

## Thermally reversible and self-healing novolac epoxy resins based on Diels–Alder chemistry

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**ABSTRACT:** The modified novolac epoxy resins with furan pendant groups were prepared by novolac epoxy resin and furfuryl alcohol and then crosslinked by bifunctional maleimide via Diels–Alder (DA) chemistry to obtain the thermally reversible and self-healing novolac epoxy resins. The as-prepared crosslinked novolac epoxy resins were characterized by FT-IR, NMR, TGA, and DMA. The results indicate that the novel crosslinked novolac epoxy resins present higher storage modulus (2.37 GPa at 30°C) and excellent thermal stability (348°C at 5% mass loss). Furthermore, the thermal reversible and self-healing properties were studied in detail by DSC, SEM, thermal re-resolution, and gel–solution–gel transition experiments. All the results reveal that the crosslinked novolac epoxy resins based on DA reaction can be used as smart material for the practical application of electronic packaging and structural materials. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42167.

**KEYWORDS:** crosslinking; Diels–Alder chemistry; recycling; resins

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### INTRODUCTION

The self-healing phenomenon in the natural world has attracted intensive attention from researchers for decades. Numerous methodologies and strategies were developed to prepare smart polymer materials with self-healing property and improve the safety and lifetime of devices.<sup>1,2</sup> There are basically two types of self-healing polymers, i.e., extrinsic and intrinsic materials.<sup>3</sup> Investigation of intrinsic self-healing polymers which can be healed by chemical and physical method without any catalysts or healing agents has attained significant achievements recently. The temperature-dependent reversible covalent crosslinking of polymers or block copolymers, such as Diels–Alder chemistry, represents an effective method for the implementation of intrinsic self-healing into functional materials.<sup>4</sup> Until now, self-healing polymers based on DA reaction of furan and maleimide, such as multifunctional furan–maleimide,<sup>5–10</sup> polyketones,<sup>11,12</sup> polyamides,<sup>13,14</sup> polyethylenes,<sup>15–17</sup> polyesters,<sup>18,19</sup> poly( $\epsilon$ -caprolactone),<sup>20,21</sup> poly(lactic acid),<sup>22</sup> and polyurethanes<sup>23–25</sup> have been widely studied.<sup>4</sup> Therefore, there are a large number of interesting possibilities in developing new self-healing polymers system based on DA reaction.

Epoxy resin as an important thermoset material has been used widely in electronics due to the excellent heat resistance, out-

standing corrosion protection, high electrical resistivity, superior electrical, and mechanical properties and adhesion to a variety of substrates. However, cracks might occur as a result of thermal stress and mechanical fatigues during processing and service of such highly crosslinked materials. It is desired that epoxy resins used in electronic packaging can be removed or repaired when cracks occur, such that the failure of the whole electronic devices can be avoided. Our group have reported a series of epoxy compounds, such as cycloaliphatic diepoxides containing thermally cleavable carbamate linkages,<sup>26</sup> carbonate linkages,<sup>27</sup> secondary, and tertiary ester linkages<sup>28</sup> and so forth. Because of weak chemical bonds, the mentioned epoxy resins can be degraded by heating (below 300°C) to achieve the purpose of removing. However, these epoxy resins could not be reused after the degradation. Comparing with the thermal degradable resins, the thermal healable epoxy resins are more economic. Some groups have developed interesting epoxy resins with self-healing property based on DA reaction.<sup>29–31</sup> In general, the epoxy compounds were modified with furan or maleimide group in one molecule. Thereinto, the epoxide groups reacted with conventional curing agent to form three-dimensional network. Meanwhile, the DA reaction between furan groups and maleimide groups introduce thermally reversible property into the epoxy network. In this way, cured epoxy resins possessed not only

similar mechanical properties as commercial epoxy but also thermal remendability that enabled elimination of cracks.

Novolac epoxy resins are widely used in area of electronic packaging owing to their excellent integrated properties. Therefore, developing functional novolac epoxy resin with self-healing property will broaden the scope of its application. In this work, the commercially available novolac epoxy resin (DEN431) was modified by furfuryl alcohol to prepare a new novolac resin bearing free furan groups. Then the resultant resin was cross-linked by *N,N*-(4,4'-methylene-diphenyl) dimaleimide (BMI) to yield thermally reversible novolac epoxy film and gels based on DA reaction. The thermomechanical, thermally reversible, and self-healing properties were also investigated.

