



# Synthesis and characterization of a novel heat resistant epoxy resin based on N,N'-bis(5-hydroxy-1-naphthyl)pyromellitic diimide

Hua Ren, Jianzhong Sun\*, Qian Zhao, Qiyun Zhou, Qincai Ling

State key laboratory of Chemical Engineering, Department of Chemical and Biochemical Engineering, Zhejiang University, Hangzhou 310027, China

## ARTICLE INFO

### Article history:

Received 26 February 2008  
Received in revised form 9 September 2008  
Accepted 26 September 2008  
Available online 4 October 2008

### Keywords:

Epoxy resin  
Heat resistant  
Naphthol

## ABSTRACT

A novel epoxy resin containing imide and naphthyl groups was synthesized, and characterized using NMR, FT-IR spectra and elemental analyses. The curing behavior was investigated with differential scanning calorimetry (DSC) using 4,4'-diaminodiphenylsulfone (DDS) as curing agent. The physical properties of the cured polymer were evaluated with dynamic thermal mechanical analysis (DMTA) and thermogravimetric analysis (TGA). The results showed that the cured polymer exhibited higher glass transition temperature ( $T_g$ ) and better thermal stability compared with those commercial available heat resistant epoxy resins.

© 2008 Elsevier Ltd. All rights reserved.

## 1. Introduction

Epoxy resins have the combined advantages of excellent chemical and corrosion resistances, good thermal and dimensional stability, and great mechanical and electrical properties, ensuring their wide applications in laminating, adhesive, surface coating and semiconductor encapsulation. However, the conventional epoxy resins are unable to satisfy some applications such as integrated circuit packaging and advanced materials which require higher thermal resistance [1]. Hence it is necessary to design and synthesize novel high heat resistant epoxy resin systems to suit these applications.

Many approaches have been reported to enhance the heat resistance as well as moisture resistance of epoxy resins by changing the structure of the starting resins which influences the properties of final cured epoxy polymers. The incorporation of a naphthalene structure into the epoxy skeleton is an effective way to increase the glass transition temperature and thermal stability [2]. Kaji and Dndo [3], Pan et al. [4], Wang et al. [5] and Castell et al. [6] synthesized the naphthalene-based epoxy resin containing naphthyl and phenyl structures. Xu et al. [7] and Ren et al. [8] reported that the naphthalene-cycloaliphatic moiety linked epoxy resins were prepared and the cured polymers showed higher glass transition temperatures. Liquid crystalline epoxy resins based on naphthalene mesogen were also studied in recent years and exhibited good thermal properties [9]. To design and synthesize

epoxy resins containing both naphthyl and aromatic or cycloaliphatic group by chemical bonding in molecular backbone are the trend of recent studies [8,9]. Polyimides are well known for their excellent heat resistant stability due to the thermal stable imide linkage. Polymers, including epoxy resins, made up of aromatic and/or heterocyclic structures have superior thermal properties than the polymers mainly based on flexible aliphatic chains [10]. Considerable attentions have been paid on introducing imide group into epoxy resin network to improve the thermal properties of the cured polymer. Most of the report focused on preparing imide group containing curing agents [10–14] and blending epoxy resins with thermoplastic polyimides or with functionalized polyimides [15]. Few reports were found about modifying the backbone structure of epoxy resins with imide group [16]. Moreover, Tao et al. [17] synthesized a novel imide ring and siloxane-containing cycloaliphatic epoxy resin. Li et al. [18] studied the properties and pyrolysis of a novel siloxane and imide modified epoxy resin from N,N'-bis(4-hydroxyphenyl)-5,5'-bis(1,1,3,3-tetramethyl disiloxane-1,2-diyl)-bis-norborane-2,3-dicarboximide. When cured with siloxane-containing dianhydride, the glass transition temperature of the cured resin was 173.2 °C. Directly blending epoxy resin with polyimide has to focus on the phase separation problem and control the morphology of the cured polymer to obtain the desired performance. Although partial modification of the skeleton of the epoxy resin or curing agent with imide group, including blending with reactive imide compound, could sometimes improve the thermal properties of the cured polymer, the increasing extent is limited. Synthesis of epoxy resin from imide group containing monomers could precisely design and control the backbone structure of the resin, which will retain in the cured

\* Corresponding author. Tel.: +86 571 87953171.  
E-mail address: [bigwig@zju.edu.cn](mailto:bigwig@zju.edu.cn) (J. Sun).

polymer network and determine the properties of the final product. Furthermore, these imide group containing epoxy resins could be cured with different commercial available hardeners, or even formulated with other epoxy resins to form various cured polymers with desired thermal properties. As a possible approach to advanced thermosets, studies aimed to synthesize a novel heat resistant epoxy resin containing both naphthyl and imide groups have been initiated in our group. The incorporation of naphthyl ring could increase the rigidity of the backbone and the presence of imide linkage could also facilitate the thermal properties of the cured resins. The combination of the special features of the naphthyl/imide structure is expected to offer the epoxy resin great improvement in glass transition temperature and thermal stability to satisfy the requirement in the field of electrical encapsulation and advanced composites.

