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Synthesis and characterization of a novel epoxy resin containing naphthyl/dicyclopentadiene moieties and its cured polymer

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Abstract

A new epoxy resin containing both naphthalene and dicyclopentadiene (DCPD) groups was synthesized to produce a highly heat-resistant network, and the curing behavior was investigated using diaminodiphenylsulfone (DDS) as curing agent. The chemical structures were characterized with FTIR spectroscopy, NMR, MS, and GPC analyses. Dynamic curing behavior was investigated using differential scanning calorimetry (DSC). The physical properties of the resulting polymers were evaluated with dynamic thermal mechanical analyses (DMTA) and thermogravimetric analyses (TGA). The cured polymer showed great improvement in heat-resistant property including remarkably higher glass transition temperature (T_g) and thermal stability. Such properties make this new epoxy resin highly promising for heat-resistant applications.

Keywords: Epoxy resin; Naphthol; Dicyclopentadiene

1. Introduction

Epoxy resins have been widely used in laminating, adhesive, surface coating and semiconductor encapsulation applications because of their heat, solvent, moisture and chemical resistance, good mechanical and electrical properties, and great adherence to many substrates. 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]. Thus, it is necessary to design and develop high thermal resistant and low moisture absorption epoxy resin systems for these applications.

Many approaches have been reported to improve the heat resistance of epoxy resins by changing the structure of the starting resins which influences the properties of final cured epoxy polymers. The introduction 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], Wang et al. [4] and Castell et al. [5] synthesized the naphthalene-based epoxy resins containing naphthyl and phenyl structures. Xu et al. [6] reported that a novel naphthalene-cycloaliphatic moieties linked epoxy resin was obtained and its cured polymers had a higher glass transition temperature. Liquid crystalline epoxy (LCE) resins were developed to enhance the mechanical and thermal properties, Lee et al. [7,8] reported several LCE resins and studied the effect of chemical structure on curing and thermomechanical properties; LCE resin based on naphthalene mesogen showed superior thermal properties [9]. Furthermore, glass transition temperature rises as crosslinking density increases [10,11]; naphthalene multifunctional epoxy resins have a higher T_g than that of the di-functional naphthalene-based epoxy resins [12−14]. To design and synthesize epoxy monomers containing both naphthyl and aromatic or cycloaliphatic group by chemical bonding in molecular backbone are the trend of recent studies. Dicyclopentadiene (DCPD) is a byproduct of C5 streams in oil refineries, because of their availability, low cost and reactivity toward aromatic rings; they were used as the moieties of some epoxy resins

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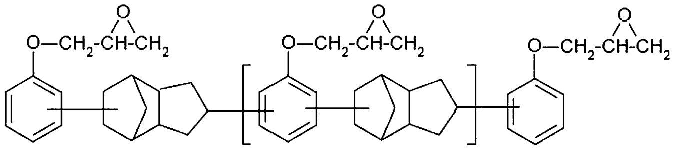


Scheme 1. Structure of Tactix 556 epoxy resin.

and curing agents. Several reports were published about the synthesis and properties of epoxy resins obtained from DCPD and phenol or its derivatives [15–23]; DCPD-based phenol novolac epoxy resins have the advantages of reduction in epoxy cure shrinkage and moisture resistance, but they are not satisfactory for some restricted applications because of relatively lower glass transition temperature.

The goal of the present study is to synthesize a novel, heat-resistant epoxy resin containing both a naphthalene structure and a DCPD group. In this work, the novel epoxy monomer was prepared through Friedel–Crafts condensation between 1-naphthol and DCPD, and then the epoxy monomer was reacted with paraformaldehyde and epichlorohydrin orderly to obtain a naphthalene–DCPD epoxy resin, both the structures of the monomer and the resin have been characterized, the thermal and mechanical properties of the cured polymers were investigated.

2. Experimental

2.1. Materials

DCPD was purchased from Fluka Co. 1-Naphthol (99.0%) from Shanghai Tingxin Chemical Engineering Reagent Co., China, paraformaldehyde from Tianjin Chemical Reagent Co., China, epichlorohydrin (ECH) from Acros were used without further purification. Benzyltrimethylammonium chloride from Acros was used as phase transfer catalyst. 4-4′-Diaminodiphenysulfone (DDS) obtained from Yinsheng Chemicals Co. Ltd., China was used as a curing agent. Tactix 556 (Scheme 1) with epoxy equivalent weight of about 225 g/eq was supplied by Huntsman Advanced Materials Americas Inc. All solvents and other chemicals were of reagent grade or better.