## EXPERIMENTAL

### Materials

Novolac epoxy (DEN431, Epoxide Equivalent Weight is 172–179 g eq<sup>-1</sup>) was obtained from Dow Chemical Company. Furfuryl alcohol (FA), tetrahydrofuran (THF), triethylamine (TEA), anhydrous diethyl ether, and dimethyl formamide (DMF) were purchased from Sinopharm Chemical Reagent Beijing, China and *N,N'*-(4,4'-diphenylmethane)bismaleimide (BMI) was supplied by Aldrich Chemical. All the chemicals were used as received.

### Measurements

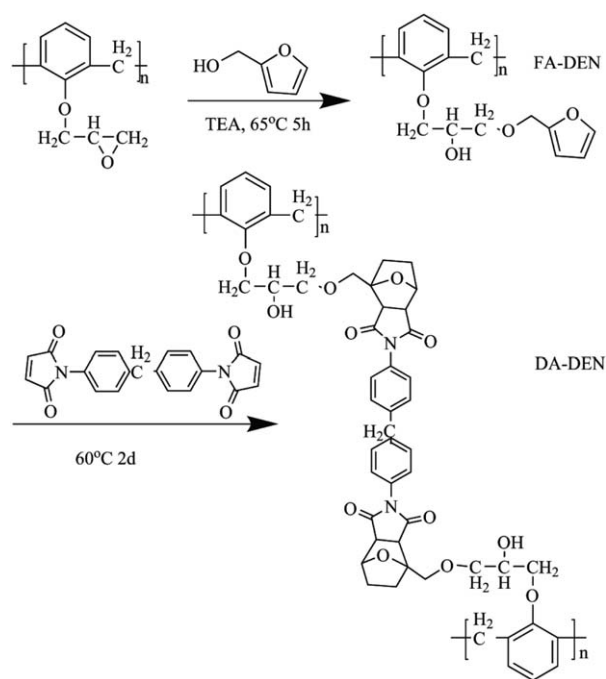
Fourier transform infrared (FTIR) spectra were recorded with Bruker Vertex 70 spectrometer (Bruker Optik GmbH, Ettlingen, Germany) in the range of 4000–400 cm<sup>-1</sup>. Proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectra were recorded at room temperature using a 400 MHz NMR spectrometer. Samples were prepared as a solution of 5–10 mg of each compound in 0.7 mL of dimethyl sulfoxide (DMSO-*d*<sub>6</sub>), using tetramethylsilane (TMS) as the internal reference. Differential scanning calorimetry (DSC) was performed on Q20–1173 DSC thermal system (TA instruments) with heating rate of 10°C min<sup>-1</sup> and ranging from 30 to 180°C. Nitrogen gas was purged at a flow rate of about 50 mL min<sup>-1</sup>. Dynamic mechanical analysis (DMA) was conducted on a TA Instruments DMA 2980 in controlled force mode with a 3 N min<sup>-1</sup> strain rate to 18 N at room temperature (RT) and multifrequency—strain mode with the heating rate was 3°C min<sup>-1</sup> from RT to 120°C. Thermal gravity analysis (TGA) was made on a TA SDTQ600 thermogravimetric analyzer; the microbalance has a precision of ±0.1 μg. Samples of about 10 mg were placed into 70 μL alumina pans. The samples were heated from 30 to 800°C under a nitrogen flow of 100 mL min<sup>-1</sup>. Scanning electronic micrographs (SEM) were recorded with a Nova NanoSEM 450.

### Sample Preparation

FA-DEN was synthesized via a ring-opening reaction between the epoxy groups of DEN431 and the hydroxyl group of furfuryl alcohol, after which the novolac epoxy resins were modified with furan pendant groups. The DA reaction occurred between FA-DEN and BMI at mild condition which resulted in DA-DEN as shown in Scheme 1.

