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Synthesis, Characterization, and Properties of Low Viscosity Tetra-functional Epoxy Resin *N,N,N′,N′*- tetraglycidyl-3,3′-diethyl-4,4′-diaminodiphenylmethane

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ABSTRACT: Tetra-functional epoxy resin *N,N,N′,N′*-tetraglycidyl-3,3′-diethyl-4,4′-diaminodiphenylmethane (TGDEDDM) was synthesized and characterized. The viscosity of TGDEDDM at 25°C was 7.2 Pa·s, much lower than that of *N,N,N′,N′*-tetraglycidyl-4,4′-diaminodiphenylmethane (TGDDM). DSC analysis revealed that the reactivity of TGDEDDM with curing agent 4,4′-diamino diphenylsulfone (DDS) was significantly lower than that of TGDDM. Owing to its lower viscosity and reactivity, TGDEDDM/DDS exhibited a much wider processing temperature window compared to TGDDM/DDS. Trifluoroborane ethylamine complex (BF_3-MEA) was used to promote the curing of TGDEDDM/DDS to achieve a full cure, and the thermal and mechanical properties of the cured TGDEDDM were investigated and compared with those of the cured TGDDM. It transpired that, due to the introduction of ethyl groups, the heat resistance and flexural strength were reduced, while the modulus was enhanced. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40009.

KEYWORDS: thermosets; viscosity and viscoelasticity; thermal properties; resins; structure-property relations

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INTRODUCTION

Epoxy resins, the most common and important thermosetting polymers, have been used extensively in industry, as coating, adhesives, composite matrix, etc., due to their excellent comprehensive properties. Multifunctional epoxy systems are of particular interest, largely because of their high temperature capabilities and mechanical properties.[1–10] Multifunctional glycidyl amine type epoxy resins, mainly represented by tetra-functional one *N,N,N′,N′*-tetraglycidyl-4,4′diaminodiphenylmethane (TGDDM) and tri-functional one triglycidyl para-aminophenol (TGPAP), are included in the most important multifunctional epoxy resins.

The synthesis of TGDDM epoxy resins (Scheme 1) was first patented by Union Carbide Corporation in 1956.[11] From 1970s, TGDDM epoxy resins have started to be used in the manufacture of carbon fiber-reinforced composites for aerospace use, because of their excellent mechanical properties, heat resistance and adhesion property. They are now among the main matrix resins for advanced composites in aerospace and aircraft applications. Nowadays, many commercial products of TGDDM are available, such as MY-720 and MY-721 produced by Huntsman, AG-80 from Shanghai Research Institute of Synthetic Resins (China), etc.

One of the main disadvantages of TGDDM is their high viscosity. The viscosity at 50°C was 8–18 Pa·s for MY-720, 3–6 Pa·s for MY-721, and 6–10 Pa·s for AG-80. The viscosity of TGDDM at 25°C was usually around hundreds of Pa·s, and the lowest reported viscosity was about 70 Pa·s.[12] The high viscosity limits their use in liquid molding process. Moreover, because the cured neat TGDDM is intrinsically fragile, toughening modification is regularly required. High-performance thermoplastic resins are often incorporated into the TGDDM epoxy systems as toughening modifier in the preparation of advanced composite matrix,[13–21] which results in a significant increase of viscosity. Therefore the addition amount of thermoplastic toughener in TGDDM is restricted; otherwise, the processability will become extremely poor. Although some reactive or inert diluents can be used to reduce the viscosity of TGDDM and then to maintain the processability when an enough amount of thermoplastic toughener is compounded, the introduction of diluents inevitably has adverse effects on the properties of the cured resin, such as a decrease in glass transition temperature (T_g) and a deterioration of heat resistance.

It has been patented that, when the 3 and 3′, positions of benzene rings in TGDDM were substituted by halogen, methyl or ethyl groups, the viscosity was reduced remarkably.[22–25] However, to the best of our knowledge, there has been no systematic investigation reported on the synthesis and the properties of this kind of epoxy resins. In this study, we present the

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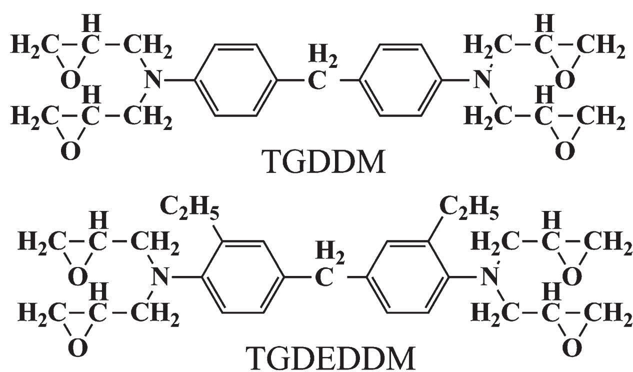


Scheme 1. The chemical structures of TGDDM and TGDEDDM.

synthesis and characterization of *N,N,N′,N′*-tetraglycidyl-3,3′-diethyl-4,4′-diaminodiphenylmethane (TGDEDDM) epoxy resin (Scheme 1). As expected, the viscosity of TGDEDDM was much lower than that of TGDDM. The reactivity of TGDEDDM with the curing agent 4,4′-diamino diphenylsulfone (DDS), and the properties of the cured resin were investigated with those of TGDDM for comparison.

