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Synthesis and characterization of novel epoxy resin bearing naphthyl and limonene moieties, and its cured polymer

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Abstract

The synthesis of novel epoxy resin containing both naphthalene moiety and cycloaliphatic group by chemical bonding in the same molecule has been conducted starting from naphthol and limonene. Its chemical structure was characterized with FTIR spectroscopy, NMR, and GPC analyses. Dynamic cure behaviors with different curing agents were investigated using differential scanning calorimetry. The physical properties of the resulting polymers were evaluated with dynamic thermal mechanical spectroscopy, thermogravimetric and thermal mechanical analysis, and X-ray diffraction. Compared to that of diglycidyl ether of bisphenol A, cured polymer of the novel epoxy resin showed remarkably higher glass transition temperature (T_g), lower coefficient of thermal expansion, higher thermal stability, better moisture resistance and dielectric property.

Keywords: Epoxy resin; Naphthol; Limonene

1. Introduction

Epoxy resins have the combination of good thermal and dimensional stability, excellent chemical and corrosion resistance, high tensile strength and modulus, and ease of handling and processability, ensuring their wide application to the aerospace and electronic industries in the form of structural adhesives, advanced composite matrices, and packaging materials [1,2]. The properties of cured epoxy polymers largely depend on the nature of chemical structure of the starting resins. Hence, it is possible to tailor and synthesize various resins through incorporating of some types of moieties into the backbone of molecules to suit particular needs.

Several scientific efforts have been expended on the study of developing novel epoxy resins that enhance the heat resistance as well as electric resistance of the thermosets for use in electrical and microelectronic devices [3–6]. For instance, cycloaliphatic epoxides in which the oxirane rings are fused to the rings of cycloaliphatic hydrocarbon are known to be one of the most common products for this purpose [7]. Characterized by the saturated cycloaliphatic ring structure and without any aromatic unsaturation, they have lower viscosity before curing; their cured polymers show the advantages of good dielectric properties and durable performance for outdoor use [8–12]. However, some inherent features of the resulting polymers such as the relatively low glass transition temperature (T_g), inferior cracking-resistance when subjected to severe temperature and moisture environment, and low reactivity towards amine curing agents, may cause limitation to their application. More recently, as a possible approach to advanced thermosets, a project aimed at the synthesis of new, more thermally stable epoxy resin has been initiated in this laboratory. This epoxy monomer contains both naphthyl moiety and cycloaliphatic group by chemical bonding in molecule backbone, and can be called ‘structural hybrid’ epoxy resin (It will be named as NL epoxy resin for description convenience). This structural design takes into account several chemical and material considerations. The presence naphthalene moiety is expected to greatly improve thermal property and moisture resistance of the obtained thermoset that possesses a high T_g as well [13–15]. Using naphthol and limonene, which are inexpensive and commercially available, as starting materials, the NL monomer

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would be practicably obtained through Friedel–Crafts condensation. The combination of the special features of cycloaliphatic structure with naphthalene would subsequently offer the NL epoxy resin better overall performance to satisfy required properties in the fields of fabrication of multilayered printed circuit boards and encapsulating of larger-scale chip.

The objective of this article was to describe the synthesis and structure of glycidyl ether derived from naphthol and limonene. The characteristics of cure and thermal and mechanical properties of the cured polymer were investigated using several methods, and compared with those of conventional diglycidyl ether of bisphenol A.

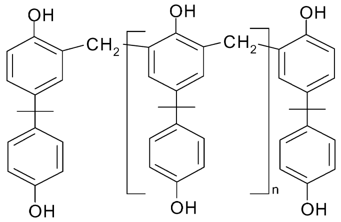
2. Experimental

2.1. Materials

Reagent grade of 1-naphthol, 2-naphthol, and paraformaldehyde were commercially available and used as received. Epichlorohydrin and methyl isobutyl ketone (MIBK) were distilled before use. Limonene (Huangpu Chemical Co., Guangzhou) was washed with 5 wt% Na_2CO_3 aqueous solution and water to remove inhibitors, and then dried over magnesium sulfate and distilled before use. Dicyanodiamide (DICY, from Aldrich) and a bisphenol A-formaldehyde novolac resin (PN, see Scheme 1, with hydroxy equivalent weight of about 120, supplied by Borden Chemical, Inc.) were used as curing agents, and 2-methylimidazole (2-MI, from Nippon Gohsei Co.) as accelerator without purification. Diglycidyl ether of bisphenol-A (DGEBA, Epikote 828, epoxy equivalent weight, EEW 188) was obtained from Shell Chemical Co.