### Synthesis of FA-DEN

FA (10 mmol), DEN431 (10 mmol) and 3–4 drops of TEA were mixed in a 100-mL three-necked round-bottomed flask with the



**Scheme 1.** The synthetic procedures of FA-DEN and DA-DEN.

thermometer and mechanical stirred equipment and heated at 65°C for 5 h at atmospheric pressure (Scheme 1). The resultant solution was poured into 250 mL of dry ether and the unreacted reactants were removed by decantation and the process was repeated for three times. The obtained reddish brown viscous liquid was dried in a vacuum oven to remove any remaining solvents at 30°C for 24 h.

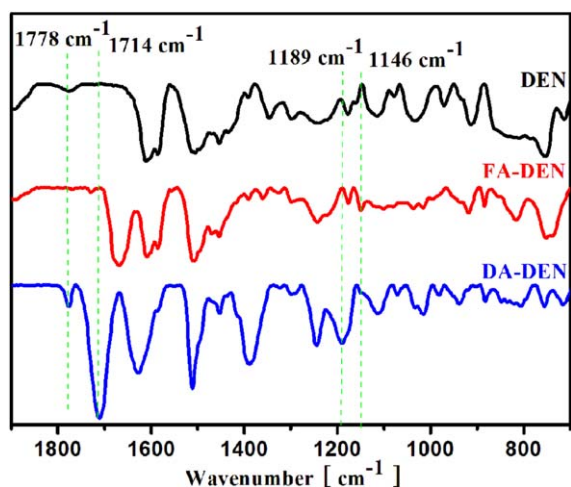
FTIR (KBr, cm<sup>-1</sup>): 3566 (—OH), 3041 (C—H in phenyl group), 3121 (C—H in furan ring), 2931 (aliphatic C—H), 1670 (unsaturation C=C), 1510 (aromatic —C=C—), 1146 (furan ring), 1016 (furan ring breathing), 885 (2-substituted furan ring).

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm, δ): 7.65 (j H), 7.09–6.80 (a H, c H, and b H), 6.42 (k H, l H), 5.12 (i H), 4.45 (f H, e H), 3.88 (h H), 3.84 (a H), 3.46 (g H).

### Synthesis of DA-DENs

FA-DEN (520 mg, 2 mmol) was dissolved in 10 mL DMF with BMI (358 mg, 1 mmol) added into the solution. After stirring for 30 min, the whole solution was poured into a polytetrafluoroethene (PTFE) mould in an oven at 60°C for 2 days. During this time, the color of the crosslinked epoxy system changed from light yellow to red. The crosslinking via DA reaction will further proceed to obtain a gelled film with higher crosslinking density in the blast oven. Meanwhile, the solvent DMF was evaporated and a flat crosslinked epoxy film was obtained as the final product. In the same way, other epoxy systems with different mole ratios of furan to maleimide groups (F : M, proportional to the content of crosslinker), i.e., 1 : 1, 2 : 1, 4 : 1, and 8 : 1 were prepared and named DA-DEN-1, DA-DEN-2, DA-DEN-4, DA-DEN-8, respectively.

FTIR (KBr, cm<sup>-1</sup>): 3566 (—OH), 3041 (C—H in phenyl group), 2931 (aliphatic C—H), 1778 (C=C in DA adduct), 1714 (C=O



**Figure 1.** FTIR spectra of DEN, FA-DEN, and DA-DEN. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

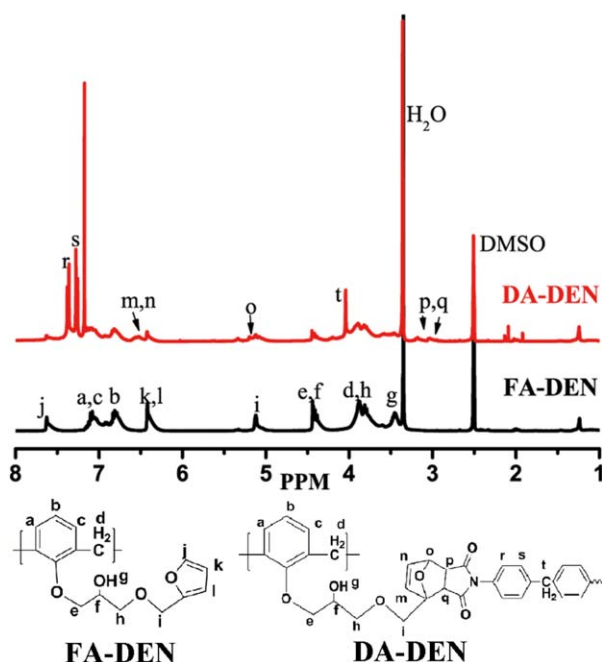
of maleimide), 1510 (aromatic  $\text{C}=\text{C}$ ), 1387 ( $\text{C}=\text{N}$ ), 1189 ( $\text{C}-\text{C}$  in DA adduct), 1112 ( $\text{C}-\text{O}-\text{C}$  in maleimide ring).

