PAPER www.rsc.org/materials | Journal of Materials Chemistry

A thermally remendable epoxy resin†

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Received 14th July 2008, Accepted 2nd December 2008
First published as an Advance Article on the web 22nd January 2009
DOI: 10.1039/b811938d

To provide epoxy resin with crack healing capability, an epoxy containing both furan and epoxide groups, *N*,*N*-diglycidyl-furfurylamine (DGFA), was synthesized through a two-step approach. When it reacted with *N*,*N*′-(4,4′-diphenylmethane) bismaleimide (DPMBMI) and methylhexahydrophthalic anhydride (MHHPA), respectively, a crosslinked polymer with two types of intermonomer linkage was yielded. That is, thermally reversible Diels–Alder (DA) bonds from the reaction between furan and maleimide groups, and thermally stable bonds from the reaction between epoxide and anhydride groups. In this way, cured DGFA possessed not only similar mechanical properties as commercial epoxy, but also thermal remendability that enabled elimination of cracks. The latter function took effect as a result of successive retro-DA and DA reactions, which led to crack healing in a controlled manner through chain reconnection.

Introduction

In recent years, there have been continuous efforts to prepare self-repairing polymers and polymer composites.[1–4] It is desired that microcracks deep inside structures can be healed in an autonomic way.

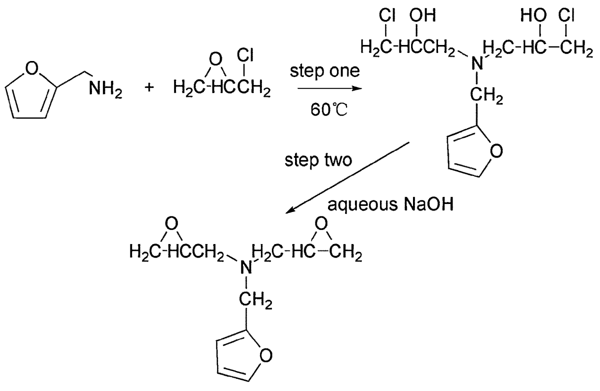
So far, the achievements in this aspect fall into two categories: extrinsic and intrinsic self-healing. In the case of extrinsic self-healing, the healing agent has to be encapsulated and embedded into the materials in advance. As soon as cracks destroy the fragile capsules, the healing agent would be released into the crack planes due to the capillary effect, re-binding the cracks.[5–7] For intrinsic self-mending, cracks can be healed by polymers themselves as a result of physical and/or chemical interactions at the broken faces. The work by Wudl and co-workers is a representative in this aspect.[8,9] They synthesized highly crosslinked polymeric materials with multi-furan and multi-maleimide *via* Diels–Alder (DA) reaction. At temperatures above 120 °C, the "intermonomer" linkages disconnect (corresponding to retro-DA reaction) but then reconnect upon cooling (i.e. DA reaction). This process is fully reversible and can be used to restore fractured parts of the polymers. In principle, an infinite of crack healing is available without the aid of additional catalysts, monomers and special surface treatment.

Following the approach of Wudl and co-workers, Liu and Hseih prepared a thermally remendable and removable crosslinked polymer through DA reactions between multifunctional furan and maleimide monomers, by using epoxy compounds as precursors.[10] In a subsequent paper, Liu and Chen reported thermally reversible crosslinked polyamides from maleimide-containing polyamides and a tri-functional furan compound.[11]

On the other hand, Ober and co-workers showed a series of reworkable epoxy compounds that incorporated thermally cleavable groups, such as secondary or tertiary esters, into the networks.[12,13] These groups were chosen to decompose between 200 and 300 °C so that the cured epoxy can be removed without damaging the underlying structure. Also, Small *et al.* made a thermally-removable encapsulant from a bis(maleimide) compound and tris(furan) or tetrakis(furan), which can be easily removed by heating to temperatures higher than 90 °C, preferably in a polar solvent.[14]

Epoxy has been extensively employed in many applications because of its excellent properties.[15,16] It is worth noting that curing reactions of epoxy with hardeners are generally irreversible. Consequently, conventional cured epoxy can hardly exhibit remendable behavior due to lack of the ability of recombination of broken molecules. Since epoxy materials mostly work under severe circumstances where long-term service is required, it would be ideal if they were integrated with multiple self-healing capability.

In this work, a novel epoxy resin, *N*,*N*-diglycidyl-furfurylamine (DGFA, Scheme 1, IUPAC name: *N*-(2-furylmethyl)-*N*,*N*-bis(oxirane-2-ylmethyl)amine) was synthesized to combine



Scheme 1 DGFA synthesized by a two-step route.

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† Electronic supplementary information (ESI) available: Synthesis and characterization of DGFA, isothermal curing kinetics, and time dependences of DA conversion. See DOI: 10.1039/b811938d

epoxide with furan groups in one molecule. The epoxide groups can react with a traditional curing agent like anhydride to form an epoxy network, providing the material with outstanding mechanical properties and thermal resistance as usual. Meanwhile, the furan groups can react with maleimide to introduce thermally reversible DA bonds into the epoxy network. Eventually, the molecular networks in the cured material are comprised of two types of intermonomer linkage. In this context, the advantages of the epoxy and an intrinsic self-healing ability join together.