The goal of this work was to describe the synthesis and structure of a novel heat resistant epoxy resin containing both naphthyl and imide groups. The characteristics of cure and physical properties of the cured polymer were investigated using several measurement methods, and compared with those of commercially available heat resistant epoxy resin.

## 2. Experimental

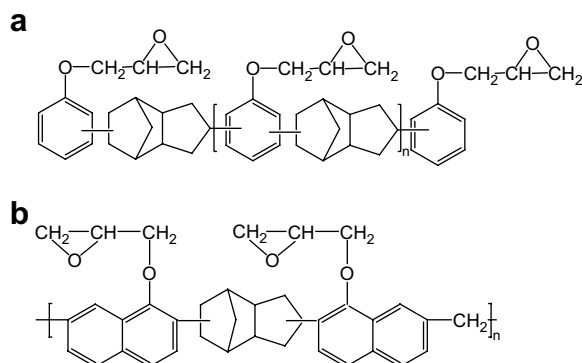
### 2.1. Materials

5-amino-1-naphthol purchased from Acros, Pyromellitic acid dianhydride and *p*-toluene sulfonic acid (pTSA) from Sinopharm Chemical Reagent Co Ltd., China and epichlorohydrin (ECH) from Tianjin Bodi Chemical Reagent Co Ltd. were used without further purification. Benzyltrimethylammonium chloride from Acros was used as phase transfer catalyst. 4,4'-diaminodiphenylsulfone (DDS) obtained from Yinsheng Chemicals Co Ltd., China was used as curing agent. Tactix 556 (Scheme 1a) with epoxy equivalent weight of about 225 g/eq. was kindly supplied by Huntsman Advanced Materials Americas Inc. Naphthalene-dicyclopentadiene epoxy resin (NDEP) is another heat resistant epoxy resin synthesized in our laboratory in the previous study [8]. The chemical structure is shown in Scheme 1b. All solvents and other chemicals were of reagent grade or better.

### 2.2. Synthesis

#### 2.2.1. Synthesis of *N,N'*-bis(5-hydroxy-1-naphthyl)pyromellitic diimide

7.95 g of 5-amino-1-naphthol and 100 ml of acetone were put into a 250 ml four-necked round-bottom flask equipped with a heating water bath, a stirrer, a reflux condenser, a dropping funnel and nitrogen inlet. The mixture was heated to 40 °C to let the 5-



Scheme 1. Structures of Tactix 556 epoxy resin (a) and NDEP (b).

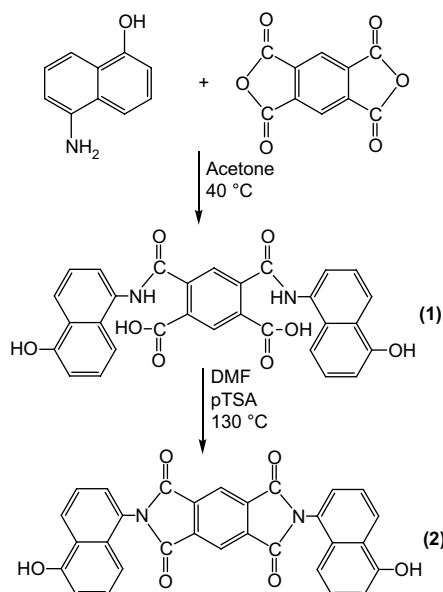
amino-1-naphthol well dissolve in the acetone. Then solution of 5.45 g pyromellitic acid dianhydride dissolved in 50 ml of acetone was added dropwise over a period of 1 h, and the mixture was maintained at 40 °C for another 5 h. After the reaction was completed, the resultant mixture was filtered and then washed with acetone three times. A lustrous green powder (indicated as **1** in Scheme 2) weighed 9.9 g was obtained.