$^1\text{H}$  NMR (DMSO- $d_6$ , ppm,  $\delta$ ): 7.37 (r H), 7.09–6.80 (a H, c H, and b H), 7.28 (s H), 6.56 (m H, n H), 5.23 (o H), 5.12 (i H), 4.45 (f H, e H), 4.04 (t H), 3.88 (h H), 3.84 (a H), 3.46 (g H), 3.17 (p H), 3.01 (q H).

## RESULTS AND DISCUSSION

### Synthesis and Characterization of FA-DEN and DA-DEN

The structure of the FA-DEN and DA-DEN were characterized by FTIR as shown in Figure 1. Comparing with the spectrum of DEN, the additional peaks at  $1146\text{ cm}^{-1}$  confirmed the presence



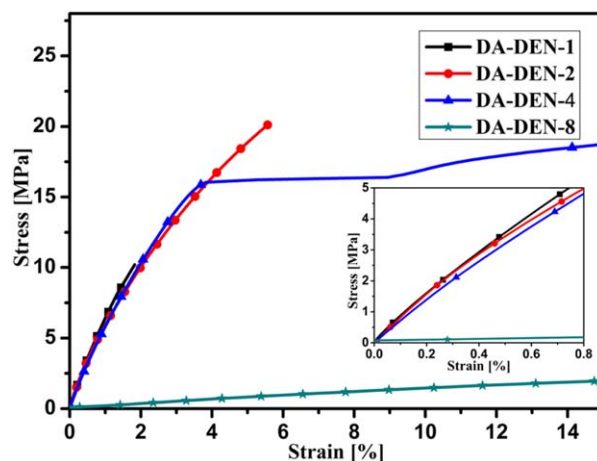
**Figure 2.**  $^1\text{H}$  NMR of (a) FA-DEN and (b) DA-DEN. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

of furan ring in FA-DEN. Furthermore, in the spectrum of DA-DEN, a peak at  $\sim 1714\text{ cm}^{-1}$  ascribing to  $\text{C}=\text{O}$  band of BMI was observed. Meanwhile, the peaks at 1778 and  $1189\text{ cm}^{-1}$  in the spectrum of DA-DEN can be ascribed to  $\text{C}=\text{C}$  and  $\text{C}-\text{C}$ , which were specific to the DA adduct.<sup>32,33</sup> Simultaneously, the intensity of the peak at  $1146\text{ cm}^{-1}$  in the spectrum of DA-DEN was lower than that of FA-DEN, which can be ascribed to that the furan ring was consumed by BMI. All these features indicated that the DEN was successfully modified by furan groups and the DA reaction between FA-DEN and BMI occurred.

The successful synthesis of FA-DEN and DA-DEN were also confirmed by  $^1\text{H}$  NMR as shown in Figure 2. Firstly, the peaks at  $\delta = 7.63, 6.42\text{ ppm}$  are assigned to the protons *j, k*, and *l* of the furfuryl ring in FA-DEN separately. The intensity of peaks of *j, k*, and *l* all decreased after 48 h at  $60^\circ\text{C}$  as a result of the formation of DA-DEN. The newly appearing peak at  $\delta = 7.17\text{ ppm}$  attribute to the protons of maleimide groups of BMI. On the other hand, there are four extra peaks at  $\delta = 6.60\text{ ppm}$  (*m* and *n*),  $5.19\text{ ppm}$  (*o*),  $3.21$  and  $3.06\text{ ppm}$  (*p* and *q*) due to the DA adduct. All of these features confirmed that the DA reaction had already proceeded successfully.