This paper discussed the synthesis and characterization of DGFA and the related substances. Thermal reversibility and remendability of the resultant were also examined for having a deeper understanding of the structure-property relationship. In addition, the newly developed epoxy is intended to possess thermal remendability below its glass transition temperature. To attain this objective, for such a DGFA molecule, the curing feature of its epoxy groups with anhydride, and the recyclability of retro-DA and DA reactions between furan and maleimide groups, were carefully studied. The kinetic inhibition effect of the epoxy network on the reversible DA reaction was revealed from retro-DA and DA reactions of the cured DGFA resin.

Experimental

Materials and reagents

Reagents and solvents used in the syntheses, including furfural amine, epichlorohydrine, ethyl acetate, hexane and sodium hydroxide, were obtained from Alfa Aesar GmbH, Germany. The curing agents, methylhexahydrophthalic anhydride (MHHPA) and *N*,*N*′-(4,4′-diphenylmethane) bismaleimide (DPMBMI), were supplied by Aldrich Chemical Co., USA. All the chemicals were used as received.

Measurements

Fourier transform infrared (FTIR) spectra were recorded with a Bruker EQUINOX55 Fourier transformation infrared spectrometer coupled with an infrared microscope spectrometer. ^{1}H-NMR and ^{13}C-NMR spectra were measured on a VARIAN Mercury-Plus 300 (300 Hz). Elemental analysis was performed with a Vario EL elemental analyzer. Dynamic viscosity of the resin at 25 °C was measured by an advanced rheometric expansion system (ARES Rheometer, TA). Differential scanning calorimetry (DSC) was performed on a TA Instruments DSC Q10 using nitrogen purge and an empty aluminium pan as a reference.

Dynamic mechanical analysis (DMA) was conducted on a TA Instruments DMA 2980 at a heating rate of 5 °C/min. Tensile and flexural properties were tested at room temperature by an Instron 4505 universal testing apparatus under a constant crosshead rate of 2 mm/min. Each batch included ten specimens to yield an averaged value.

Synthesis of DGFA

Synthesis of DGFA followed the routine processes of producing a glycidyl amine-type epoxy resin. The experimental details and interpretation of the characteristic spectra can be found in the ESI.†

FTIR max(KBr)/cm^{-1}: 3144; 3117; 3051; 1503; 1346; 1250; 1148; 1013; 918; 851; 752. δ_H (300 MHz; CDCl$_3$, ppm): 7.3 (1 H); 6.3 (1 H); 6.2 (1 H); 3.8 (2 H); 3.1–2.4 (10 H). δ_C (300 MHz; CDCl$_3$, ppm): 151; 141; 110; 109; 66.6; 66.1; 61.1; 60.9; 60.6; 44.8; 44.5. Elemental analysis: (Found: C, 62.49; H, 7.15; N, 6.47. $C_{11}H_{15}NO_3$ requires C, 63.14; H, 7.23; N, 6.69%). Viscosity of DGFA at 25 °C is 0.02 Pa·s.

DA adduct of DGFA and DPMBMI

To achieve the retro-DA reaction feature of the adduct of DGFA and DPMBMI, a solution method was chosen to obtain the adduct as entirely as possible. Firstly, 5.71 g (0.016 mol) DPMBMI was dissolved in 50 mL anhydrous tetrahydrofuran (THF). The solution was charged into a 100 mL three-necked round-bottom flask equipped with magnetic stirring. Then, 6.68 g (0.032 mol) DGFA was slowly added into the solution. Afterwards, the solution was refluxed at about 66 °C for 24 h under N_2 atmosphere, and cooled down to room temperature. The reaction solution was poured into a large excess of diethyl ether. The precipitate was filtered, washed with methanol, and then dried under vacuum ($<1.3 \times 10^3$ Pa) at room temperature.

Preparation of DGFA/MHHPA/DPMBMI crosslinked polymer

First, 17.13 g (0.048 mol) DPMBMI was dissolved in 20 g (0.096 mol) DGFA liquid under stirring at 90 °C for 10 min without the help of solvent. Then, 25.86 g (0.1536 mol) MHHPA was mixed with the above mixture at 80 °C for an additional 10 min. The resultant homogeneous liquid was degassed, poured into a closed silicone rubber mold, and cured at 70 °C for 24 h. The curing temperature was selected according to the optimal temperature for DA bond formation (see the sub-section in the Results and discussion section: DA and retro-DA reactions between DGFA and DPMBMI), so that most furan and maleimide groups could take part in the reaction prior to the solidification of the system. Furthmore, a non-stoichiometric ratio of epoxy ring/anhydride of 1 : 0.8 was used to slow down curing of the resin.

Remendability assessment

The crosslinked polymer plates (5 mm thick) were impacted with an iron ball to generate visible cracks. The samples were then thermally treated at different temperatures for 20 min and annealed at 80 °C for different times. Variations in the damage patterns during annealing were monitored with a camera.