2.2. Synthesis of C-alkylated product of 1-naphthol with limonene (*1*)

Into a 2000 ml four-neck round-bottom flask equipped with Dean–Stark trap and metering pump were added 1-naphthol (288 g, 2 mol) and toluene (900 ml), and the mixture was heated to azeotropic point and refluxed for 2 h under nitrogen atmosphere to remove water in Dean–Stark trap with toluene. Then boron trifluoride–ether complex (4 g) and limonene (27.2 g, 0.2 mol) were charged into the flask via metering pump at 60 °C.The mixture was further stirred for 6 h at 120 °C. After cooling down, the resultant mixture was neutralized with 5 wt% aqueous $NaCO_3$ solution followed by washing with water. The organic phase was concentrated to remove the toluene and excess 1-naphthol. A gray product with softening point around ambient temperature was obtained in 80% yield. IR (KBr): 3390 (–OH), 1622, 1592, 1510, 810 (aromatic C–C), 1260 cm^{-1} (C–O). Fig. 1 displayed the ^1H NMR spectrum of **1**.



Scheme 1. Structure of bisphenol A-formaldehyde novolac (PN).

2.3. Synthesis of limonene alkylated naphthol-formaldehyde resin (*2*)

In 350 ml of MIBK, 85 g of **1** and 6.3 g of paraformaldehyde were dissolved. To this solution 1 g of *p*-toluene sulfonic acid (PTSA) was added and the solution was refluxed for 8 h. The generated water was removed from the reaction mixture by azeotropic distillation. After the solvent was evaporated, the dark brown-colored solid product **2** was obtained (88 g). M_n 1330, M_w/M_n 1.82. ^1H NMR: δ (ppm) 8.3 (–OH), 6.5–7.9 (broad peak, aromatic proton), 3.7–4.2 and 4.5–4.7 (multiplet, CH_2 linkage between naphthyl ring), 1.0–3.1 (alicyclic CH, CH_2, CH_3). The FTIR spectrum was shown in Fig. 3(a).

2.4. Glycidyl ether of the limonene alkylated naphthol-formaldehyde resin (*3*)

Seventy grams of **2**, 2 g of polyethylene glycol (PEG-400) and 235 ml of epichlorohydrin were put into a 500 ml four-necked flask equipped with stirrer, a modified Dean–Stark trap with condenser and a vacuum controller. To the resultant solution was added continuously 25 g of 48 wt% aqueous sodium hydroxide solution via metering pump over a period of 4 h while maintaining temperature at 65 °C under a reduced pressure, and the mixture was stirred for an additional 2 h. Both of the water generated by reaction and that contained in the aqueous solution of sodium hydroxide were removed continuously from the reaction system by azeotropic distillation, and the distilled epichlorohydrin was returned to the reaction system. Then the reaction mixture was filtered to remove salt, and the organic phase was washed with water three times. The excess epichlorohydrin was subsequently distilled to give a light amber-colored semisolid product **3** (81 g). EEW was 295 g/equiv. M_n 1690, M_w/M_n 1.95. IR (KBr): 1624, 1597,1510 (aromatic C–C), 1088 (C–O–C), 908 cm^{-1} (epoxy). ^1H NMR: δ (ppm) 6.7–8.0 (br, aromatic proton), 1–4.6 (br, $-CH_2$, $-CH$, $-CH_3$).

2.5. Preparation of cured polymers

The epoxy resins and curing agents in a molar stoichiometric ratio of 1:1 were dissolved in the mixture of acetone and DMF at room temperature. 0.5 wt% of 2-MI was added to the mixture. The solvent was evaporated under vacuum. The samples were kept in the refrigerator before performing the DSC experiment. The cured samples were

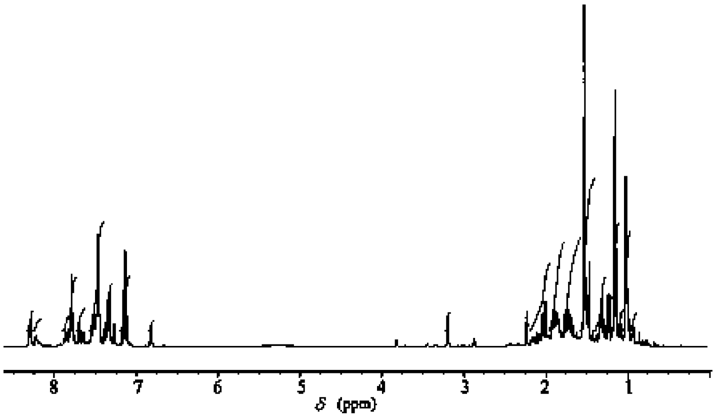


Fig. 1. ^{1}H NMR spectrum of **1**.