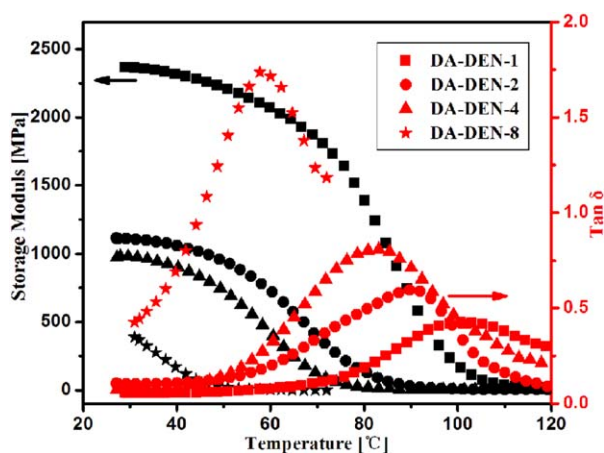
### Thermomechanical Properties of DA-DEN

The tensile test of DA-DENs was investigated by DMA and the rectangular-shaped specimens with a thickness of 0.1–0.5 mm were prepared by the solvent cast method in DMF. Figure 3 shows the stress–strain curves of DA-DENs with different mole ratios of furan to maleimide. DA-DEN-1 was too brittle and broke at a very small strain of 1.83%. DA-DEN-2 showed similar behavior and the strain at break was 5.57%. For DA-DEN-4, a yield stress region appeared in the stress–strain curve which can be attributed to the decreased restraints of polymer segments in the vicinity of the crosslinker. The curve of DA-DEN-8 is almost linear and the modulus of DA-DEN-8 is much smaller as can be seen from Figure 3. The result suggest that with the reduction of maleimide groups, the degree of the crosslinked DA-DENs decreases, which consequently leads to reduction in the modulus and mechanical strength of DA-DENs.



**Figure 3.** Stress–strain curves of DA-DENs. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

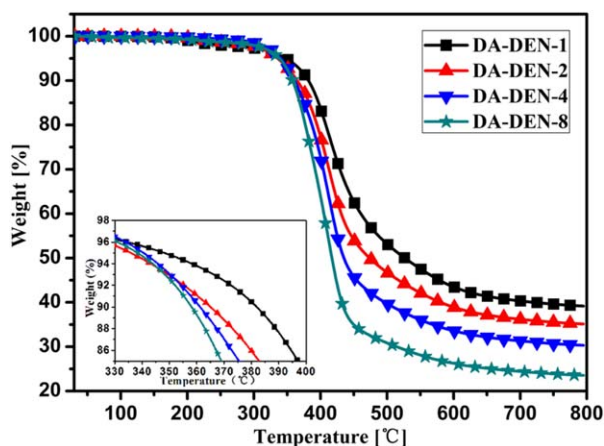




**Figure 4.** Storage modulus and  $\tan \delta$  of DA-DENs. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

The modulus of DA-DENs were conducted in DMA and a marked drop of the storage modulus from DA-DEN-1 to DA-DEN-8 can be seen in Figure 4. The storage modulus of DA-DEN-1 is 2.37 GPa at RT which is two times higher than that reported in the literature<sup>34</sup> and it is still 1.39 GPa when the temperature is 80°C. The storage modulus of DA-DEN-2 is only 1.11 GPa at RT. For DA-DEN-8, the storage modulus (390 MPa) is only 1/8 of that of DA-DEN-1. The obvious change shown in Figure 4 is mostly result from the reduction of cross linking rate of the furan groups in the novolac epoxy resins which is mainly influenced by the addition of BMI. Figure 4 also shows the change of  $\tan \delta$  as a function of temperature of for all the DA-DENs. The glass transition temperature ( $T_g$ ) revealed by  $\tan \delta$  profiles are 102, 90, 83, and 58°C corresponding to DA-DEN-1, DA-DEN-2, DA-DEN-4, and DA-DEN-8 respectively. The reduction in  $T_g$  is thought to be related to the lower degree of crosslinking in DA-DENs.