Results and discussion

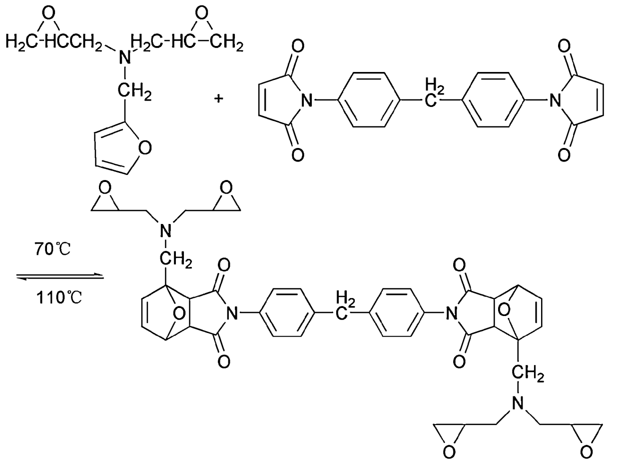
Synthesis and characterization of DGFA

The novel epoxy resin, DGFA, was synthesized according to a two-step reaction mechanism (Scheme 1). In the first step, a ring-opening addition reaction between the oxirane ring of epichlorohydrine and the amine group of 2-furfurylamine occurred to produce a chlorohydrine end-group compound. In the second step, DGFA formed through the ring-closing reaction of chlorohydrine groups owing to the dehydrochlorination action of NaOH solution. After purification by chromatography on a silica gel column, the product of DGFA was characterized with FTIR (ESI, Fig. S1†), ^{1}H-NMR (ESI, Fig. S2), ^{13}C-NMR (ESI, Fig. S3) and elemental analysis.

The data shown in the Experimental section provide sufficient evidences for the chemical structure of DGFA. Further analysis of the spectra is available in the ESI.

To highlight the effect of purification during the preparation of DGFA, the FTIR spectrum of the raw DGFA product is compared to that of its purified version (cf. ESI, Fig. S1A and S1B). A broad absorption at 3471 cm^{-1} appears on the former, which is ascribed to the stretching mode of the chlorohydrine groups (O–H). It means that the ring-closing reactions of the chlorohydrine groups in the second step (Scheme 1) were not completely carried out, which explains the necessity of purification by chromatography to obtain high purity DGFA.

Since the structure of DGFA has been confirmed, the reactivity of the attached epoxide groups has to be checked. Accordingly, the isothermal curing kinetics of DGFA with MHHPA at a stoichiometric ratio were studied by DSC using a modified Avrami equation (see ESI, Table S1†).[17] It is found that DGFA can perform the curing reaction with MHHPA like a conventional epoxy resin, implying that the synthesized DGFA might be applicable for the field in which conventional epoxy resin is employed. In addition, the activation energy, 61.5 kJ/mol, agrees well with that of a similar epoxy-anhydride system (71.6 kJ/mol).[18] On the other hand, DGFA can be cured by MHHPA at a temperature as low as ~50 °C (see ESI, Fig. S4), which contrasts sharply with the case of conventional epoxy cured by anhydride even in the presence of an accelerant (i.e. 100~150 °C). The catalytic effect of the tertiary amine group on the DGFA molecules (see Scheme 1) should take the responsibility.



Scheme 2 DA and retro-DA reactions between DGFA and DPMBMI.

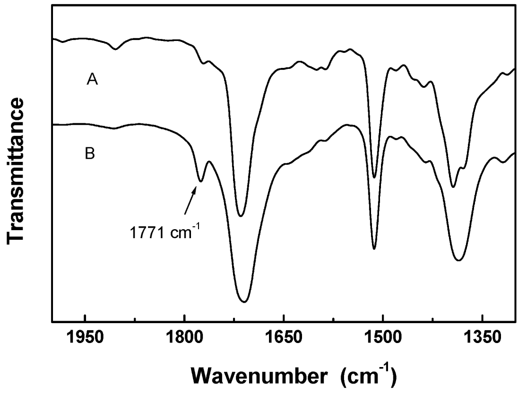


Fig. 1 FTIR spectra of (A) a mixture of DGFA and DPMBMI, and (B) a mixture of DGFA and DPMBMI treated at 66 °C for 24 h.

DA and retro-DA reactions between DGFA and DPMBMI

The objective of this work is to develop a thermally remendable epoxy resin by introducing thermally reversible groups into the cured networks. Therefore, the reversibility of the DA reaction between DGFA (containing furan ring, electron-rich diene) and DPMBMI (involving maleimide, electron-poor dienophile) should be verified in addition to the above-proved reactivity of the epoxide groups of DGFA.

According to the literature,[19] DA and retro-DA reaction temperatures of the current system were set at 70 and 110 °C (Scheme 2), respectively. First, DA reaction of the furan and maleimide groups in an equivalent molar mixture of DGFA and DPMBMI was monitored by FTIR and ^{1}H-NMR spectroscopy as well. The mixture solution in acetone (50% w/v) was coated on the surface of a KBr tablet, and then the FTIR spectrum was collected after the tablet had been dried at room temperature. As shown in Fig. 1A, there is only a negligible peak at 1771 cm^{-1}, which is specific to DA adducts of maleimides.[20] This peak appears obviously after keeping the mixture solution in THF at about 66 °C for 24 h (see details in the Experimental section) (Fig. 1B). It manifests that the DA reaction can take place very slowly at room temperature, while is accelerated at around 70 °C.