2.2. Synthesis

2.2.1. Preparation of alkylated product of 1-naphthol with DCPD

Into a 500 ml four-necked round-bottom flask equipped with a heating oil bath, stirrer, reflux condenser and argon inlet, were charged 86.4 g of 1-naphthol and 200 ml of toluene. The mixture was heated to 90 °C to let the 1-naphthol to dissolve in the toluene. Then 1.5 g of $AlCl_3$ powder was charged into the flask as the catalyst of Friedel–Crafts condensation. DCPD toluene solution of 15 ml (4 mol/l) was added gradually over a period of 1 h, and then the mixture was heated to 120 °C and maintained for another 7 h. After the reaction was completed, the resultant mixture was washed with 5 wt% aqueous $NaHCO_3$ to terminate the reaction followed by washing with water three times. The organic phase was separated and recrystallized to remove the excess 1-naphthol, then distilled in a rotary evaporator to remove the solvent, finally placed in the vacuum oven to eliminate the traces of toluene and 1-naphthol. A brown product (indicated as Product A) weighed 22.85 g was obtained. The reaction equation is shown in Scheme 2. ESI-MS: $m/z = 419.1$ (Fig. 1) IR (KBr): 3411 cm^{-1} (–OH of naphthyl); 1269 cm^{-1} (C–O); 1653 cm^{-1}, 1597 cm^{-1}, 1511 cm^{-1} (aromatic C–C); ^1H NMR ($CDCl_3$) δ (ppm): 8.30 (–OH of naphthyl), 6.87–7.86 (aromatic proton), 1.0–3.0 (saturated protons of DCPD ring) (Fig. 2).

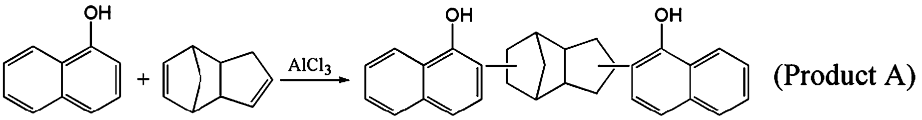
2.2.2. Preparation of naphthol–DCPD novolac

Product A (21 g), paraformaldehyde (1.5 g) and methyl isobutyl ketone (MIBK) (150 ml) were added to a four-necked round-bottom flask equipped with a heating oil bath, stirrer, reflux condenser and argon inlet. After the Product A and paraformaldehyde were completely dissolved in the MIBK, 0.2 g of *p*-toluene sulfonic acid (PSTA) was added, then the mixture was heated to 120 °C and refluxed for 6 h. When the reaction was completed, the solvent was evaporated under vacuum. A dark brown-colored solid product (indicated as Product B) weighed 21.9 g was obtained. The reaction equation is shown in Scheme 3.

IR (KBr): 3443 cm^{-1} (–OH of aromatic ring); 1386 cm^{-1} (C–O); 1658 cm^{-1}, 1598 cm^{-1}, 1508 cm^{-1} (aromatic C–C) (Fig. 3a). ^1H NMR ($CDCl_3$) δ (ppm): 8.29 (d, –OH), 6.72–7.76 (b, aromatic protons), 4.53–4.72 (m, $-CH_2$ between naphthyl), 1.0–3.0 (b, saturated –CH, $-CH_2$). GPC: $M_n = 973$ g/mol, polydispersity: 1.61.

2.2.3. Preparation of naphthalene–DCPD epoxy resin

Product B of 21.9 g and 100 ml of epichlorohydrin were put into a 250 ml four-necked round-bottom flask equipped with a heating oil bath, stirrer, and argon inlet. Benzyltrimethylammonium chloride of 0.5 g was also added as phase transfer catalyst. The reaction mixture was heated to 100 °C, and then 0.09 mol of 40 wt% aqueous NaOH was added gradually over a period of 2 h and the mixture was maintained at 100 °C for 4 h. After cooling down, the reaction solution was filtered



Scheme 2. Synthesis of Product A.