ESI-MS:  $m/z = 534.9$ ;  $^1\text{H NMR}$  (DMSO- $d_6$ )  $\delta$  (ppm): 13.59 (s, 2H, -COOH), 10.49 (s, 2H, aromatic hydroxyl), 8.14 (s, 2H, protons of phenyl), 8.09 (d, 2H), 7.77 (d, 2H), 7.65 (d, 2H), 7.50 (t, 2H), 7.36 (t, 2H), 6.93 (d, 2H) (protons of naphthyl). Elemental analysis: Calc. %: C: 67.16, H: 3.73, N: 5.22; Found %: C: 67.39, H: 3.65, N: 5.63.

9.9 g of **1**, 45 ml of *N,N'*-dimethylformamide and 15 ml of toluene were added to a 100 ml four-necked round-bottom flask equipped with a heating oil bath, a magnetic stirrer, Dean-Stark condenser and nitrogen inlet. After completely dissolved, 0.1 g of *p*-toluene sulfonic acid (pTSA) was added, then the mixture was heated to 130 °C and refluxed for 8 h. The generated water was removed from the mixture by azeotropic distillation. After the reaction was completed, the mixture was concentrated to remove some of the solvent and then poured into distilled water at 0 °C and stirrer for 0.5 h. The mixture was filtered and washed with water three times, the solid product was then placed in the vacuum oven to remove the traces of solvent and water. A brown-colored solid product (indicated as **2**) weighed 7.7 g was obtained. The reaction equation is shown in Scheme 2. ESI-MS:  $m/z = 499.1$ ;  $^1\text{H NMR}$  (DMSO- $d_6$ )  $\delta$  (ppm): 10.54 (s, 2H, -OH), 8.49 (s, 2H, protons of phenyl), 8.35 (d, 2H), 7.70 (b, 2H), 7.61 (t, 2H), 7.36 (t, 2H), 7.24 (m, 2H), 6.97 (d, 2H) (protons of naphthyl) (Fig. 1) IR (KBr): 3410  $\text{cm}^{-1}$  (-OH of naphthyl ring); 1273  $\text{cm}^{-1}$  (C-O); 1776  $\text{cm}^{-1}$ , 1726  $\text{cm}^{-1}$ , 1375  $\text{cm}^{-1}$ , 727  $\text{cm}^{-1}$  (imide bands); 1630  $\text{cm}^{-1}$ , 1598  $\text{cm}^{-1}$ , 1519  $\text{cm}^{-1}$ , 1581  $\text{cm}^{-1}$ , 1416  $\text{cm}^{-1}$  (C-C of naphthyl and phenyl) (Fig. 2a). Elemental analysis: Calc. %: C: 72.00, H: 3.22, N: 5.60; Found %: C: 71.98, H: 3.25, N: 5.59.

#### 2.2.2. Synthesis of glycidyl ether of *N,N'*-bis(5-hydroxy-1-naphthyl)pyromellitic diimide

7.5 g of **2** and 50 ml of epichlorohydrin were put into a 100 ml four-necked round-bottom flask equipped with a heating oil bath, a magnetic stirrer, a syringe pump and a modified reflux condenser. Benzyltrimethylammonium chloride of 0.1 g was added as phase



Scheme 2. Synthesis of *N,N'*-bis(5-hydroxy-1-naphthyl) pyromellitic diimide.

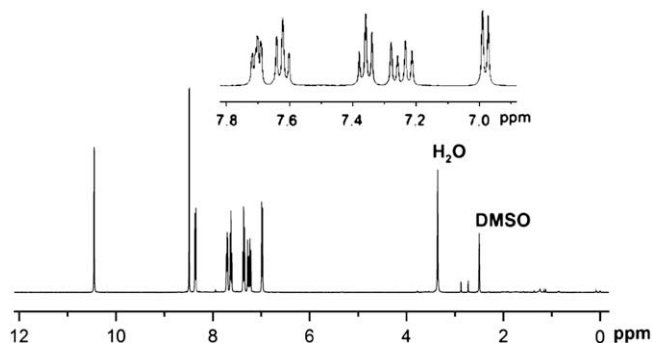


Fig. 1.  $^1\text{H}$  NMR spectrum of **2**.