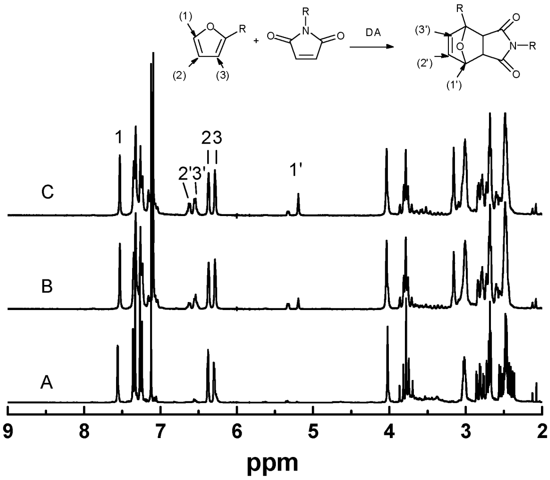


Fig. 2 ^{1}H-NMR spectra of a mixture of DGFA and DPMBMI kept at 70 °C for (A) 0 h, (B) 2 h, and (C) 6 h.

The DA reaction between DGFA and DPMBMI was further evaluated by in-situ ^{1}H-NMR spectroscopy. An equivalent molar mixture of DGFA and DPMBMI was dissolved in DMSO-d$_6$ (76 mmol/L) and then sealed in a glass tube under N_2

atmosphere. Then, ^{1}H-NMR spectra were collected at specific time intervals to monitor the DA reaction proceeding in the mixture solution at 70 °C. The results show that at the beginning of the reaction, no characteristic peaks between 5.1 and 5.3 ppm corresponding to the DA adduct are observed (Fig. 2A). After 2 h, these peaks appear (Fig. 2B), and become more evident when the reaction has proceeded for 6 h (Fig. 2C). The feasibility of the DA reaction between DGFA and DPMBMI is thus confirmed.

On the other hand, the content of the DA adduct and unreacted DGFA can be characterized by the integrals of H_2' and H_3' peaks, and those of H_2 and H_3 peaks, respectively (Fig. 2). This is because H_2' and H_3' peaks at 6.6 and 6.5 ppm are due to the H_2' and H_3' protons of the DA adduct,[21,22] while the peaks at 6.3 and 6.2 ppm are assigned to the H_2 and H_3 protons of unreacted DGFA. As a result, time-dependent reaction conversion of the DA adduct, x, is known:

$$x = \frac{\text{Integral area of } (H'_2 + H'_3)}{\text{Integral area of } (H'_2 + H'_3 + H_2 + H_3)} \qquad (1)$$

Also, first- and second-order kinetics of the reaction can be estimated from:

$$\ln 1/(1 - x) = kt \qquad (2)$$

$$1/(1 - x) = kt \qquad (3)$$

where k stands for the rate constant. Quantification of the DA reaction between DGFA and DPMBMI based on in-situ ^{1}H-NMR spectroscopy (see ESI, Fig. S5†) indicates that a linear fit of the data at 70 °C gives a rate constant with a regression coefficient of 0.9882 for the first-order plot and 0.9960 for the second-order one, suggesting that the second-order kinetics reaction should be more reasonable. Similarly, the reaction at 60 °C also exhibits a greater regression coefficient for the second-order plot than that of the first-order one. The activation energy derived from the second-order kinetics is 42.9 kJ/mol, which falls in the similar ranges reported for the other furan-maleimide DA reactions.[10,23–26]

In order to reveal the temperature range of the DA reaction between DGFA and DPMBMI, a DSC heating experiment was conducted (Fig. 3). The sample mixture of DGFA and DPMBMI was obtained by dissolving stoichiometric DPMBMI into DGFA at 90 °C for 5 min, and then quickly cooling down to room temperature. Upon being heated in a DSC cell, the mixture performs a DA reaction from 27 to 86 °C with an exothermal peak at 65 °C. Afterward, an endothermic peak appears at 110 °C representing the retro-DA reaction, followed by two evident exothermal peaks at 160 and 214 °C due to the epoxide ring-opening reaction and polymerization of maleimide moieties, respectively. This DSC analysis proves that the DA reaction can take place at 70 °C. Therefore, an isothermal DSC scanning was subsequently carried out at 70 °C to evaluate the extent of the DA reaction. After 200 min of reaction, the exothermal enthalpy is found to be 216 J/g, corresponding to 83.8 kJ/mol (per DA bond). The value agrees with that reported in the literature.[19]

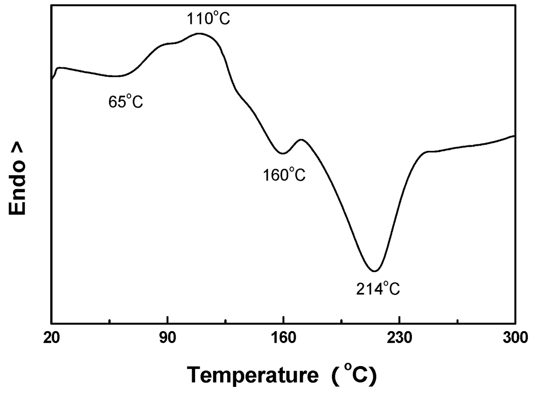


Fig. 3 DSC heating trace of a mixture of DGFA and DPMBMI. Heating rate: 2 °C/min.