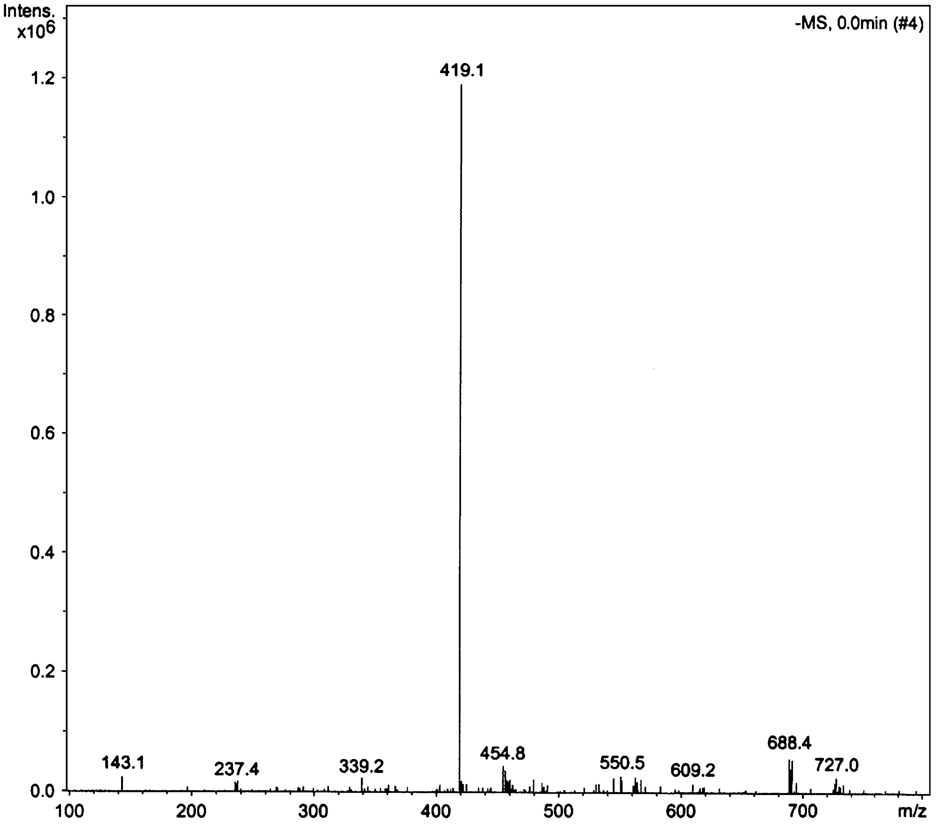


Fig. 1. ESI-MS spectrum of Product A.

to remove the salt, and the organic phase was washed with water three times. The excess epichlorohydrin was distilled in a rotary evaporator. Then the crude product was washed with water and dried in a vacuum oven. A dark yellow-colored product was obtained in almost quantitative yield. The reaction equation is shown in Scheme 4.

IR (KBr): 3421 cm^{-1} (–OH), 1090 cm^{-1} (C–O), 1622 cm^{-1}, 1597 cm^{-1}, 1506 cm^{-1} (aromatic C–C), 907 cm^{-1} (oxirane ring) (Fig. 3b). ^{1}H NMR (DMSO-d_6) δ (ppm): 6.82–7.96 (b, aromatic protons), 4.50–4.76 (m, –CH$_2$ between naphthyl), 1.0–3.9 (b, saturated –CH, –CH$_2$ of DCPD ring and 1,2-epxoypropyl). ^{13}C NMR (DMSO-d_6) δ (ppm): 148.2, 134.4, 130.0–122, 120.1, 113.6 (naphthalene), 70.1, 51.6, 43.6 (oxirane ring), 55.1 (CH$_2$ between naphthyl) 46.9, 46.7, 39.2–20.7 (DCPD ring) (Fig. 4). GPC: $M_n = 1264$ g/mol, polydispersity = 1.76.

2.2.4. Curing procedure

The epoxy resins 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 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 110 °C for 1 h, 160 °C for 1 h and 200 °C for 2 h. Then, the cured samples were cooled slowly to room temperature to prevent cracking.

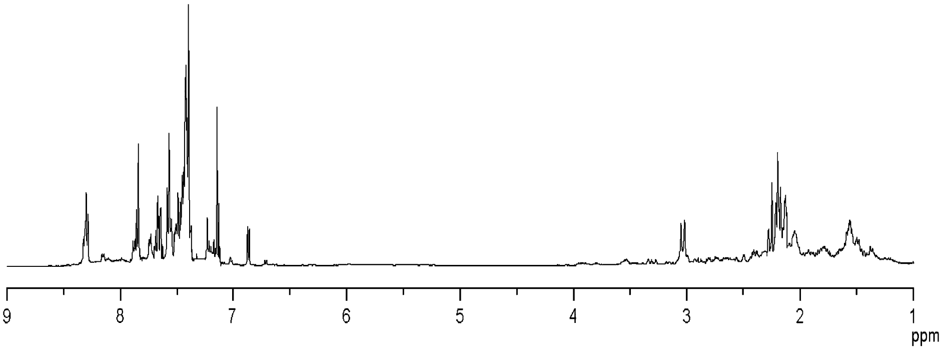
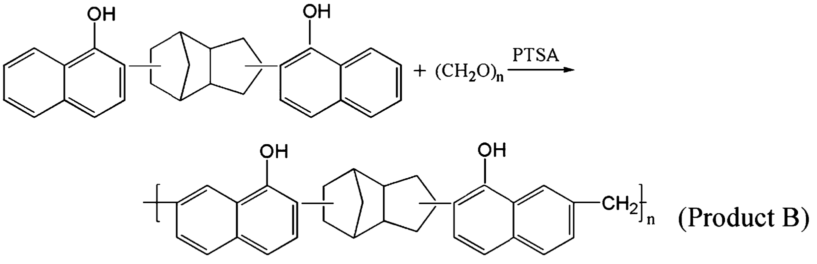


Fig. 2. ^{1}H NMR spectrum of Product A.



