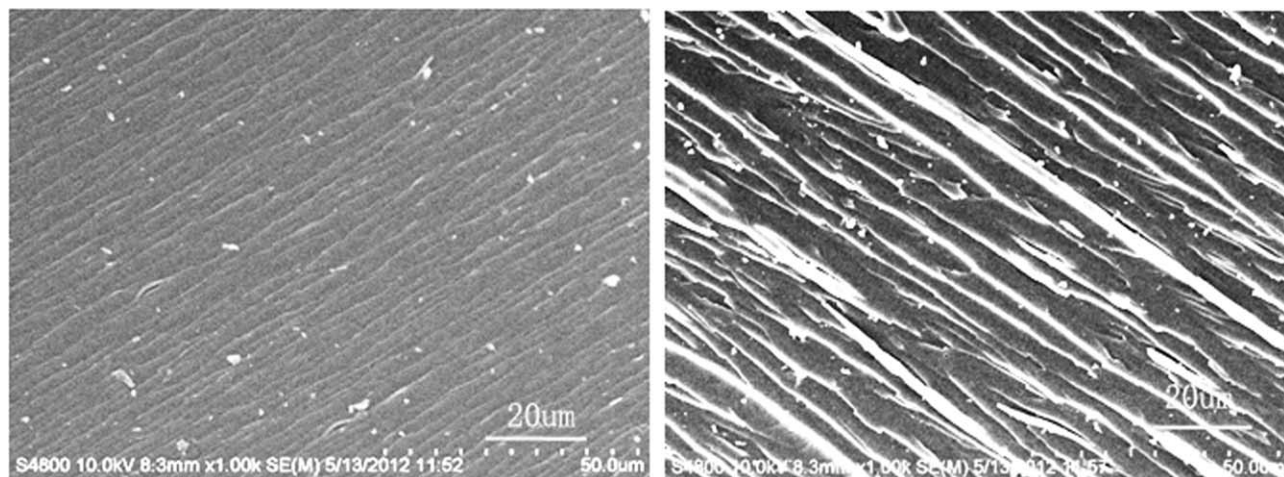| Sample	Tensile strength (MPa)	Tensile modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)	Impact Strength (kJ/m²)
TGPAP/DDS	60.02	2.72	126.02	3.96	10.02
TGAPP/DDS	66.12	2.77	118.20	3.85	15.10

Figure 10. SEM micrographs of fractured surface of cured TGPAP/DDS (left) and TGAPP/DDS (right).

the α-relaxation in the tanδ curve of TGAPP/DDS shifted toward lower temperature to 242.1°C, 8.1°C lower than that of TGPAP/DDS. Generally, there are two factors which affect the glass transition temperature. One is the crosslinking density, the other is the stiffness of polymer chain.[30] With the introduction of the flexible oxyphenylene unit, the crosslinking density, and the stiffness of polymer chain was decreased, which decreased the glass transition temperature and the storage modulus.

The thermal stability of the cured epoxy resins was investigated by TGA. The thermogram curves are depicted in Figure 9 and the decomposition temperature (T_d), the temperature at 5% weight loss (T_5), and residual weight at 800°C (W_{800}) are summarized in Table II. T_5 and W_{800} of TGAPP/DDS were 2.4°C and 1% lower than those of TGPAP/DDS, indicating the slightly decreased thermal stability of TGAPP.

Mechanical Properties of Epoxy Resins

The mechanical properties of the cured epoxy resins were investigated and the results are listed in Table III. The tensile strength and tensile modulus of TGAPP /DDS were 66 MPa and 2.77 GPa, respectively, 10% and 1.8% higher than those of TGPAP /DDS. The flexural strength and flexural modulus of TGAPP /DDS were 118 MPa and 3.85 GPa, 6.3% and 2.8% lower than those of TGPAP /DDS, which is consistent with the result of DMA analysis. It was interesting to observe that the impact strength of TGAPP/DDS was improved by 50%, from 10.02 kJ/m^2 of TGAPP/DDS to 15.10 kJ/m^2 of TGPAP/DDS. The increased toughness of TGAPP/DDS was due to the introduction of flexible oxyphenylene unit which improved the chain segment mobility. On the other hand, the presence of oxyphenylene unit reduced the flexural strength and flexural modulus of TGAPP/DDS, indicating the slightly decreased rigidity of the three-dimensional structure.

Fracture Morphology

The fracture surfaces of the epoxy resins are shown in Figure 10. As can be seen that the fracture surface of the TGPAP/DDS was smooth and glassy. This suggested that no large scale plastic deformation occurred during fracture, which was typical of

a brittle thermosetting polymer[31,32]; hence, a low impact strength of 10.02 kJ/m^2 was measured. For comparison, the fracture surface of TGAPP/DDS was rougher than that of the TGPAP/DDS, the ridges on the fracture surface acted as obstacles to cause the deflection of the crack, therefore, the required energy for the propagation of the cracks on the surfaces increased.[20,33] As a result, the impact strength of TGAPP/DDS was increased by 50% to 15.10 kJ/m^2. As TGAPP was synthesized via the three-step procedure, the overall yield of TGAPP was relatively low, which would add to its production cost, resulting in the high cost of the toughness increase of the epoxy.

CONCLUSIONS

A novel epoxy resin, containing oxyphenylene unit in the molecular structure, was synthesized and characterized. DSC and rheological analysis showed that the reactivity of TGAPP was lower than that of the TGPAP epoxy resin, and the processing window of TGAPP/DDS was 20°C wider compared to that of TGPAP/DDS. The cured TGAPP showed a lower T_g, a lower thermal stability, a lower flexural strength, a higher tensile strength, and a higher impact strength compared with TGPAP. SEM characterization of TGAPP/DDS demonstrated that ridges appeared on the fracture surfaces morphology. The improved tensile strength and impact strength of the cured TGAPP/DDS were due to the the introduction of oxyphenylene unit into the molecular structure of TGAPP. The improved tensile strength, impact strength, and excellent processability might make TGAPP promising candidate for advanced composite matrix.

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