EXPERIMENTAL

Materials

3,3′-Diethyl-4,4′-diaminodiphenylmethane (DEDDM) was donated by Jiangyin Wayfar Synthetic Material Co., China, and purified by vacuum distillation before use; epichlorohydrin (ECH), 2-methoxyethanol, sodium hydroxide, toluene, and 4,4′-diaminodiphenylsulfone (DDS) were supplied by Beijing Chemical Reagents Company (China) and used as received; TGDDM with a epoxy equivalent weight of 118 was obtained from Shanghai Research Institute of Synthetic Resins; trifluoroborane ethylamine complex (BF_3-MEA) and lanthanum nitrate were purchased from TCI, Japan, and used as received.

Synthesis of TGDEDDM

DEDDM (30 g) dissolved in toluene (45 g) and 50% lanthanum nitrate in 2-methoxy-ethanol (1.2 g) were placed in a 250 mL three-necked flask equipped with a mechanical stirring bar, a constant-voltage funnel, a thermometer, a water separator, and a reflux condenser. After the solution temperature was maintained at 60°C by means of vacuum reflux, epichlorohydrin (48 g) was added dropwise over 3 h, and the vacuum reflux was held for 9 h. Then 50% aqueous of benzyltrimethylammonium chloride (0.45 g) was added and the system set up for vacuum azeotrope. 50% aqueous sodium hydroxide (75.5 g) was then added over 3h, and water was distilled out under vacuum at 60°C. After the addition, the temperature and vacuum were held for another 2 h. Then 100 mL toluene was added and the mixture was washed with deionized water to the neutral pH. The organic layer was separated and evaporated in vacuo to give the product TGDEDDM, a clear brown viscous liquid at room temperature. Yield: 48.05 g (86%). FTIR (KBr, cm^{-1}): 3529, 3048, 2983, 2872, 1600, 1496, 1450, 1203, 1107, 915. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): 7.14 (*d*, 2H), 7.07(*s*, 2H), 6.99 (*d*, 2H), 3.89 (*s*, 2H), 3.24 (*m*, 4H), 3.06 (*m*, 8H), 2.79 (*m*, 4H), 2.69 (*m*, 4H), 2.46 (*m*, 4H), 1.22 (*m*, 6H).

Preparation of Cured Epoxy Resins

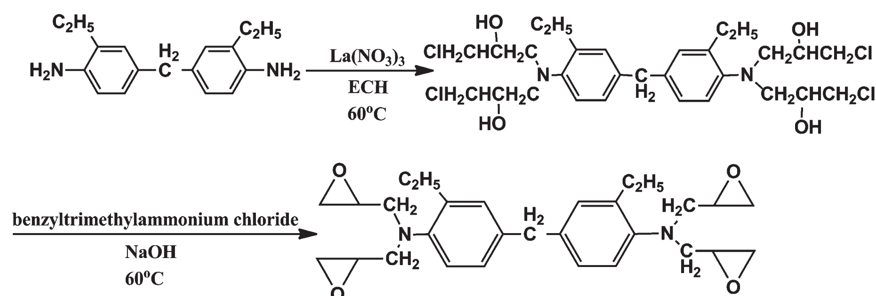
The reactant compositions were mixed homogeneously in a 1 : 1 molar ratio according to the EEW values. To prepare the samples for Differential scanning calorimetry (DSC) measurement and rheology test, the DDS powder was mixed with epoxy resin with continuous mechanical stirring at 80°C for 10 min to get a homogeneous dispersion. To prepare the samples for mechanical properties test, dynamic thermomechanical analysis (DMA) and thermal gravimetric analysis (TGA), the epoxy/amine mixture was heated to 150°C with continuous mechanical stirring until a homogenous solution was formed, then the mixture was poured into the silicon rubber molds after degassing under reduced pressure. When accelerant BF_3-MEA was used, the epoxy/amine solution was cooled to 80°C, and mixed homogeneously with BF_3-MEA before casting. The curing regimes were shown in Table II.

Characterization and Measurement

The structure of TGDEDDM 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 as solvent and tetramethylsilane as internal reference. The FTIR AQ2 measurement was performed on a BRUKER TENSOR-27 FTIR spectrometer at room temperature in the range of 4000–400 cm^{-1}. The bulk viscosities of epoxy resins were measured on a Brookfield model DV-II cone and plate viscometer (Brookfield). The reversed phase HPLC was carried out using Waters 600 inversed phase chromatography with C 18 columns at 35°C, using methanol as eluent and UV detection at 254 nm. The molecular weight, based on polystyrene standard, was determined by Waters 1515 gel penetration chromatography (Waters Co.).