Scheme 3. Synthesis of Product B.

2.3. Characterization

The electrospray ionization (ESI) MS was carried on a Bruker Esquire-LC-00075 spectrometer. FTIR spectra were recorded on a Nicolet 5700 FT-IR spectrophotometer. ^{1}H NMR and ^{13}C NMR characterizations were carried out by Bruker Avance DMX 500 NMR spectrometer using tetramethylsilane (TMS) as internal standard. Gel permeation chromatography (GPC) was performed by Waters 1525/2414 GPC instrument. The epoxide equivalent weight (EEW) of epoxy resin was determined by HCl/acetone titration method. Thermogravimetric analysis (TGA) was performed using a Pyris 1 thermogravimetric analyzer (Perkin–Elmer Cetus Instruments, Norwalk, CT) at a heating rate of 10 °C/min under nitrogen and air atmosphere. Dynamic curing kinetics was measured on a Perkin–Elmer DSC-7 under nitrogen atmosphere with the heating rate of 10 °C/min used for comparison of naphthalene–DCPD epoxy resin/DDS and Tactix 556/DDS systems. Dynamic mechanical thermal analysis (DMTA) was carried out with a TA DMA Q800 instrument using 2 mm × 10 mm × 30 mm rectangular samples at a programmed heating rate of 3 °C/min from 50 °C to 300 °C at a frequency of 1 Hz under air atmosphere. Moisture absorption was tested as follows: 10 mm × 10 mm × 2 mm rectangular samples were dried under vacuum at 120 °C for 24 h until trace water had been expelled, then cooling to room temperature, the samples were weighed and placed in 100 °C water for 144 h and weighed again. Dielectric constant (D_k) were measured with Agilent 4294 precision impedance analyzer at a frequency of 1 MHz. Tensile properties were measured on a Zwick Roell Z202 Universal Material Testing Machine at a testing rate of 1 mm/min, the specimens were dumbbell-shaped with the testing part in the middle (dimension of cross section is 6 mm × 4 mm and the length of the testing part is 40 mm). Flexural properties were measured on a Zwick Roell Z202 Universal Material Testing Machine at a testing rate of 0.5 mm/min, with the dimension of the specimens 3 mm × 9 mm × 90 mm.

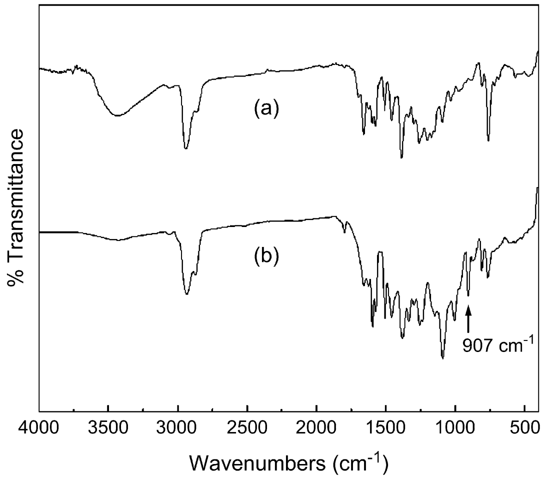
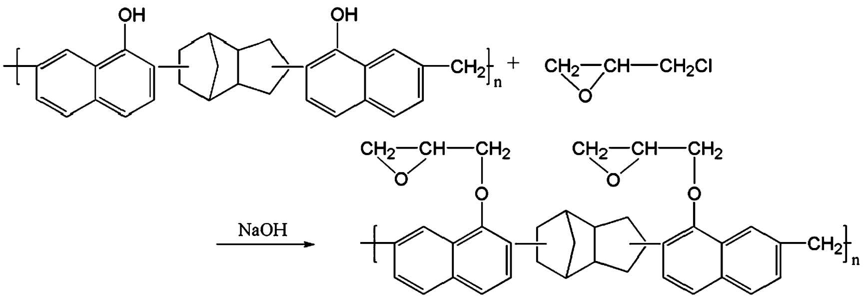


Fig. 3. FTIR spectroscopy of Product B and naphthalene–DCPD epoxy resin.