transfer catalyst. The reaction mixture was heated to  $100\text{ }^\circ\text{C}$ , and then 4 g of 30 wt% aqueous NaOH was added gradually over a period of 1 h by syringe pump and further reacted at the reflux temperature for 4 h. After cooling down, the reaction solution was filtered to remove the salt, and the organic phase was washed with water three times. The solution was concentrated and poured into ethyl ether with stirring, then filtered to collect the solid product. The crude product was washed with ethyl ether and dried in a vacuum oven. A yellow-colored solid product (indicated as **3**) weighed 8.5 g was obtained. The chemical reaction is outlined in Scheme 3. IR (KBr):  $1777\text{ cm}^{-1}$ ,  $1724\text{ cm}^{-1}$ ,  $1373\text{ cm}^{-1}$ ,  $727\text{ cm}^{-1}$  (imide bands);  $1631\text{ cm}^{-1}$ ,  $1582\text{ cm}^{-1}$ ,  $1511\text{ cm}^{-1}$ ,  $1374\text{ cm}^{-1}$ ,  $1415\text{ cm}^{-1}$  (C–C of naphthyl and phenyl);  $911\text{ cm}^{-1}$  (oxirane ring);  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  (ppm): 8.51 (s, 2H, protons of phenyl), 8.40 (d, 2H), 7.78 (b, 2H), 7.71 (b, 2H), 7.50–7.39 (m, 4H), 7.16–6.98 (m, 4H) (naphthyl), 4.16–4.06 (m, 2H), 3.96–3.81 (m, 2H), 2.94 (t, 2H), 2.87 (m, 2H), 2.50 (b, 2H) (saturate protons of 1,2-epoxypropyl).  $^{13}\text{C}$  NMR (DMSO- $d_6$ )  $\delta$  (ppm): 166.5 (C=O), 154.4, 137.7, 131.6, 128.6–127.8, 126.6–123.6, 118.8, 115.6, 106.5 (naphthyl and phenyl), 69.9, 50.0, 44.1 (oxirane ring). Elemental analysis: Calc. %: C: 70.59, H: 3.95, N: 4.57; Found %: C: 70.44, H: 4.12, N: 4.55.

### 2.3. Curing procedure

The epoxy resin and the curing agent DDS were mixed in a 1:1 equivalent ratio and some were dissolved in the mixture of N,N-dimethylformamide and acetone in room temperature. Then the

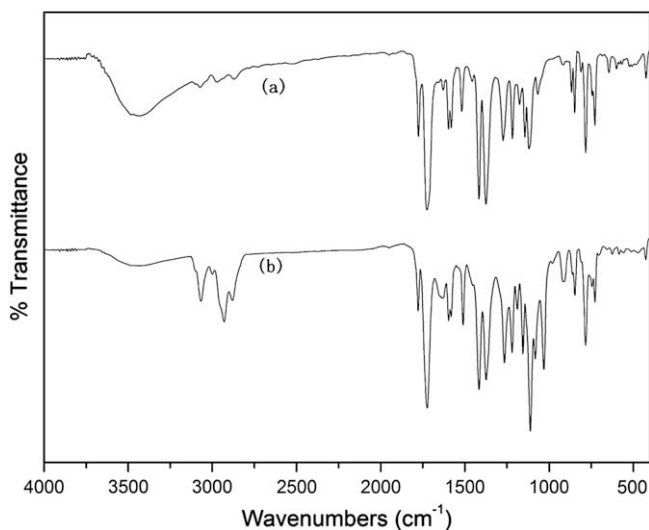
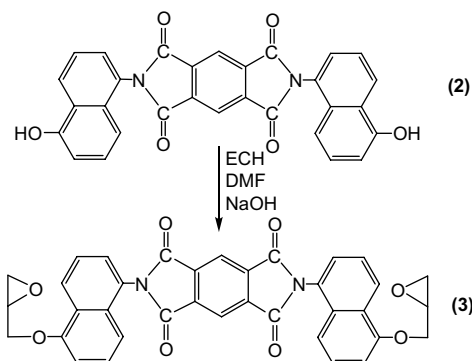


Fig. 2. FT-IR spectroscopy of **2** and **3**.



Scheme 3. Synthesis of glycidyl ether of N,N'-bis(5-hydroxy-1-naphthyl)pyromellitic diimide.

mixed solvent was evaporated under vacuum and the blends were placed in the refrigerator before performing the DSC measurement. The other reactants were heated on hot plates and cured at  $120\text{ }^\circ\text{C}$  for 1 h,  $180\text{ }^\circ\text{C}$  for 1 h,  $240\text{ }^\circ\text{C}$  for 1 h. Then, the cured resins were cooled slowly to room temperature to get the required specimens for DMTA and TGA measurements.