prepared by mixing the reactant compositions homogeneously at 100 °C, and then cured at 200 °C for 4 h under vacuum. For thermomechanical analysis (TMA), dielectric analysis and water-absorption experiment, the curing formulations were dissolved in acetone/DMF and immersed with glass fiber cloth to obtain prepreg. The prepreg were dried at 60 °C, and then cured at 200 °C for 4 h, and were cut to get required specimens for evaluation.

2.6. Methods of measurements

^{1}H and ^{13}C NMR characterizations were carried out by Bruker DRX 400 NMR spectrometer using chloroform-d_1 ($CDCl_3$) as the solvent and tetramethylsilane (TMS) as internal standard. FTIR spectra were recorded on Nicolet MAGNA 760 infrared spectrometer. Gel permeation chromatography (GPC) was performed by a Agilent 1100 HPLC equipped with polystyrene gel columns and a UV detector (eluent THF) at 40 °C at a flow rate of 1 ml/min. The EEWs of epoxy resin were determined by HBr titration method.

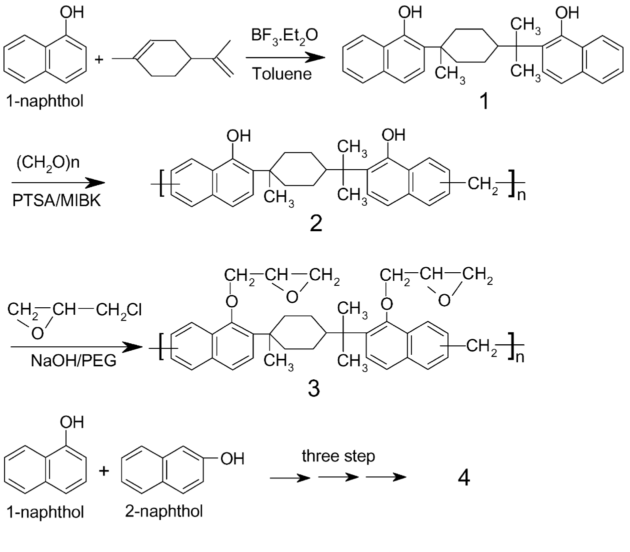
Dynamic curing kinetics was measured with a Perkin–Elmer DSC-7 under nitrogen atmosphere. The glass transition temperature (T_g) and the coefficient of thermal expansion (CTE) were measured with TA DSC 2010 instrument in differential scanning calorimetry (DSC) module and TMA module at a heating rate of 10 °C/min under air atmosphere, respectively. Thermogravimetric analysis (TGA) was performed by a Perkin–Elmer TGA-6 at a heating rate of 10 °C/min under nitrogen or air atmosphere. Dynamic mechanical thermal analysis was carried out with a NETZSCH DMA 242 using 2 mm × 5 mm × 50 mm rectangular samples. The sample was subject to three-point flexure deformation mode at a programmed heating rate of 2 °C/min from ambient to 250 °C at a frequency of 10 Hz under air atmosphere.

Dielectric constants (ε) were measured with HP-4291B dielectric analyzer at a frequency of 1 MHz. Wide-angle X-ray diffraction patterns (WAXD) were obtained on a Rigaku D/max-1200 diffractometer at room temperature using copper filtered Cu Kα radiation (40 KV, 30 mA).

3. Results and discussion

3.1. Synthesis and characterization of epoxy resins

The structural hybrid epoxy resin **3** bearing naphthalene and limonene moieties was designed and prepared according to the chemical reaction s outlined in Scheme 2. As described in detail in Section 2, the overall synthesis involves three steps: (1) alkylation of naphthol with limonene in the presence of Friedel–Crafts catalyst, (2) introduction of methylene linkage between naphthalene rings to obtain product **2** with higher molecular weight, and subsequently (3) epoxidation of **2** with epichlorohydrin in the presence of sodium hydroxide and polyethylene glycol to give epoxy resin **3**. The first step involves an acid-catalyzed electrophilic aromatic substitution of limonene on naphthol ring. One of the mechanistic basis for this lies on the formation of carbocation by reaction of carbon–carbon