3. Results and discussion

3.1. Synthesis and characterization

The alkylated product of 1-naphthol with DCPD was synthesized by Friedel–Crafts condensation between 1-naphthol and DCPD. It involves an electrophilic aromatic substitution of DCPD on naphthol ring. First, DCPD reacted with $AlCl_3$ to form carbocations with three possible structures [22] (Scheme 5), then the three possible active carbocations attack the naphthalene ring and C–C linkage was created. It is similar to the reaction between phenol and DCPD [21,23]. Several isomeric compounds would be obtained because of the three different carbocations from DCPD; mass spectrum (Fig. 1) showed that the alkylate had the same molecular weight ($m/z = 419.1$); ^{1}H NMR analysis of Product A indicated that the product was not just a single compound but a mixture of isomeric compounds obtained from the alkylation between different carbocations and naphthalene. In this work, no efforts were made to separate the product into pure isomeric compounds and all of the isomeric compounds can obtain the final epoxy resins. In addition, the molar ratio of naphthol to DCPD and the reaction temperature could influence the resultant product. It was found that if the reaction temperature was too low, the predominant product was DCPD single-substituted alkylate, which was the compound created via the alkylation process between one DCPD molecule and one naphthol molecule. When the molar ratio of naphthol to DCPD increased, the DCPD single-substituted alkylate decreased evidently. Therefore, large molar excess of naphthol to DCPD and the appropriate reaction temperature made the optimized naphthol–DCPD alkylate to be obtained. The Product A was characterized by ESI-MS, FTIR and ^{1}H NMR spectra. Mass spectrum showed that the Product A has a single mass–charge ratio ($m/z = 419.1$) and contains



Scheme 4. Synthesis of the naphthalene–DCPD epoxy resin.

no single-substituted alkylate. ^{1}H NMR spectrum (Fig. 2) exhibited broad peaks at 1.0–2.6 due to the saturated protons of DCPD ring, supporting the suggestion that Product A contains two or more isomeric compounds. No signals were found at 5.0–6.0 ppm which is the signal range for unsaturated protons of DCPD ring, also proving that no single-substituted alkylate or unreacted DCPD is contained in Product A.

Naphthalene–DCPD novalac was prepared by the condensation reaction between Product A and paraformaldehyde with the presence of PSTA as catalyst. The molecular weight was increased and more hydroxy groups would be contained in one molecule so that multifunctional epoxy resin could be obtained in the next step. The GPC measurement showed that Product B had a M_n of 973 g/mol and a M_w of 1561 g/mol, thus, two or three molecules of Product A had been linked together by the methylene bridge.

Finally, naphthalene–DCPD epoxy resin was synthesized by the reaction between Product B and epichlorohydrin with the aqueous NaOH added to control the reaction and benzyltrimethylammonium chloride added as phase transfer catalyst to facilitate the reaction. The FTIR spectra of Product B and the naphthalene–DCPD epoxy resin are shown in Fig. 3(a) and (b), respectively. The strong absorption peak of –OH at 3443 cm^{-1} observed in Fig. 3(a) disappeared in Fig. 3(b) because of the reaction of the hydroxy group with epichlorohydrin, and the characteristic absorption peak at 907 cm^{-1} for oxirane ring emerged in Fig. 3(b). ^{13}C NMR spectrum of the naphthalene–DCPD epoxy resin (Fig. 4) also confirmed the chemical structure of the synthesized resin, the peaks of 70.1, 51.6, 43.6 were assigned to the carbons in epoxy group and 148.2, 113.6 to the carbons linked with glycidyl ether and DCPD group, respectively. According to the result of the EEW titration, the EEW of naphthalene–DCPD epoxy resin is 286 g/eq, which is close to the theoretical EEW of 269 g/eq.

3.2. Dynamic thermal curing

The blend of naphthalene–DCPD epoxy resin and DDS was employed to study the thermal curing behavior by DSC measurement. The kinetic analysis was performed using the Kissinger model [24,25]. According to the Kissinger's method, the activation energy can be obtained from the maximum reaction rate at the peak exotherm temperature. The relation could be expressed as the following equation:

$$\frac{\mathrm{d}\left[\ln\left(q/T_{\mathrm{p}}^{2}\right)\right]}{\mathrm{d}\left(1/T_{\mathrm{p}}\right)} = -\frac{E_{\mathrm{a}}}{R} \qquad (1)$$

where T_p is the peak exotherm temperature, q is the 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. The cure reaction order could also be obtained when Crane [26] method as depicted in Eq. (2) is applied.