DA-DEN-1 has the highest storage modulus (2.37 GPa) and  $T_g$  (102°C), it is selected for further investigation. DA-DEN-1 is in glassy state when the temperature is below 80°C and the storage modulus is very high. With the increase of temperature, DA-



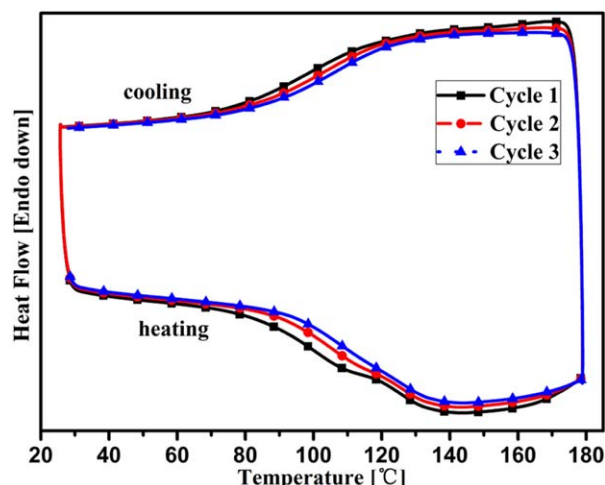
**Figure 5.** TGA curves of the DA-DENs. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table I.** Thermal Properties of DA-DENs

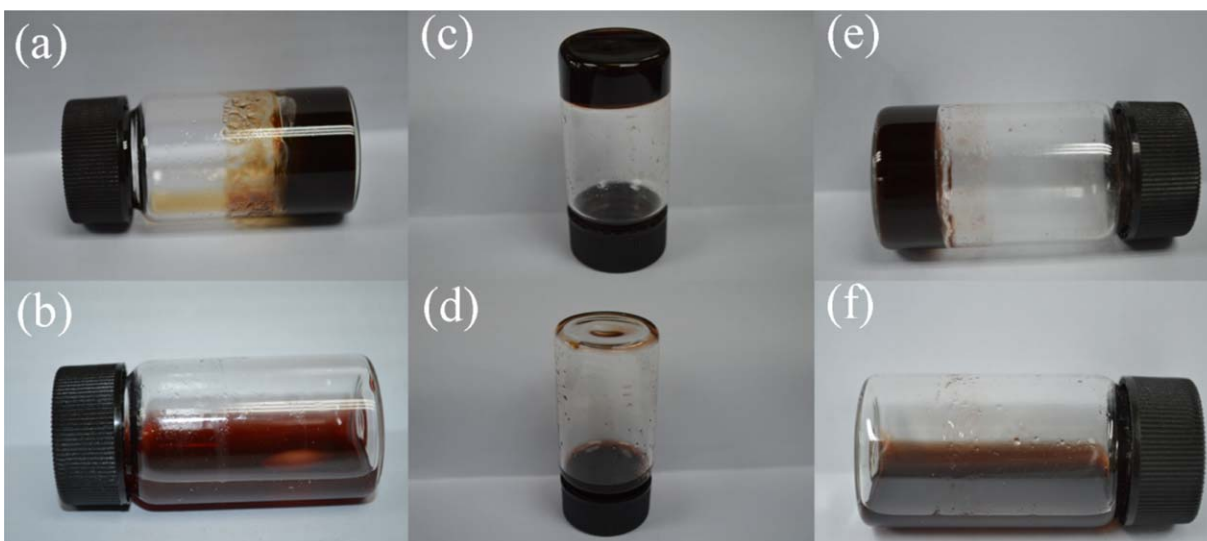
Sample	Weight-loss temperature ( $T_5$ ) (°C)	Weight-loss temperature ( $T_{10}$ ) (°C)	$T_{max}$ (°C)	Char yield at 800°C (%)
DA-DEN-1	348	382	401	39.31
DA-DEN-2	335	365	405	35.09
DA-DEN-4	340	361	404	29.98
DA-DEN-8	338	358	379	23.46

DEN-1 enters into a rubbery state at 80–100°C and the storage modulus drops rapidly. When the temperature is above 102°C, DA-DEN-1 is going to get into a viscous state and the storage modulus becomes very small. Also, when the temperature is above 100°C the retro-DA reaction happens obviously which accelerates the decrease of the modulus. In summary, DA-DEN-1 can be used at much higher temperature reliably and safely.