### 2.4. Characterization

The electrospray ionization (ESI)-MS was carried on a Bruker Esquire-LC-00075 spectrometer. FT-IR spectra were recorded on a Nicolet 5700 FT-IR spectrophotometer.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR characterizations were carried out by Bruker Avance DMX 500 NMR spectrometer using tetramethylsilane (TMS) as internal standard. Elemental analyses were performed by a ThermoFinnigan EA-1112 elemental analyzer. The epoxide equivalent weight (EEW) of epoxy resin was determined by HCl/acetone titration method. Dynamic curing kinetics was measured with a Perkin-Elmer DSC-7 under nitrogen atmosphere with heating rates of  $5\text{ }^\circ\text{C}/\text{min}$ ,  $10\text{ }^\circ\text{C}/\text{min}$ ,  $15\text{ }^\circ\text{C}/\text{min}$  and  $20\text{ }^\circ\text{C}/\text{min}$ . Thermogravimetric analysis (TGA) was performed using a Pyris 1 thermogravimetric analyzer (Perkin-Elmer Cetus Instruments, Norwalk, CT) at a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$  under nitrogen and air atmospheres. Dynamic mechanical thermal analysis (DMTA) was carried out with a TA DMA Q800 instrument using  $2\text{ mm} \times 10\text{ mm} \times 30\text{ mm}$  rectangular samples at a programmed heating rate of  $3\text{ }^\circ\text{C}/\text{min}$  from  $50\text{ }^\circ\text{C}$  to  $300\text{ }^\circ\text{C}$  at a frequency of 1 Hz under air atmosphere.

## 3. Results and discussion

### 3.1. Synthesis and characterization

N,N'-bis(5-hydroxy-1-naphthyl)pyromellitic diimide (**2**) was synthesized from the condensation reaction between 5-amino-

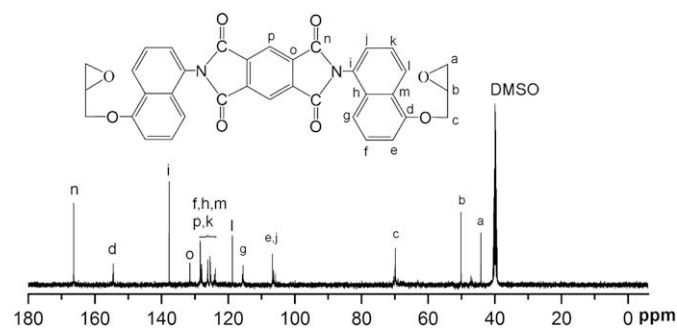


Fig. 3.  $^{13}\text{C}$  NMR spectrum of **3**.

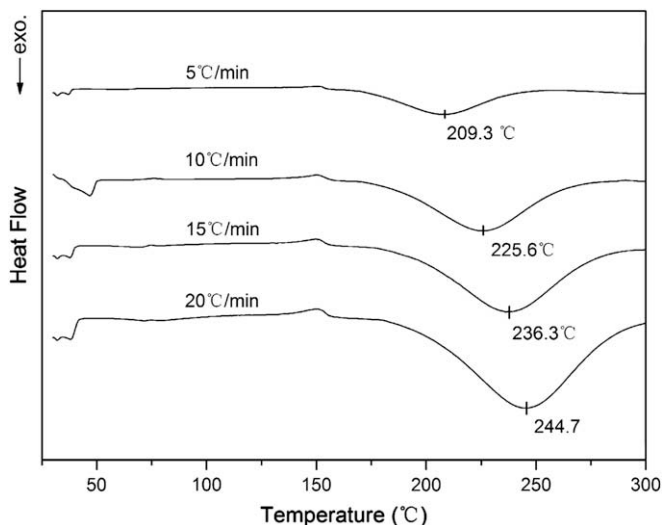


Fig. 4. DSC measurement of 3/DDS curing system at different heating rates.

1-naphthol and pyromellitic acid dianhydride. Mass spectrum showed that **2** has a single mass-charge ratio of 499.1 and indicates that two molecules of 5-amino-1-naphthol reacted with one molecule of pyromellitic acid dianhydride to obtain a new product with a molecular weight of 500.1 g/mol, which is the same as the designed molecule of **2**. Fig. 2(a) shows the FT-IR spectrum of **2**, in which the absorption around  $3410\text{ cm}^{-1}$  attributed to the vibration of naphthyl-OH stretching can be found. The absorption peaks for the asymmetrical and symmetrical stretching of C=O can be observed at  $1776\text{ cm}^{-1}$  and  $1726\text{ cm}^{-1}$ , respectively. The characteristic absorption for C-N linkage of imide bond can be detected at  $1375\text{ cm}^{-1}$ . Moreover, no signals were found in  $^1\text{H NMR}$  spectrum at 11–13 ppm which is the signal range for protons of -COOH, also proving that the carboxyl has totally reacted with imine and the nitrogen atom has linked with three carbon atoms.