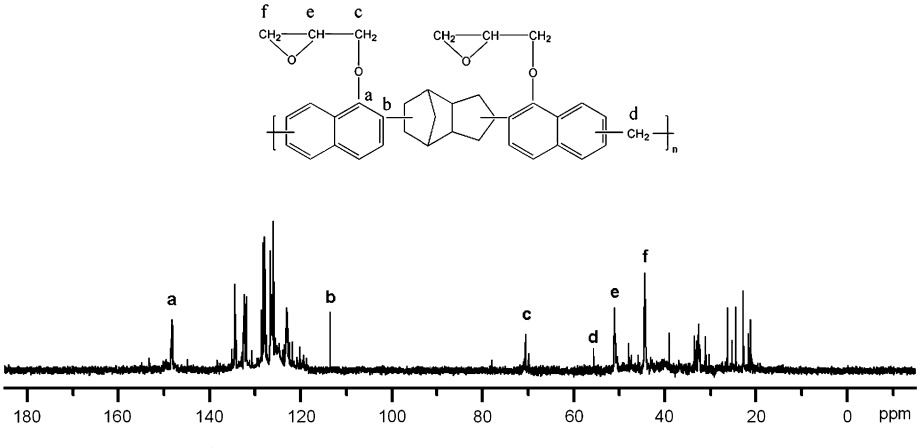
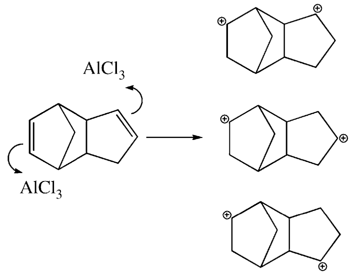


Fig. 4. ^{13}C NMR spectrum of Product B naphthalene–DCPD epoxy resin.



Scheme 5. Three possible carbocations after DCPD reacted with AlCl$_3$.

$$\frac{\mathrm{d}\left[\ln\left(q/T_\mathrm{p}^2\right)\right]}{\mathrm{d}\left(1/T_\mathrm{p}\right)} = -\frac{E_\mathrm{a}}{nR} \tag{2}$$

where n is the reaction order. It could be calculated from the slope of the plot of $\ln(q/T_\mathrm{p}^2)$ versus $1/T_\mathrm{p}$.

Tactix 556 is a kind of phenol–DCPD-based commercial epoxy resin with good thermal properties, which was used to compare and evaluate the reactivity of naphthalene–DCPD epoxy resin toward DDS. Fig. 5 shows the DSC trace of the blend of naphthalene–DCPD epoxy resin/DDS and Tactix 556/DDS systems at a heating rate of 10 °C/min and the dynamic cure reaction parameters are summarized in Table 1. The curing onset temperature (T_o) and exothermic peak temperature (T_p) of Tactix 556/DDS system were relatively lower. Besides, the activation energy of naphthalene–DCPD epoxy/DDS system calculated from the slope of Eq. (1) was higher than Tactix 556/DDS, which could conclude that naphthalene–DCPD epoxy resin represented lower reactivity toward amines. The cure kinetic model should be particularly investigated in the further study.

3.3. Characteristics of the cured polymer

3.3.1. Dynamic mechanical thermal analyses

Dynamic mechanical observations were performed to analyze the dynamic elastic modulus and the occurrence of molecular mobility transitions such as glass transition [7]. The DMTA scans of the naphthalene–DCPD epoxy resin and Tactix 556 cured with DDS are shown in Fig. 6. The peak temperature of tan δ was taken as the glass transition temperature. The DMTA measurement indicated that the T_g of the cured polymer from naphthalene–DCPD/DDS system is 236.2 °C, which is higher than Tactix 556/DDS system ($T_\mathrm{g} = 201.2$ °C) and the phenyl-DCPD epoxy system reported in the literatures [22,23]. These results confirmed that the heat-resistant properties of cured epoxy polymer depend strongly on the chemical structure. Glass transition temperature of the cured polymers could rise remarkably by introducing the naphthalene and DCPD group into the molecular backbone. The reason for this result is that the motion of the cured polymer chain is restrained due to the rigid structure of naphthalene and a high crosslink density.

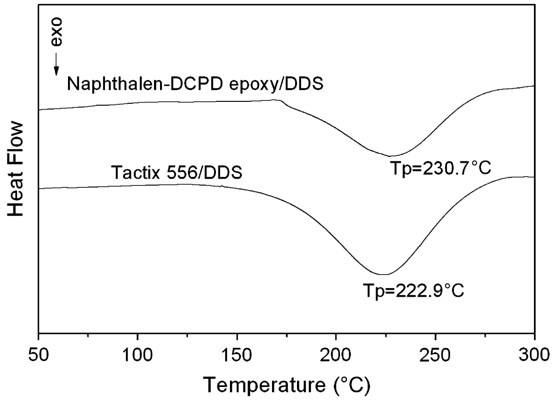


Fig. 5. DSC measurement of the curing systems at a heating rate of 10 °C/min.