DSC was used to investigate the curing behavior of epoxy blends by scanning with a SII EXSTAR6000-DSC6220 from 30 to 350°C at a heating rate of 5, 10, 15, 20°C/min, respectively. The instrument was calibrated with a high-purity indium standard, and α-Al_2O_3 was used as the reference material. 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. Samples of dimensions 80 mm × 10 mm × 4 mm were prepared for mechanical properties test. The flexural properties were determined at room temperature on an Instron model 3365 universal tester (Instron, Canton, MA) according to ASTM D-790 in a three-point bending mode. The span was 64 mm, and the strain rate was 1 mm/min. 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.



Scheme 2. Synthesis of TGDEDDM.

The reported mechanical properties were the average of at least five samples.

RESULTS AND DISCUSSION

Synthesis and Characterization of TGDEDDM

The epoxy resin TGDEDDM was synthesized through a two-step epoxidation of DEDDM as shown in Scheme 2. The first step was the ring-opening of epichlorohydrin with DEDDM catalyzed by lanthanum nitrate. It has been reported that di- or higher-valent metal salts of inorganic oxy-acid were effective catalysts to promote the aromatic amine-epichlorohydrin reaction in the synthesis of glycidyl amine type epoxy resins.[25,26] Lanthanum nitrate was especially favorable to achieve a low viscosity in the preparation of epoxy resins with high epoxide content. An inert solvent, 2-methoxyethanol, which can dissolve lanthanum nitrate and is miscible with reaction solvent (toluene) was used to enhance the catalytic effectiveness of lanthanum nitrate. The second step was a ring-closure process by dehydrochlorination with a phase-transfer catalyst, benzyltrimethylammonium chloride, and a base, 50% NaOH aqueous solution.

The obtained TGDEDDM is a clear brown viscous liquid, with a viscosity of 7.2 Pa·s at 25°C, which is about 1/10th of the lowest reported viscosity of TGDDM.[9] This low viscosity is of a great advantage for processing. The expected low viscosity is due to the introduction of ethyl group, resulting in the reduction intermolecular force. The purity of TGDEDDM, determined by the HPLC chromatography, was 94.28%. The product also contained a small amount of oligomers, and its average number molecular weight was 488 as measured by GPC.

Figure 1(a) shows the ^{1}H NMR spectrum of TGDEDDM, the resonance signals of epoxide protons appeared in the region of 3.06–2.46 ppm. Compared to the ^{1}H NMR spectrum of TGDDM [Figure 1(b)], the resonance signals at 1.24–1.20 and 2.81–2.74 in Figure 1(a) were assigned to the protons in the methyl and methylene groups, respectively. The epoxy value of TGDEDDM, calculated from the ^{1}H-NMR spectra, was 0.77, which was 92.4% of theoretical epoxy value. The FTIR spectrum of TGDEDDM is given in Figure 2. The characteristic band of oxirane rings was detected at 915 cm^{-1}. The absorption in the range of 3300–3500 cm^{-1} was assigned to the hydroxyl groups which existed in the oligomers. The above structural characterization demonstrates the successful synthesis of TGDEDDM epoxy resin.

Curing of Epoxy Resins

DDS, an epoxy curing agent commonly employed for preparing high-performance composite matrix, was used to cure epoxy resins. Figure 3 shows the DSC curves for TGDEDDM/DDS and TGDDM/DDS at a heating rate of 10°C/min. The exothermic

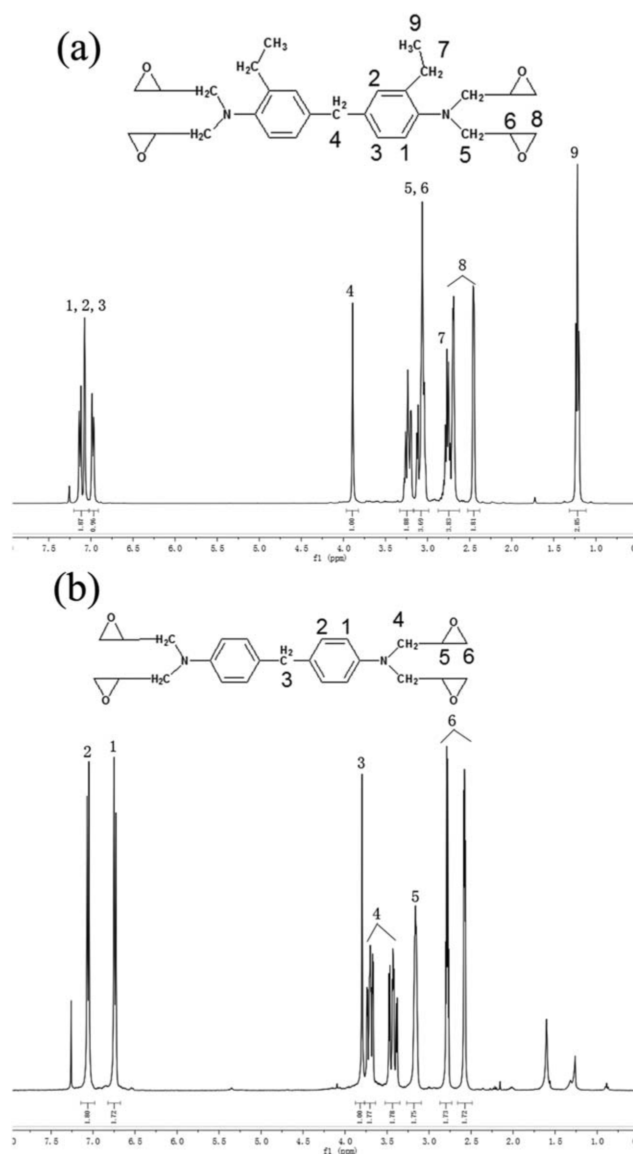


Figure 1. ^{1} H-NMR spectra of (a) TGDEDDM and (b) TGDDM.