The naphthyl/imide based epoxy resin was synthesized by the reaction between **2** and epichlorohydrin with the aqueous NaOH added to control the reaction and benzyltrimethylammonium chloride added as phase transfer catalyst to facilitate the reaction. The FT-IR spectra of **2** and the naphthyl/imide based epoxy resin are shown in Fig. 2(a) and (b), respectively. The strong absorption peak of -OH at  $3410\text{ cm}^{-1}$  observed in Fig. 2(a) almost disappeared in (b) because of the reaction of the hydroxyl group with epichlorohydrin, and the characteristic absorption peak at  $911\text{ cm}^{-1}$  for oxirane ring could be observed in (b).  $^{13}\text{C NMR}$  spectrum of the naphthyl/imide based epoxy resin (Fig. 3) also confirmed the chemical structure of the synthesized resin; the peaks of 69.9, 50.0, 44.1 were assigned to the carbons in epoxy group and 154.4 to the carbons linked with glycidyl ether group. According to the result of the EEW titration, the EEW of naphthyl/imide based epoxy resin is 311.0 g/equiv., which is close to the theoretical EEW of 306.3 g/equiv.

Table 1  
Dynamic cure parameters of the epoxy systems.

| Curing system <sup>a</sup> | $T_0^b$ (°C) | $T_p^c$ (°C) | $T_f^d$ (°C) | $\Delta H$ (kJ/mol) | $E_a$ (kJ/mol) |
|----------------------------|--------------|--------------|--------------|---------------------|----------------|
| Naphthyl-imide             | 182.9        | 225.6        | 279.3        | 111.58              | 73.3           |
| NDEP                       | 176.5        | 230.7        | 285.8        | 73.24               | 90.9           |
| Tactix 556                 | 151.7        | 222.9        | 277.6        | 106.01              | 82.1           |

<sup>a</sup> At a heating rate of  $10\text{ °C/min}$ .

<sup>b</sup> The curing onset temperature.

<sup>c</sup> The peak temperature of the exotherm area.

<sup>d</sup> The curing finish temperature.

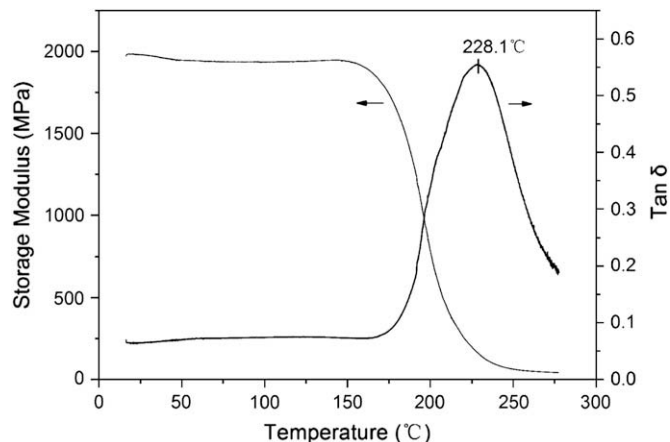


Fig. 5. DMTA results of 3/DDS cured polymer.

### 3.2. Dynamic thermal curing

The blend of naphthyl/imide based epoxy resin and DDS were employed to study the thermal curing behavior by DSC measurement. The kinetic analysis was performed using the Kissinger model [19, 20]. According to Kissinger's method, the activation energy can be obtained from the peak exotherm temperatures at