Table 1
Dynamic cure reaction parameters of the epoxy system

Curing system	T_o (°C)	T_p (°C)	T_f (°C)	ΔH (kJ/mol)	E_a (kJ/mol)	n
Naphthalene–DCPD	176.5	230.7	285.8	73.24	90.9	1.008
Tactix 556	151.7	222.9	277.6	106.01	82.1	0.997

3.3.2. Thermogravimetric analyses

Fig. 7(a) and (b) is the TGA and its differential curves (DTG) of the cured polymer under nitrogen and air, respectively. TGA traces provided information regarding their thermal stability and thermal degradation behavior. The results indicated that the 10% degradation temperature of the cured polymer is 392.9 °C under nitrogen and 373 °C under air. It exhibited a higher thermal stability than phenol–DCPD epoxy resins because of the three resonance structures of naphthalene compared to two resonance structure for phenyl [12]. The percent char yield for the cured polymer at 800 °C was 29% under nitrogen. It is much higher than phenol–DCPD-based epoxy polymers. But the weight loss increased obviously since 600 °C under air, the presence of oxygen results in a complicated decomposition mechanism of the cured polymer [27]

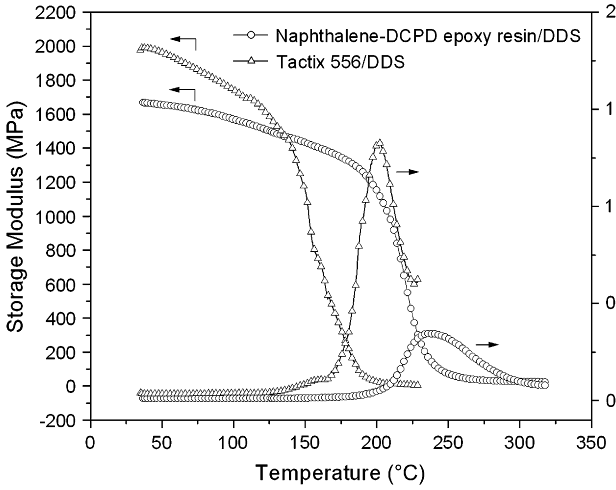


Fig. 6. DMTA results of the cured polymer.

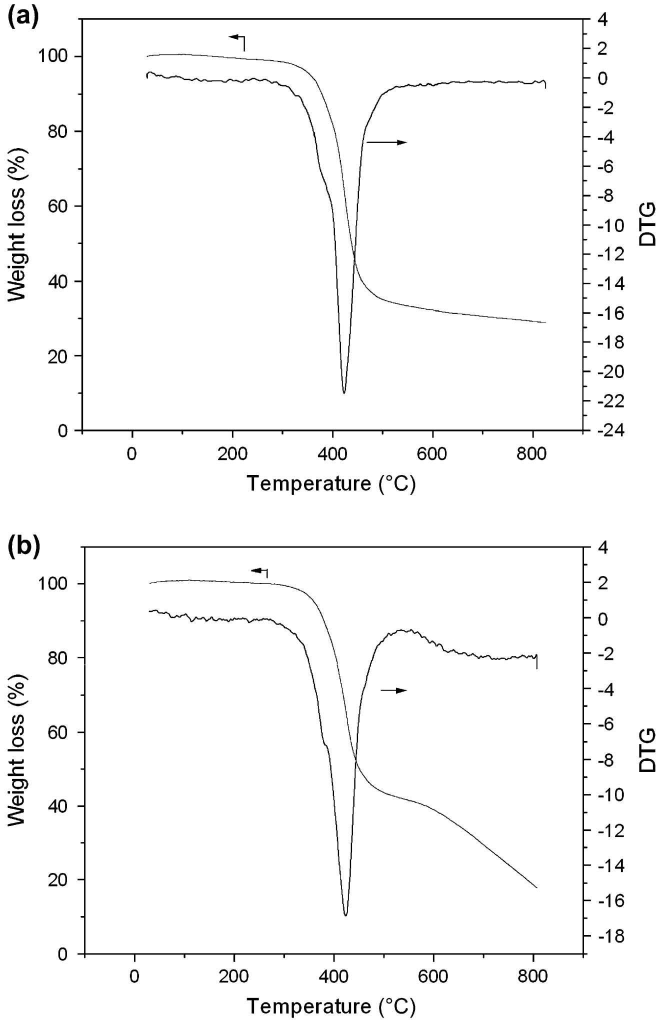


Fig. 7. Weight loss of the cured polymer: (a) under nitrogen and (b) under air.

and the pyrolysis reaction was activated by the existence of oxygen.

3.3.3. Moisture absorption

Moisture absorption will increase the dielectric constant of the cured polymer and have a disadvantageous effect on mechanical properties [28]. Furthermore, it will ionize the ionic impurities and thus corrode the integrated circuits. Thus, to obtain a higher performance epoxy polymer, it is necessary to decrease the moisture absorption. The moisture absorption was calculated as percent weight gain:

$$\text{Moisture absorption\%} = (W/W_o - 1) \times 100\%$$

where W is the weight of the sample after dipping in 100 °C water for 144 h, W_o is the weight of the sample after placing in vacuum oven for 24 h. Conventionally, the moisture absorption increases as the T_g increases in the cured polymers from novolac type epoxy resin and phenol novolac [29]. However, because of the hydrophobic nature of both aliphatic DCPD and naphthyl structure, the cured polymer from naphthalene/DDS system exhibited a high T_g and relatively low moisture absorption of 0.736%, compared to that of Tactix 556/DDS of 1.210%.