The TGA curves are shown in Figure 5. A slight weight loss was observed at around 200°C of DA-DEN-1 and DA-DEN-2 which might be attributed to evaporation of the residual solvents due to their high crosslinking. It can be seen from the inset in Figure 5, another weight loss stage was observed at around 350°C. The thermal stability of these systems are compared by consideration of the temperatures for 5% ( $T_5$ ) and 10% ( $T_{10}$ ), the maximum weight loss temperature ( $T_{max}$ ), and the char yields at 800°C. These data were presented in Table I. As can be seen, values for  $T_5$ ,  $T_{10}$ , and char yield of the DA-DEN-1 are much higher than those of the controlled ones. This indicates that more BMI provides the higher degree of crosslinking and improves the inherent thermal stability of the novolac epoxy resin dramatically. With the reduction of BMI, the thermal stability of DA-DENs decrease obviously which can be seen from the change of  $T_{10}$  and the char yields of DA-DENs. For the DA-DEN-1, 348°C for  $T_5$  indicates that the new novolac epoxy resin based DA reaction can be applied as latent advanced composites in harsh condition.



**Figure 6.** Repeated DSC curves of DA-DEN-1. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



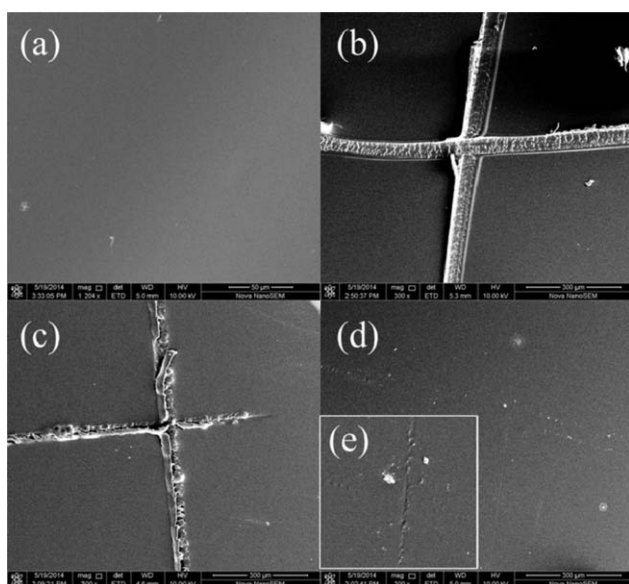
**Figure 7.** Polymer gels were formed after 2 h at 60°C (a, c, and e) and, polymer solutions were obtained after reheating the gels at 130°C for 10 min (b, d, and f). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### Thermally Reversible Property of DA-DEN

According to the above results, DA-DEN-1 presents superior thermal and mechanical properties and was selected for thermally-reversible investigation. Figure 6 depicts the thermal behavior of DA-DEN-1 which was measured between 30 and 180°C by repeated DSC cycles. Thereinto, the first cycle showed a glass transition process at about 90°C which was in accordance with  $\tan \delta$  of DMA analysis. While the following two cycles did not show the same process. Meanwhile, an overlapping of the obvious endothermic and exothermic transitions in

the range of 130–150°C can be observed during successive thermal cycles. The repeated endothermic and exothermic transitions of DA-DEN-1 should be predominately attributed to the retro-DA and DA reactions, respectively. The slight deviations of the repeated DSC traces and negligible glass transition in 2nd and 3rd cycles can be attributed to the incomplete reconstruction of the DA network within the relatively short time scale of the DSC experiments.<sup>35,36</sup> In short, the above results clearly demonstrate DA-DENs can be used as a thermal remendable and recyclable materials.<sup>35</sup>