In addition, the retro-DA reaction of the DA adduct between DGFA and DPMBMI in solution (see details in the Experimental section) was evaluated by ^{1}H-NMR and ^{13}C-NMR spectroscopy. The DA adduct was dissolved in DMSO-d$_6$ in a glass tube and heated at 110 °C for 20 min to disconnect the DA adduct. After the retro-DA reaction, the product was

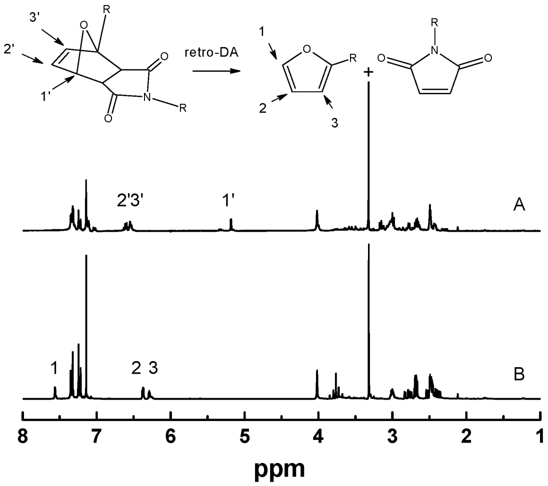


Fig. 4 ^{1}H-NMR spectra of (A) the adduct of DGFA and DPMBMI, and (B) the retro-DA product of the adduct of DGFA and DPMBMI by heating the adduct at 110 °C for 20 min.

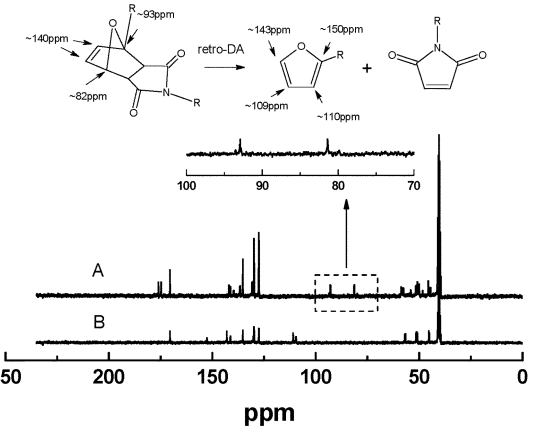


Fig. 5 ^{13}C-NMR spectra of (A) the adduct of DGFA and DPMBMI, and (B) the retro-DA product of the adduct of DGFA and DPMBMI by heating the adduct at 110 °C for 20 min.

immediately cooled down to room temperature and analyzed. From the ^{1}H-NMR spectra in Fig. 4, it is seen that the peaks at 5.1–5.3 ppm ascribed to the DA adduct (Fig. 4A) entirely disappear in the spectrum of the retro-DA product (Fig. 4B). Also, the characteristic peaks at 82 and 93 ppm,[8] which are clearly found in the ^{13}C-NMR spectrum of the DA product (Fig. 5A), are no longer perceived in the spectrum of the retro-DA product (Fig. 5B). These data demonstrate that the retro-DA reaction can be completed at 110 °C for 20 min.

Thermal reversibility of DGFA/MHHPA/DPMBMI crosslinked polymer

The curing reaction of DGFA with MHHPA and DPMBMI was carried out at 70 °C for 24 h. In the FTIR spectrum of cured DGFA (Fig. 6), the peaks attributed to the epoxide groups at 918 cm^{-1} (oxirane ring breathing) and 851 cm^{-1} (C–O–C) disappear, indicating that all epoxide groups have reacted with anhydride groups of MHHPA to form epoxy networks. An evident peak of hydroxyl groups emerges at 3500 cm^{-1} as a result of this reaction. Besides, the DA reaction of furan and maleimide groups in the cured sample is also proved by the existence of the peak at 1771 cm^{-1}.

As mentioned in the Introduction, the cured DGFA polymer should contain two types of crosslinedk covalent bonds: (i) thermally stable bonds from the reaction between the epoxide and anhydride groups, and (ii) thermally reversible bonds from the DA reaction of the furan and maleic groups. Although the DA and retro-DA reactions between DGFA and DPMBMI have been proved by the simulation tests (see Fig. 1–5), it is still unknown whether these thermally reversible reactions would be inhibited by the stable crosslinked epoxy networks. Therefore, the thermal reversibility of the cured DGFA polymer should be studied, as it is directly related to thermal remendability of the material.