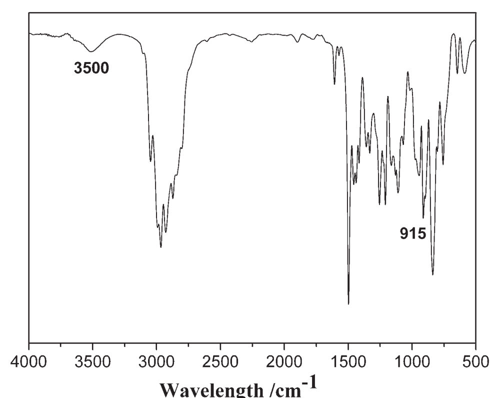


Figure 2. FTIR spectrum of TGDEDDM.

peak of TGDEDDM/DDS appeared at 261.2°C, about 30°C higher than that of TGDDM/DDS, implying the reactivity of TGDEDDM with DDS is significantly lower than that of TGDDM.

DSC thermograms of epoxy/DDS at a series of heating rate (5, 10, 15, and 20°C/min) in a N_2 atmosphere are shown in Figure 4 and the curing kinetics of epoxy/DDS are investigated. Table I lists the exothermic peak temperatures (T_P) obtained from the DSC curves, which increase with increasing heating rate. The apparent activation energies (E_a) of curing reaction can be calculated using Ozawa's[27–29] and Kissinger's[30] methods, as shown eqs. (1) and (2), respectively, where E_a is the activation energy (kJ/mol); R is gas constant (8.314 J/mol K); β is the heating rate (°C/min) and T_p is the peak temperature in K.

$$E_a = \frac{Rd(1\text{n}\beta)}{1.052d(1/T_p)} \tag{1}$$

$$E_a = \frac{Rd\left[1\text{n}\left(\beta/T_p^2\right)\right]}{d(1/T_p)} \tag{2}$$

Figure 5 shows the plots of ln β versus $1000/T_p$ and ln (β/T_p^2) versus $1000/T_p$ for the curing of TGDDM and TGDEDDM with DDS. E_a values calculated from the slope of the lines are listed in Table I. Moreover, the reaction order was determined using Crane equation shown in eq. (3):

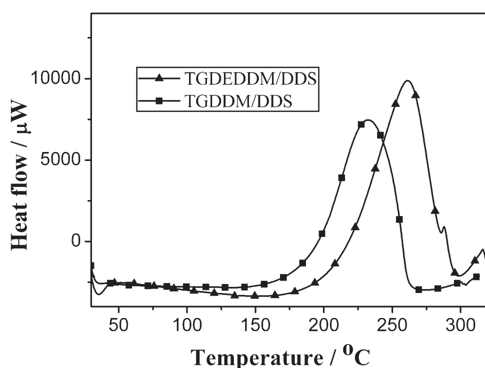
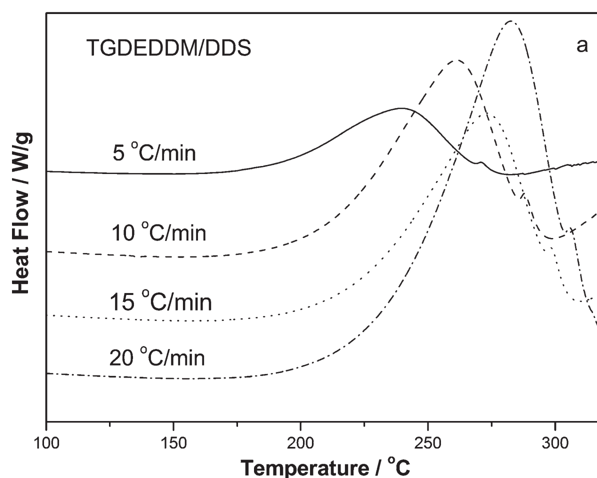


Figure 3. DSC scans at 10°C/min for TGDEDDM/DDS and TGDDM/DDS.