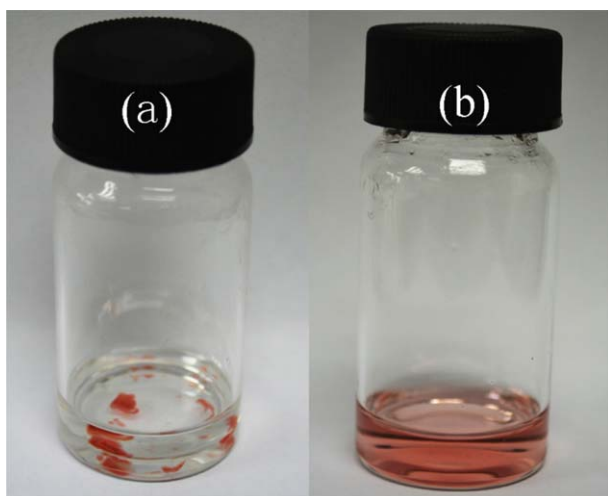
Thermal reversibility of DA-DEN was further investigated by the polymer sol-gel transition experiments in DMF (10 wt % concentration) and the detailed phase changes versus temperature can be observed as shown in Figure 7. DA-DEN-1 could form polymer gels through DA crosslinking reaction between maleimide groups of BMI and furan groups of modified novolac epoxy resins at 60°C for 2 h [Figure 7(a)]. Then the retro-DA reaction happened at 130°C for 10 min which transformed polymer gel into clear solution [Figure 7(b)]. Furthermore, sample *b* was cooled down from 130 to 60°C and held for some time, the viscosity was increased gradually and the gel reformed completely without fluidity after 2 h [Figure 7(c)]. This could be explained by the regeneration of the DA bond. Repeating the cooling-heating cycles on the same sample, the clear solution phase appeared again as shown in Figure 7(d). This cycle could be repeated at least three times [Figure 7(e,f)], which indicated that DA-DEN-1 present good thermal reversibility. This result also suggested that DA-DENs can be used as removable and recycled materials.



**Figure 8.** Visual inspection of thermal repair of DA-DEN-1. (a) The pristine crosslinked material, (b) a fissure was made by a knife, (c) the surface of the sample after thermally treated at 130°C for 10 min, (d) the surface of the sample after thermally treated at 60°C for 24 h, and (e) Enlargement of picture d.

### Self-Repairing and Resoluble Property of DA-DENs

The self-repairing behavior of DA-DEN-1 was characterized by SEM (Figure 8). The pristine crosslinked material showed a smooth surface [Figure 8(a)]. A fissure was made on the surface of the sample by a knife [Figure 8(b)]. The cut sample was thermally treated at 130°C for 10 min and then at 60°C for 24 h.



**Figure 9.** (a) DA-DEN-1 in DMF after 24 h at 25°C; (b) DA-DEN-1 in DMF after 3 min at 130°C. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

Firstly, retro-DA reaction occurred at 130°C to provide chance of chain reformation, and DA reaction occurred at 60°C to heal the fissure ascribing to reforming the crosslinked structure. As shown in Figure 8(c), after the thermally treatment at 130°C for 10 min, the thermal repair of DA-DEN-1 is partially happened. And after the treatment at 60°C for 24 h the fissure finally almost disappeared as it can be seen in Figure 8(d,e). The crack-healing ability of the modified novolac epoxy resin based on DA reaction is demonstrated in this way.

In addition to self-healing property, the resolubility is also meaningful to the crosslinked novolac epoxy resins. The cross-linked novolac epoxy resin DA-DEN-1 was insoluble in DMF at room temperature [Figure 9(a)] and became readily soluble after heating at 130°C [Figure 9(b)]. Therefore, the DA-DENs could be utilized as a new class of thermally reversible cross-linked polymers which reserve its properties at low temperatures and show removability and solubility at high temperatures and this means the resins could be reused and recycled.

## CONCLUSIONS

In summary, modified novolac epoxy resins containing furan groups were prepared and crosslinked by Diels–Alder reaction to yield novel self-healing materials. The as-prepared novolac epoxy resin revealed excellent thermal stability (348°C at 5% mass loss) and mechanical properties (storage modulus: 2.37 GPa at 30°C). Furthermore, the crosslinked novolac epoxy resin exhibits good thermally reversible and self-healing property which means the resins could be reused and recycled. These new findings open up a facile route for self-healing epoxy resin production with commercial material and tremendous opportunities for smart materials, structural materials, and electronic packaging. Investigation of crosslinking of the modified novolac epoxy resins by multimaleimide and other conventional curing agents (such as amine and anhydride) together to improve integrated properties are currently underway in our laboratory.

## ACKNOWLEDGMENTS

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