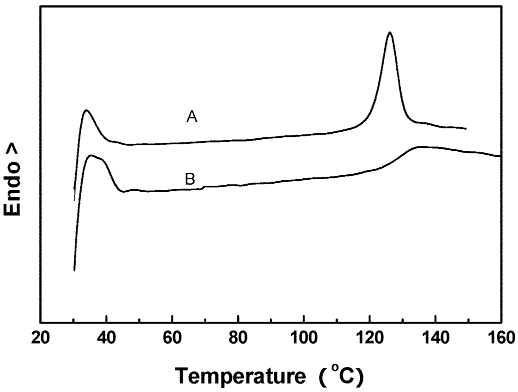


Fig. 7 DSC heating traces of DGFA/MHHPA/DPMBMI crosslinked polymer (heating rate: 5 °C/min). The sample was first heated for recording curve (A), and then naturally cooled down to room temperature in the DSC cell, followed by a second heating to record curve (B).

Fig. 7 shows the heating DSC curves of the cured DGFA polymer. The first heating curve has an endothermic peak at 126 °C, while the second one shows no peak except for a transition at 128.5 °C. It is thus reasonable to deduce that the endotherm appearing on the first curve must result from the retro-DA reaction. Because there is not enough time for the recovered furan and maleimide moieties to be reconnected during the subsequent cooling and reheating processes, no more retro-DA reaction but the glass transition of the cured epoxy is detected by the second DSC heating scan. In comparison to the retro-DA reaction at 110 °C in solution (Fig. 4 and 5), the higher retro-DA reaction temperature in the solid (126 °C) is indicative of the restraining effect of the cured epoxy. It can also be concluded that reconnection of the furan and maleic groups in the cured DGFA has to proceed at a rate much slower than that in solution, due to the same restriction of the epoxy network. Nevertheless, the DSC results demonstrate that the retro-DA reaction is an accessible reaction pathway under heating circumstances that is preferred over the bond-breaking degradation reaction in the cured epoxy network.

The reversibility of the crosslinked DGFA polymer was further studied by applying cyclic retro-DA (heat treatment at 140 °C for 20 min to attain a retro-DA sample) and DA (heat treatment at 80 °C for 72 h to attain a DA sample) reactions up to

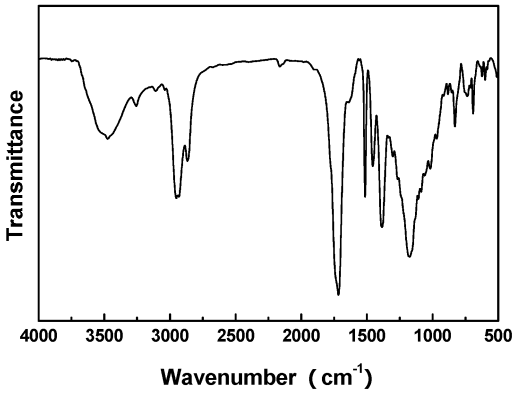


Fig. 6 FTIR spectra of DGFA/MHHPA/DPMBMI crosslinked polymer.

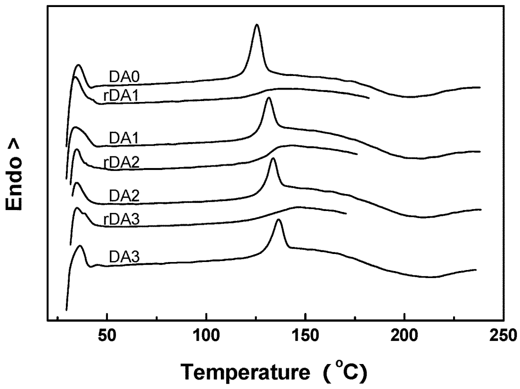


Fig. 8 DSC heating traces of DGFA/MHHPA/DPMBMI crosslinked polymer (heating rate: 5 °C/min). DA0: as-manufactured sample; rDA1: DA0 treated at 140 °C for 20 min, and then quenched to room temperature; DA1: rDA1 treated at 80 °C for 72 h, and then cooled inside oven by switching off the electricity supply; rDA2: DA1 treated at 140 °C for 20 min, and then quenched to room temperature; DA2: rDA2 treated at 80 °C for 72 h, and then cooled inside the oven by switching off the electricity supply; rDA3: DA2 treated at 140 °C for 20 min, and then quenched to room temperature; DA3: rDA3 treated at 80 °C for 72 h, and then cooled inside the oven by switching off the electricity supply.

four times. The higher heating temperatures for both retro-DA and DA reactions were chosen to increase the reaction efficiency. Again, the reactions were monitored by DSC (Fig. 8). The original cured DGFA (DA0) gives an endothermic peak of the retro-DA reaction at 126 °C, while the rDA1 only shows a glass transition at 128.5 °C. This implies that the retro-DA reaction has already been completed during the heat treatment at 140 °C for 20 min. Subsequently, the rDA1 is allowed to reconnect the cleavage groups by the DA reaction, and then an endothermic peak appears again at 131 °C for DA1. It is evident that the DA reaction between the disconnected furan and maleimide moieties has definitely taken place in the thermal treatment process. The recovery efficiency of the second DA reaction in comparison to the original cured DGFA polymer is about 77% as given by the ratio of ΔH_1 (enthalpy of DA1) over ΔH_o (enthalpy of DA0). It is noted that ΔH_o is 122.9 J/g, corresponding to 80.2 kJ/mol (per DA bond), which is quite close to the aforesaid exothermal enthalpy per mole of DA bond formation. This means that all of the DA bonds can be cleaved during the first retro-DA reaction, and the crosslinked epoxy networks do not block the retro-DA reaction.