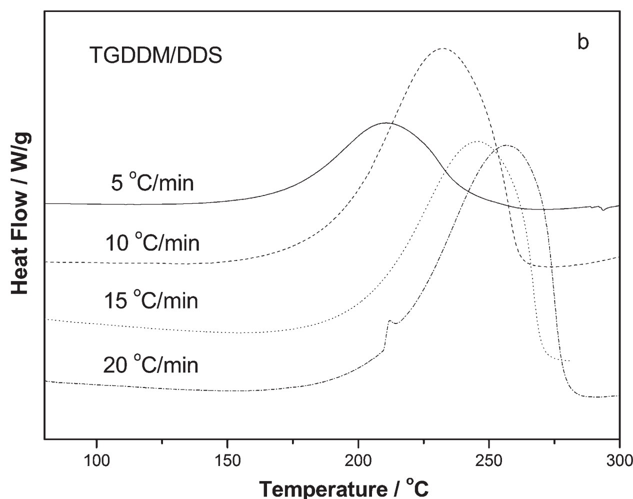


Figure 4. DSC thermograms of TGDEDDM/DDS (a) and TGDDM/DDS (b) at 5, 10, 15, 20°C/min heating rates in N_2 atmosphere.

$$\frac{d(1\text{n}\beta)}{d(1/T_p)} = \frac{-E_a}{nR} \tag{3}$$

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

As seen in Table I, TGDEDDM/DDS and TGDDM/DDS show the same reaction order of 1.1, demonstrating that they share the same reaction mechanism. This is quite understandable considering that TGDEDDM and TGDDM have the same functionality and a similar structure of reactive epoxy groups. However, the apparent activation energy of TGDEDDM/DDS is 5 kJ/mol higher than that of TGDDM/DDS. It transpires that, compared to TGDDM, the reactivity of TGDEDDM is reduced with the ethyl substitution in the 3 and 3′ positions of benzene rings, which is definitely due to the steric hindrance effect.

To understand the rheological behavior of the epoxy resins during curing, a dynamic rheology test was performed at a heating rate of 5°C/min. The plots of the complex viscosity vs. test temperature are shown in Figure 6. It can be seen that the initial viscosity of TGDEDDM/DDS was much lower than that of TGDDM/DDS. The viscosity first decreased with increasing temperature, then reached a plateau, at which the viscosity kept

Table I. DSC Analysis Results for TGDEDDM/DDS and TGDDM/DDS

Samples	Exothermic peak temperature (°C) at different heating rate (°C/min)				Ozawa E_a (kJ/mol)	Kissinger E_a (kJ/mol)	Reaction order
	5	10	15	20			
TGDDM/DDS	210.5	232.1	245.6	256.4	61.35	56.14	1.09
TGDEDDM/DDS	239.3	261.2	273.2	282.5	72.25	67.15	1.10

Table II. The Tan δ Peak Temperatures in DMA Curves for the Cured Epoxy Resins with Different Curing Procedures

Samples	Accelerant BF_3-MEA (%)	Curing procedure (h)					T_g(°C) (Tan δ)
		120°C	150°C	180°C	200°C	220°C	
TGDDM	0	–	2	2	2	–	273.5
TGDEDDM-1	0	–	2	2	2	–	271.7
TGDEDDM-2	0	–	2	3	3	–	268.5
TGDEDDM-3	0	–	2	3	3	2	258.8
TGDEDDM-4	0.5	1	2	3	3	–	259.4
TGDEDDM-5	1	1	2	3	3	–	258.6
TGDEDDM-6	2	1	2	3	3	–	253.5

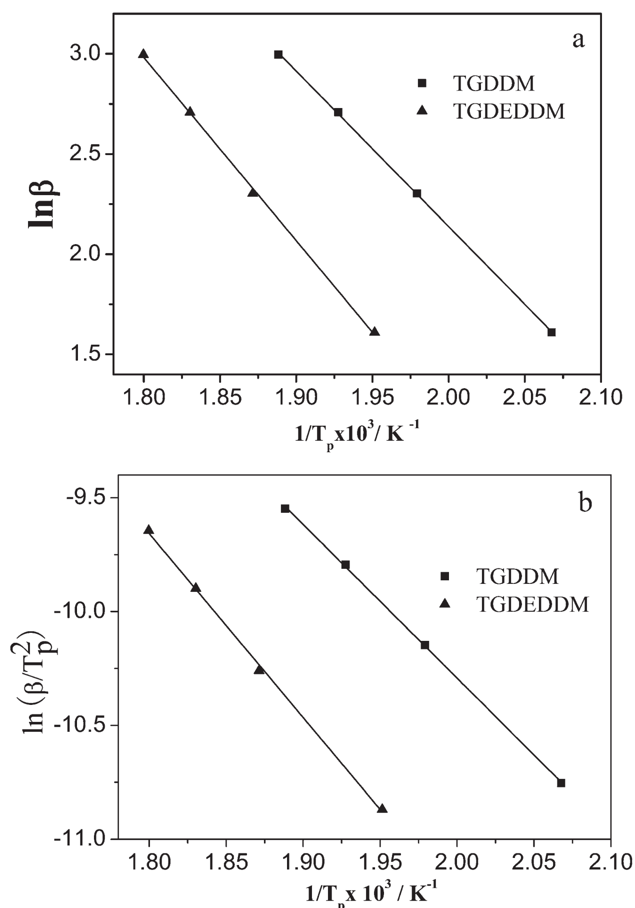


Figure 5. Plots of ln β versus $1000/T_p$ (a) and ln $(\beta/T_p{}^2)$ versus $1000/T_p$ (b) for the curing of TGDDM and TGDEDDM with DDS.

almost constant. TGDEDDM/DDS and TGDDM/DDS exhibited a nearly equivalent viscosity of 0.2 Pa·s at the plateau. As the temperature increased up to a critical value, the viscosity increased dramatically, indicating the gelation occurred. The gelation temperature of TGDEDDM/DDS was around 205°C, about 30°C higher than that of TGDDM/DDS. The temperature range of viscosity plateau is termed as "processing temperature window." As seen in Figure 6, TGDEDDM/DDS demonstrates a processing temperature window of 60–205°C, about 70°C wider compared to that of TGDDM/DDS, indicating the much improved processability of TGDEDDM/DDS.