Table 2
Mechanical properties and dielectric constant of the cured polymer

Tensile properties			Flexural properties			D_k
Tensile strength (MPa)	Tensile Modulus (MPa)	Strain at break (%)	Flexural strength (MPa)	Flexural strength (MPa)	Displacement at break (mm)	
12.94	1598.3	0.98	27.79	3006.84	1.79	3.07

3.3.4. Mechanical and dielectric properties

Table 2 shows the mechanical properties and dielectric constant (D_k) of the cured polymer. The D_k at 1 MHz is 3.07, this relatively lower dielectric constant may be attributed to the better hydrophobicity, larger free volume and lower polarization of the molecule [30]. The tensile and flexural strengths are not enough for practical application, appropriate modifications have begun in our laboratory to improve the tensile and flexural properties of the cured epoxy system.

4. Conclusions

A novel naphthalene–DCPD-based epoxy resin was synthesized from 1-naphthol and DCPD by three steps. The structures of the resin and its precursors were confirmed by MS, NMR, FTIR spectra and GPC analyses. With the introduction of naphthyl and DCPD moieties into the skeleton, the resulting epoxy polymer cured with DDS exhibited higher glass transition temperature, good thermal stability and lower moisture absorption. These pronounced good properties make it an attractive candidate for electronic encapsulation applications and composite materials.

References

[1] Ho TH, Wang CS. J Appl Polym Sci 1999;74:1905–16.
[2] Duann YF, Liu TM, Cheng KC, Su WF. Polym Degrad Stab 2004;84: 305–10.
[3] Kaji M, Dndo T. J Polym Sci Part A Polym Chem 1999;37:3063–9.
[4] Wang CS, Leu TS, Hsu KR. Polymer 1998;39:2921.
[5] Castell P, Serra A, Galia M. J Polym Sci Part A Polym Chem 2003;41: 1536.
[6] Xu K, Chen MC, Kui Z, Hu JW. Polymer 2004;45:1133.
[7] Lee JY, Jang J, Hong SM, Hwang SS, Kim KU. Polymer 1998;39:6121.
[8] Lee JY, Jang J. Polymer 2006;47:3036.
[9] Lee JY, Jang J. J Polym Sci Part A Polym Chem 1999;37:419.
[10] Ochi M, Shimizu Y, Nakanishi Y, Murata Y. J Polym Sci Part B Polym Phys 1997;35:397.
[11] Wang CS, Lee MC. Polymer 2000;41:3631.
[12] Wang CS, Lee MC. J Appl Polym Sci 1998;70:1907.
[13] Wang CS, Lee MC. J Appl Polym Sci 1999;73:1611.
[14] Ho TH. Macromol Mater Eng 2000;283:57.
[15] Nelson DL. US Patent 4,390,680; 1983.
[16] Makoto Y. Japanese Pat. 61-168618; 1986.
[17] Hishinuma M. Japanese Pat. 61-293219; 1986.
[18] Hiroakt N. Japanese Pat. 62-135539; 1987.
[19] Hsiue GH, Shiao SJ, Wei HF, Kuo WJ, Sha YA. J Appl Polym Sci 2001; 79:342.
[20] Tseng FP, Chang FC, Lin SF, Lin JJ. J Appl Polym Sci 1999;71:2129.

[21] Hsiue GH, Wei HF, Shiao SJ, Kuo WJ, Sha YA. Polym Degrad Stab 2001;73:309.

[22] Lin GH, Chiang JC, Wang CS. J Appl Polym Sci 2003;88:2607.

[23] Tseng FP, Chang FC, Lin SF, Lin JJ. J Appl Polym Sci 1999;74:2196.

[24] Kissinger HE. Anal Chem 1957;29:1072.

[25] Kissinger HE. J Res Natl Bur Stand 1956;57(4):217.

[26] Crane LW, Dynes PJ, Kaelble DH. J Polym Sci Polym Lett Ed 1973;11:533.

[27] Liu YL, Hsiue GH, Lee RH, Chiu YS. J Appl Polym Sci 1997;63:895.

[28] Boinard P, Banks WM, Pethrick RA. Polymer 2005;46:2218.

[29] Ogata M, Kinjo N, Kawata T. J Appl Polym Sci 1993;48:583.

[30] Hougham G, Tesoro G, Shaw J. Polym Mater Sci Eng 1989;61:369.