In this manner, the recyclability of retro-DA and DA reactions in the crosslinked DGFA polymer has been verified by the repeated endotherms and T_g transitions for the DA and retro-DA samples. The characteristic parameters of the reactions inspected by DSC (Fig. 8) are summarized in Table 1. It is noted that the endothermic peak temperature of the DA sample slightly increases with heat treatment time, implying that the retro-DA reaction becomes more difficult with the heating cycles. This phenomenon may be related with the increase in crosslink density of the epoxy resin after heat treatment, as evidenced by the gradual increase in the T_g of rDA1 (128.5 °C), rDA2 (132.5 °C) and rDA3 (136 °C). Accordingly, the enthalpy of each endothermic peak, ΔH, of the retro-DA reaction gradually decreases as of the second heating cycle, indicating that the increased crosslink density of the epoxy part somewhat hinders recovery of the DA bonds. Nevertheless, the decrease of each retro-DA endothermic enthalpy is marginal. The DA and retro-DA reactions in the cured DGFA can still be considered as reversible.

In fact, the crosslink density of the epoxy network would not ceaselessly change after a couple of heating-cooling cycles, so that the reversibility of the DA and retro-DA reactions in the cured DGFA can eventually be fixed. Moreover, the epoxy network should favor the disconnected furan and maleimide moieties remaining at their original places during cooling. As a result, they can be reconnected very efficiently upon being heated at 80 °C. In other words, the epoxy network would help to retain the integity of the material when the retro-DA or DA reaction occurs.

Table 1 Quantification of endothermic peaks of cured DGFA polymer measured by DSC heating scan

Sample ID[a]	Onset temperature (°C)	Peak temperature (°C)	Enthalpy (J/g)
DA0	120.7	126.2	122.9
DA1	126.2	131.6	94.7
DA2	128.4	133.7	92.6
DA3	129.2	136.5	90.0

[a] Descriptions of the samples are listed in the caption of Fig. 8.

Fig. 8 also exhibits that there is an exothermic peak at around 225 °C on the heating curves of DA0–DA3 samples. It should be ascribed to the polymerization of the free maleimide moieties resulting from the retro-DA reaction. This reaction is detrimental to the thermal reversibility of the cured DGFA polymer because it converts maleimide to irreversible bonds. To avoid the negative effect, therefore, the material should not be heated to an elevated temperature, *e.g.* 180 °C.

DMA spectra of the cured DGFA polymer are shown in Fig. 9. For the original sample, its storage modulus exhibits a two-stage behavior with a rise in temperature. At around 110 °C, a drastic decrease in the modulus starts, and then a plateau appears at 118 °C. When temperature is further raised, the modulus drops again at 121 °C. Meanwhile, the temperature dependence of tan δ shows a knee point at 119 °C and a peak at 128 °C, respectively. In contrast, after retro-DA reaction at 140 °C for 20 min, the sample only shows a single transition on the curve of storage modulus versus temperature. The corresponding tan δ plot also has only one peak and the aforesaid knee point is absent. Clearly, the two-stage variation of storage modulus of the original cured DGFA polymer reflects the retro-DA reaction and glass transition, respectively. The retro-DA reaction happens below the glass transition temperature of the material, but there is still certain overlap between the two processes. Furthermore, the DMA analysis coincides with previous DSC data, which also show a retro-DA reaction peak at around 120 °C and a glass transition at around 128 °C.

It is interesting to see from the DMA measurements (Fig. 9) that after retro-DA reaction, the cured DGFA polymer possesses a higher T_g and significantly lower room temperature storage modulus. The former phenomenon should result from the increased crosslinking density of the epoxy network, which has been discussed when analyzing Fig. 8. The latter can be explained by the disconnection of DA bonds, which may lead to an increased amount of chain ends or low molecular weight substances, and hence reduces the stiffness of the material.

When the temperature is higher than T_g, all the DA bonds are broken. Consequently, the storage modulus is only related with the crosslinking density of epoxy network. In other words, the

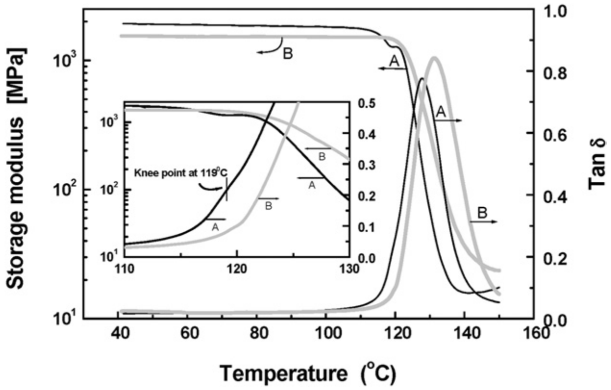


Fig. 9 DMA spectra of DGFA/MHHPA/DPMBMI crosslinked polymer. (A) as-manufactured sample; (B) as-manufactured sample treated at 140 °C for 20 min, and then quenched to room temperature.

effect of the crosslinking density variation on the storage modulus of the polymer can be perceived in the rubbery region. It is seen that the sample that experienced the retro-DA reaction exhibits a higher modulus in the rubbery region than the as-manufactured one. It again reveals that the crosslinking density of the epoxy network can be further enhanced by a heating treatment above T_g.