Dynamic Mechanical Thermal Analysis

DMA was carried out for the TGDEDDM/DDS resin systems with different curing conditions. The storage modulus and tan δ are shown as a function of temperature in Figures 7 and 8.

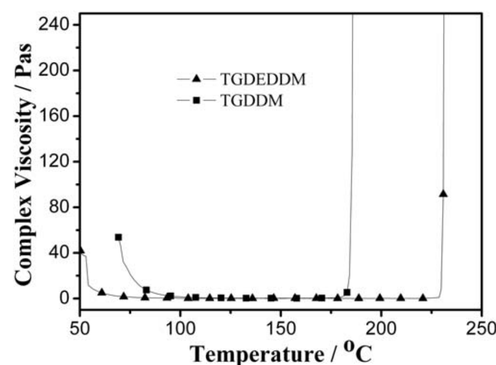


Figure 6. The rheological curves of TGDDM and TGDEDDM cured with DDS.

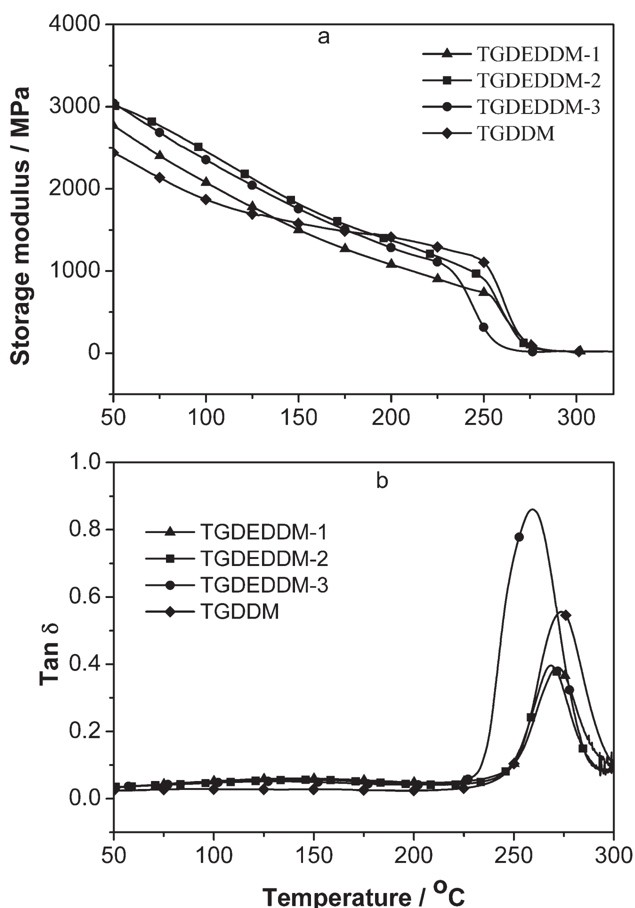


Figure 7. DMA curves of the cured TGDEDDM/DDS and TGDDM/DDS: (a) storage modulus; (b) tan δ.

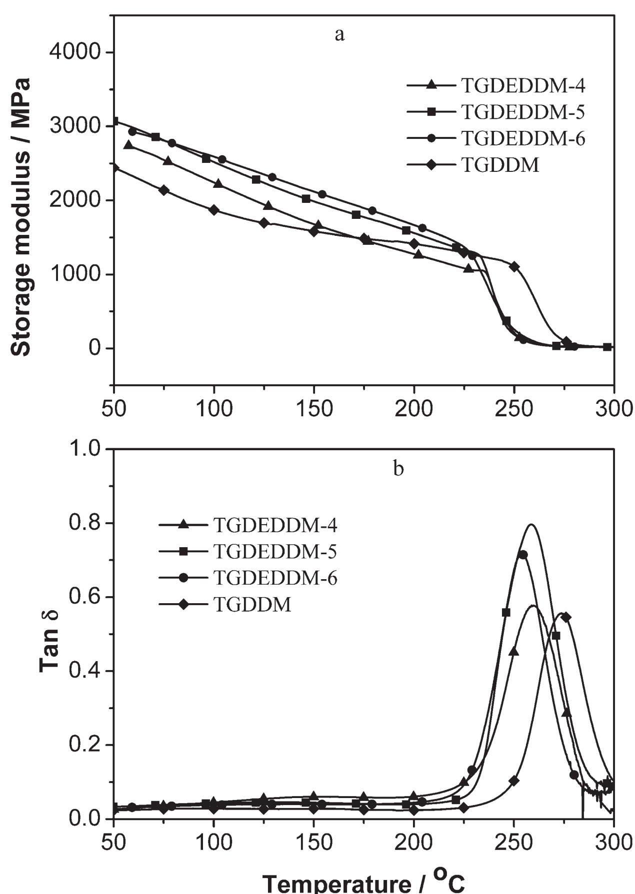


Figure 8. DMA curves of the cured TGDEDDM/DDS with BF_3-MEA as catalyst: (a) storage modulus; (b) tan δ.