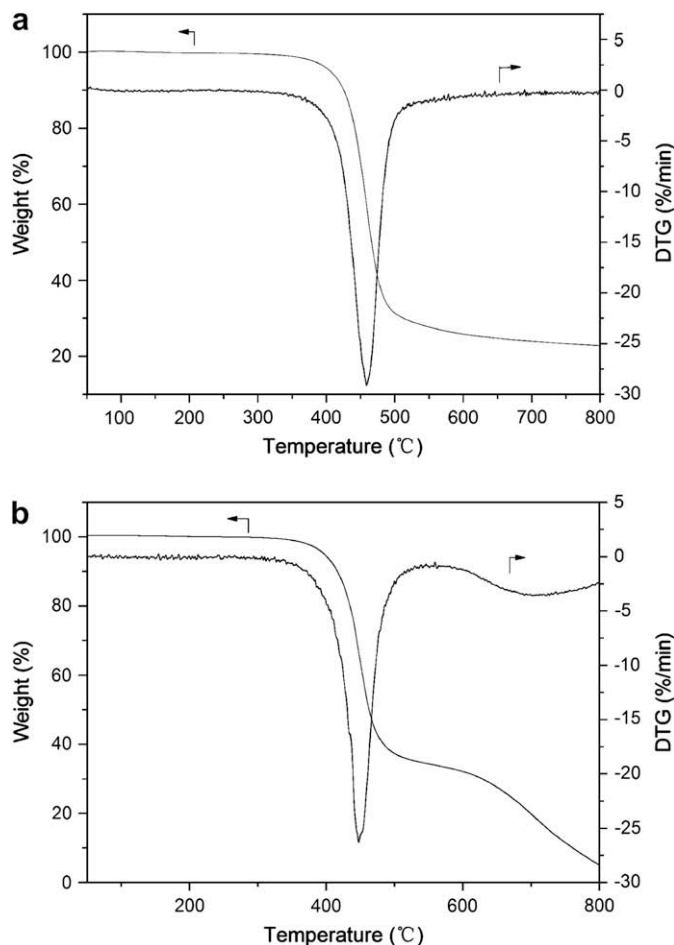


Fig. 6. (a) Weight loss of 3/DDS cured polymer under nitrogen atmosphere. (b) Weight loss of 3/DDS cured polymer under air atmosphere.



**Table 2**  
TGA analysis data and  $T_g$  of the cured epoxy resins.

| Epoxy resin    | Nitrogen atmosphere |                 |                | Air atmosphere |                 |                | $T_g$ (°C) |
|----------------|---------------------|-----------------|----------------|----------------|-----------------|----------------|------------|
|                | $T_{5\%}$ (°C)      | $T_{10\%}$ (°C) | Char yield (%) | $T_{5\%}$ (°C) | $T_{10\%}$ (°C) | Char yield (%) |            |
| Naphthyl-imide | 405.9               | 425.5           | 22.81          | 397.2          | 416.5           | 5.95           | 228.1      |
| NDEP           | 375.6               | 392.9           | 29.09          | 361.8          | 373.0           | 15.90          | 236.2      |
| Tactix 556     | 371.7               | 386.5           | 24.21          | 363.0          | 375.8           | 13.26          | 201.2 [8]  |

different heating rates. The relation could be expressed as the following equation:

$$\frac{d \left[ \ln \left( \frac{q}{T_p^2} \right) \right]}{d(1/T_p)} = -\frac{E_a}{R} \quad (1)$$

where  $T_p$  is the peak exotherm temperature,  $q$  is a constant heating rate,  $E_a$  is the activation energy, and  $R$  is the gas constant. Therefore,  $E_a$  could be calculated from slope of the plot of  $\ln(q/T_p^2)$  versus  $1/T_p$  without the need of any assumption about the conversion-dependent equation.

Fig. 4 shows the DSC traces of the blend of naphthyl/imide epoxy resin/DDS system at different heating rates and the dynamic cure reaction parameters are summarized in Table 1. Compared with Tactix 556/DDS and NDEP/DDS curing systems, the curing onset temperature ( $T_o$ ) of naphthyl/imide epoxy resin/DDS system is relatively higher and the curing finish temperature ( $T_f$ ) is relatively lower. Moreover, the activation energy of naphthyl/imide epoxy resin/DDS system calculated from the slope of Eq. (1) is lower than both Tactix 556/DDS and NDEP/DDS systems, even lower than some diglycidyl ether of bisphenol-A/amine systems ( $\sim 90$  kJ/mol) [21–23], which could indicate that naphthyl/imide epoxy resin represented higher reactivity toward amines. Further investigation should be particularly carried out to study the cure kinetic models in future.

### 3.3. Thermal resistance properties of the cured polymer

#### 3.3.1. Dynamic mechanical thermal analyses

Dynamic mechanical observations were performed to analyze the dynamic elastic modulus and occurrence of molecular mobility transitions such as glass transition [24]. Fig. 5 shows the DMTA scans of the cured epoxy resin. The peak temperature of  $\tan \delta$  was taken as the glass transition temperature. The DMTA measurement showed that the cured polymer had a  $T_g$  of 228.1 °C, which exhibited higher  $T_g$  than Tactix 556/DDS system ( $T_g = 201.2$  °C). This result may confirm that glass transition temperature of the cured polymers could be elevated drastically by introducing the rigid naphthalene group into the molecular backbone, which could restrain the thermal movements. Besides, the thermal stable imide bonds could also facilitate to form cured polymers with better thermal stability.