Mechanical properties and thermal remendability of the cured DGFA polymer

The tensile and flexural properties of the DGFA/MHHPA/DPMBMI crosslinked polymer were measured at room temperature, in comparison with those of conventional bisphenol-A epoxy cured by MHHPA (Table 2). The cured version of the newly synthesized epoxy has a higher modulus but a moderately lower strength as compared to the cured bisphenol-A epoxy.[27] On the whole, the data of the cured DGFA are still close to those of commercial epoxy resins. It means that DGFA possesses the potential ability to replace traditional epoxy resin in future applications.

Table 2 Mechanical properties of the cured epoxy

Properties	DGFA/MHHPA/ DPMBMI crosslinked polymer	Bisphenol-A epoxy cured by MHHPA[27]
Young's modulus (GPa)	2.5	1.8
Tensile strength (MPa)	53	65
Elongation at break (%)	1.5	—
Flexural modulus (GPa)	4.6	2.6
Flexural strength (MPa)	110	128

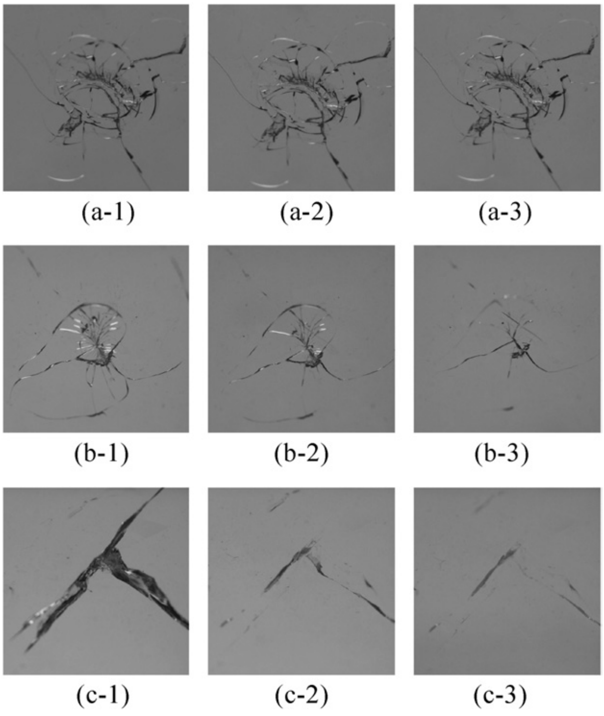


Fig. 10 Visual inspection of thermal remendability of the cured DGFA polymer. The damaged samples were firstly treated at (a) 100 °C, (b) 119 °C and (c) 125 °C for 20 min, respectively. Next, they were moved to an oven preset at 80 °C for (1) 0 h, (2) 12 h and (3) 72 h, respectively.

Thermally remendable processes of artificial damage on the cured DGFA are illustrated in Fig. 10. Since the interfaces of the cracks have a higher refractive index, they are easily visually monitored. All the samples were thermally treated at different temperatures (100~125 °C) for 20 min for disconnecting DA covalent bonds *via* retro-DA reaction, before being annealed at 80 °C for a while to repair the cracks by DA reaction between the disconnected furan and maleimide moieties.

As shown in Fig. 10a, no crack repair is observed when the heat treatment temperature (100 °C) is lower than the starting temperature of the retro-DA reaction (110 °C). When heat treatment is carried out at a temperature (119 °C) higher than the onset temperature of the retro-DA reaction, most of the cracks can be healed after DA reaction treatment at 80 °C (Fig. 10b). Some larger cracks finally remain unhealed, probably due to the relatively low retro-DA treatment temperature, and/or material loss during damaging, and/or misalignment of the cracked portions. In the case of the higher retro-DA reaction temperature (125 °C), which is close to the T_g of the cured DGFA polymer (128 °C), larger cracks can also be repaired owing to the enhanced segment mobility (Fig. 10c). These results clearly demonstrate that the synthesized epoxy has been provided with thermal remendability as expected.

Conclusions

A novel epoxy resin DGFA was synthesized by a two-step route, which combined epoxide with furan groups into one molecule. The resultant was a liquid with low viscosity and good processability, and can be cured by using anhydride and maleimide without the help of solvent. Cured DGFA contained two types of intermonomer linkage: thermally reversible DA bonds from the reaction between furan and maleimide groups, and thermally stable bonds from the reaction between epoxide and anhydride groups. It possessed mechanical properties similar to those of commercial epoxy resin. The thermal reversibility of the DA bonds in cured DGFA proved to be workable below the glass transition temperature of the material. Taking advantage of the above feature, cracks in cured DGFA can be mended in a controlled manner through chain reconnection resulting from successive retro-DA and DA reactions.

Acknowledgements

The authors thank the support of the Natural Science Foundation of China (Grants: 50573093, U0634001 and 20874117).

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