The glass transition temperatures (T_g, the tanδ peak temperatures) are listed in Table II.

In our previous study, it transpires that post-curing at 200°C/2 h can ensure the complete cure of TGDDM/DDS.[31] The fully cured TGDDM/DDS exhibits a T_g around 270°C. When TGDEDDM/DDS was post-cured at 200°C/2 h (TGDEDDM-1), it demonstrated a T_g a little lower than that of TGDDM/DDS. As the post-cure time was extended to 3 h (TGDEDDM-2), T_g almost maintained, while the storage modulus evidently increased as seen from Figure 7(a). The cured TGDEDDM exhibited a higher storage modulus compared to the cured TGDDM at 50°C. However, the modulus of TGDEDDM decreased more quickly with temperature than that of TGDDM, and the former became lower than the latter at above 130°C for TGDEDDM-1, and at above 190°C for TGDEDDM-2, indicating that TGDEDDM-2 had a higher curing degree, and TGDEDDM-1 was not fully cured. It is concluded that it is more difficult for TGDEDDM/DDS to achieve a full cure than for TGDDM/DDS due to the lower reactivity of TGDEDDM/DDS.

In order to achieve a full cure, TGDEDDM/DDS was post-cured at 220°C/2 h (TGDEDDM-3). It is surprising to find that T_g decreased by about 10°C compared to TGDEDDM-2, whereas the storage showed a slight decrease. Morever, the tanδ peak became higher and broader. These results were not observed for TGDDM/DDS.[26] These observations were attributed to the partial degradation of TGDEDDM/DDS due to the poorer thermal stability discussed later.

Because when curing at a very high temperature, such as 220°C the epoxy resins have the tendency of oxidation and decomposition, a small amount of BF_3-MEA complex was added to promote the curing reaction and then to lower the post-cure temperature. It is known that BF_3-MEA can effectively accelerate the curing reaction of TGDDM/DDS.[32] It is interesting to observe that the storage modulus of TGDEDDM-4 (cured with 0.5 wt % BF_3-MEA) shows a little abnormal increase with temperature from 230 to 235°C in Figure 8(a) (more clearly in the insert). This should result from the further curing during DMA test, and meaning that TGDEDDM-4 is still undercure. When 1 wt % (TGDEDDM-5) or 2 wt % (TGDEDDM-6) BF_3-MEA was used, this phenomenon was not observed.

TGDEDDM-5 and TGDEDDM-6 show a similar storage modulus, always evidently higher than that of TGDDM and TGDEDDM-4 until the storage modulus inflection, which is quite different from the cured TGDEDDM without BF_3-MEA. It was considered that full cure was attained for TGDEDDM-5 and TGDEDDM-6. This result indicated that BF_3-MEA did

Table III. Flexural Properties and Impact Strength of the Cured Epoxy Resins

Samples	Flexural strength (MPa)	Flexural modulus (GPa)	Impact strength (kJ/m ^{2})
TGDDM	124.53 ± 2.81	3.58 ± 0.096	8.68 ± 3.02
TGDEDDM-2	101.47 ± 12.63	3.68 ± 0.060	9.93 ± 0.97
TGDEDDM-6	102.79 ± 6.59	3.66 ± 0.046	7.54 ± 0.32

promote the curing reaction. It is just because of the acceleration of BF_3-MEA, TGDDM-4 was subjected to a quick post-cure during DMA test, and thus abnormal storage modulus increase with temperature was observed.

Furthermore, it can be seen clearly from Table II that, with the same curing procedure, the T_g of TGDEDDM/DDS decrease with increasing the addition of BF_3-MEA. This is probably because more polyether structure was formed with more BF_3-MEA, as BF_3-MEA can catalyze not only the amine-epoxy reaction, but also the homopolymerization of epoxy.[33,34]

From theoretical analysis, ethyl substitution has two opposite effects on the storage modulus and T_g: one is a decrease as a result of reduced intermolecular force; the other is an increase arising from decreased molecular mobility. The overall result, as revealed by DMA analysis, is that a decrease in T_g and an increased in storage modulus.

Mechanical Properties and Fracture Toughness of the Cured Epoxy Resins

The flexural strength and modulus and impact strength of the cured TGDEDDM (TGDEDDM-2 and TGDEDDM-6) were measured at room temperature, and the results are listed in Table III, with that of the cured TGDDM for comparison. Typical stress–strain curves from the flexural tests for TGDEDDM/DDS and TGDDM/DDS are shown in Figure 9. As seen in Figure 9, the stress-strain behavior for TGDEDDM/DDS and TGDDM/DDS is linear up to the failure point. The curing degree difference between TGDEDDM-2 and TGDEDDM-6 seems have no discernible effect on mechanical strength and modulus. The flexural modulus of TGDEDDM is a little higher than that of TGDDM, which is consistent with the DMA analysis. Whereas the flexural strength of TGDEDDM is lower by about 20% than that of TGDDM. The lower flexural strength of TGDEDDM can be interpreted by the reduced intermolecular force. Otherwise, TGDEDDM and TGDDM show comparable impact strength, indicating they have similar toughness, this is likely due to their similar crosslinking density.