#### 3.3.2. Thermogravimetric analyses

TGA is the most favored technique for rapid evaluation in the thermal stability and degradation behaviors of various polymers. Fig. 6(a) and (b) is the TGA and its differential curves (DTG) of the naphthyl/imide epoxy resin/DDS cured polymer under nitrogen and air atmospheres, respectively. The results indicated that the temperature of 5% degradation of the cured polymer is 405.9 °C under nitrogen and 397.2 °C under air, the temperature of 10% degradation of the cured polymer is 425.5 °C under nitrogen and

416.5 °C under air. It exhibits much higher thermal stability than NDEP/DDS cured epoxy resin in the previous study [8] and commercial heat resistant epoxy resin Tactix 556. (See Table 2) This may suggest that introducing of stable imide structure to link the naphthyl groups could effectively improve the stability of the epoxy resin. However, naphthyl-imide/DDS system exhibits lower char yield of 22.81% in nitrogen and 5.95% in air, respectively. The rapid weight loss started obviously from 600 °C under air atmosphere, the presence of oxygen results in a complicated decomposition mechanism of the cured polymer and the pyrolysis reaction was activated by the existence of oxygen [25].

## 4. Conclusions

A novel naphthyl/imide epoxy resin was synthesized from 5-amino-1-naphthol and pyromellitic acid dianhydride. The structures of the resin were confirmed by MS, NMR, FT-IR spectra and elemental analyses. The results of cure kinetics investigation showed that the naphthyl/imide epoxy resin had higher reactivity toward amine groups than commercial heat resistant epoxy resin Tactix 556 and some DGEBA epoxy resins. With the incorporation of naphthyl and imide groups into the backbone, the resulting epoxy polymer cured with DDS showed higher glass transition temperature and excellent thermal stability. These pronounced good properties make it an attractive candidate for packaging materials and advanced composites.

## References

- [1] Ho TH, Wang CS. *J Appl Polym Sci* 1999;74:1905.
- [2] Duann YF, Liu TM, Cheng KC, Su WF. *Polym Degrad Stab* 2004;84:305.
- [3] Kaji M, Dndo T. *J Polym Sci Part A Polym Chem* 1999;37:3063.
- [4] Pan GY, Du ZJ, Zhang D, Li CJ, Yang XP, Li HQ. *Polymer* 2007;48:3686.
- [5] Wang CS, Leu TS, Hsu KR. *Polymer* 1998;39:2921.
- [6] Castell P, Serra A, Galia M. *J Polym Sci Part A Polym Chem* 2003;41:1536.
- [7] Xu K, Chen MC, Kui Z, Hu JW. *Polymer* 2004;45:1133.
- [8] Ren H, Sun JZ, Wu BJ, Zhou QY. *Polymer* 2006;47:8309.
- [9] Lee JY, Jang J. *J Polym Sci Part A Polym Chem* 1999;37:419.
- [10] Sharma P, Choudhary V, Narula1 AK. *J Appl Polym Sci* 2006;101:3503.
- [11] Adhinarayanan K, Packirisamy S, George RS, Rao VL, Ramaswamy R. *J Appl Polym Sci* 1991;43:783.
- [12] Sasaki S, Hasuda Y. *J Polym Sci Part C Polym Lett* 1987;25:377.
- [13] Abraham G, Packirisamy S, Adhinarayanan K, Feby AG, Ramaswamy R. *J Appl Polym Sci* 2000;78:1729.
- [14] Serafini TT, Delvigs P, Vannucci RD. US Patent 4244857; 1981.
- [15] Hodgins JH, Simon GP, Varley RJ. *Polym Adv Technol* 1998;9:3.
- [16] Serra A, Cadiz V, Martinez PA, Mantecon A. *Angew Makromol Chem* 1986;138:185.
- [17] Tao ZQ, Yang SY, Chen JS, Fan L. *Eur Polym J* 2007;43:1470.
- [18] Li HT, Chuang HR, Wang MW, Lin MS. *Polym Int* 2005;54:1416.
- [19] Kissinger HE. *Anal Chem* 1957;29:1072.
- [20] Kissinger HE. *J Res Natl Bur Stand* 1956;57(4):217.
- [21] Zvetkov VL. *Polymer* 2001;42:6687.
- [22] Karkanas PI, Partridge IK. *J Appl Polym Sci* 2000;77:1419.
- [23] Barral L, Cano J, Lopez-Bueno I, Nogueira P, Torres A, Ramirez C, et al. *Thermochim Acta* 2000;344:127.
- [24] Lee JY, Jang J, Hwang SS, Hong SM, Kim KU. *Polymer* 1998;39:6121.
- [25] Liu YL, Hsiue GH, Lee RH, Chiu YS. *J Appl Polym Sci* 1997;63:895.