Thermal Stability of the Cured Epoxy Resins

The thermal stability of the cured epoxy resins was investigated by TGA. The thermogram curves are shown in Figure 10 and the decomposition temperature (T_d), the temperature at 5% weight loss ($T_{5\%}$), and residual weight at 600°C (R_w) are summarized in Table IV.

T_d and R_w of the cured TGDEDDM are about 25°C and 8% lower than those of the cured TGDDM, respectively, indicating the poorer thermal stability of TGDEDDM. The residual weight of TGDEDDM at 600°C ranges between 20.9–21.9%, which is consistent with the results of related research,[31,35] and the mechanism of thermal degradation has been reported.[36] In addition, TGDEDDM-2 and TGDEDDM-6 exhibit almost the same T_d and R_w, but TGDEDDM-6 shows a lower $T_{5\%}$, probably due to more polyether structure. It turns out that the introduction of ethyl groups results in the decline of thermal stability. This is quite reasonable since the aliphatic groups are easy to decompose at high temperature. It is worth to point out that the weight proportion of ethyl groups in the whole formulation is 8.3%, which is very close to the R_w difference between TGDEDDM and TGDDM. That is to say, ethyl groups contribute almost nothing to residual weight.

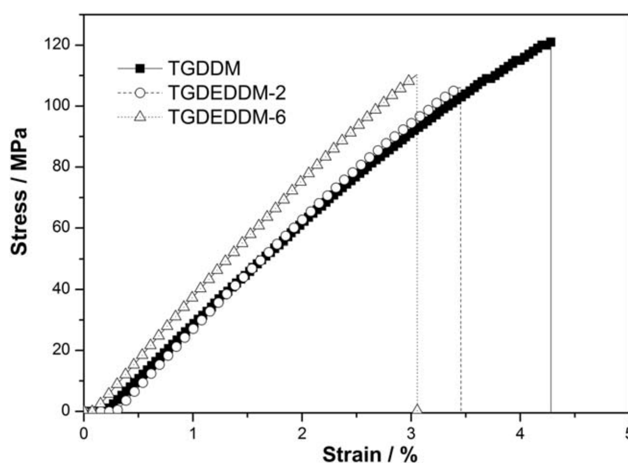


Figure 9. Stress–strain curve of flexure test results for TGDDM and TGDEDDM samples.

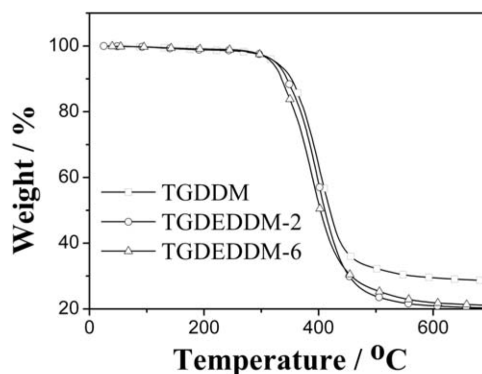


Figure 10. TGA curves for the cured TGDDM and TGDEDDM epoxy resins.

Table IV. TGA Results for the Cured TGDEDDM/DDS and TGDDM/DDS

Samples	T_d [a] (°C)	$T_{5\%}$ [b] (°C)	R_w [c] (%)
TGDDM	361	326	29.5
TGDEDDM-2	336	325	20.9
TGDEDDM-6	336	318	21.9

[a] Decomposition temperature.
[b] Temperature of 5% weight loss.
[c] Residue char at 600°C.

CONCLUSIONS

In this study, tetra-functional glycidyl amine type epoxy resin TGDEDDM was successfully synthesized and characterized. The viscosity is much lower than that of TGDDM because of the reduced intermolecular force after introducing ethyl groups. The viscosity of TGDEDDM at 25°C is about 1/10th that of TGDDM. Due to steric hindrance effect, TGDEDDM demonstrates a lower reactivity with curing agent DDS compared to TGDDM; the apparent activation energy of TGDEDDM/DDS is about 5 kJ/mol higher that of TGDEDDM/DDS. Compared to TGDDM/DDS, TGDEDDM/DDS exhibited a much wider processing temperature window owing to its lower viscosity and reactivity. BF_3-MEA can effectively accelerate the curing of TGDEDDM/DDS. The cured TGDEDDM shows a lower T_g, a lower thermal stability and a lower mechanical strength compared to the cured TGDDM. Although the heat resistance and mechanical were partially scarified resulting from the introduction of methyl groups, the high mechanical modulus and excellent processability make TGDEDDM promising candidate for some special applications, such as liquid molding process.

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