Scheme 2. Synthesis of epoxy resins starting from naphthol and limonene.

double bond with BF_3. The two non-conjugated double bond, i.e. methyl cyclohexene and isopropenyl group, generate two tertiary carbocation, respectively, which are resonance stable. These active carbocation acts as electrophile and attacks naphthalene ring at the *ortho* or *para* position of hydoxy. Bis-alkylation between limonene and two naphthol molecules proceed, and two C–C linkage between them are created. Similar reaction was reported in the literature that described the reaction of phenol and the non-conjugated dicyclopentadiene [16,17]. It should be noted that the starting material limonene consisted of a mixture of stereoisomers. Therefore, the alkylate was obtained as mixtures that in fact contained both stereoisomers and geometric isomers. Their NMR and GPC analyses could confirm this suggestion. In this work, no efforts were made to separate these complex mixtures into their 'pure' isomeric components. With the large molar excess of naphthol to limonene (10:1) and combined with lower reaction temperature (60 °C), the optimized alkylate **1** was obtained. The condensation reaction between **1** and formaldehyde was carried out to obtain **2** with higher molecular weight. The third step involves a heterogeneous reaction of **2** with epichlorohydrin where aqueous NaOH was used as reagent to yield corresponding glycidyl ether; thereby PEG with an average molecular weigh of 400 was added as phase-transfer catalyst to facilitate the reaction.

The compounds **1**, **2**, and **3** were characterized by FTIR, NMR spectra and GPC measurements. The ^{1}H NMR spectrum of **1** (see Fig. 1) exhibits multiplet peaks at 1–3.1 ppm due to the saturated protons for cycloaliphatic hydrocarbon, supporting the assumption that **1** consists of a mixture of isomers. The chemical shifts of the aromatic protons ($-C_{10}\mathit{H}_6$) were observed at 6.8–7.8 ppm. The original signals for double bonds protons in limonene molecule at 4.7 ppm and 5.4 ppm disappeared in Fig. 1. This result indicated that the two C=C double bonds completely proceeded to the reaction, which was different from the results reported on the partial reaction of phenol and dicyclopentadiene [16,17]. On the basis of integral intensities of protons, the ratio of naphthalene to limonene in alkylate **1** was calculated as 65/35. Fig. 2 depicts the ^{13}C NMR distortionless enhancement by polarization transfer (DEPT) spectrum of **3**. The DEPT technique can be used to identify clearly the carbon groups and the epoxides [18,19], because methyl and methine signals appeared as upward peaks in DEPT-90, while methylene signals appeared as downward peaks in DEPT-135, and the quaternary carbons disappeared in above spectra. The single peaks at 75, 50, and 44 ppm were assigned to the carbon for $C_{10}H_6-O-\mathit{C}H_2-$, methine carbon and methylene carbon in oxirane. The carbon for $C_{10}H_6-\mathit{C}H_2-$ appeared at 52 ppm. The simple appearance for glycidyl group suggested that the occurrence of polymerization of glycidyl ether would proceed minimally when a large excess amount of epichlorohydrin was used in the preparation of epoxide. It is in agreement with report from Wang et al. on the glycidyl etherification of phenol [20].

As shown in the FTIR spectra of **3** and its precursor **2**, the strong absorption peaking at 3380 cm^{-1} corresponds to the vibration of –OH in **2** (Fig. 3(a)). Its complete loss in Fig. 3(b) revealed the occurrence of glycidyl etherification. The characteristic absorption peak for oxirane was observed at 910 cm^{-1} in **3**.

By using the mixture of 1-naphthol and 2-naphthol as starting material and keeping the same feed ratios of alkylate to formaldehyde, a series of NL epoxy reins **4**s were obtained according to the above-mentioned steps, and their characteristics were given in Table 1. It can be observed that the molecular weights (M_n) of epoxy resins decreased with the amount of 2-naphthol ranging from 0 to 40, whereas the EEW changed slightly. This interesting result might be due to the relatively low reactivity of 2-naphthol towards formaldehyde.

3.2. Dynamic thermal cure

For theoretical and practical purpose, **3** and the blend of **3** and conventional epoxy resin DGEBA were employed to discuss the thermal cure behaviors of NL epoxy resins by DSC technique. PN and dicyanodiamide were used as counterpart curing agents to compare their reactivities towards the epoxy resins and their influences upon the properties of cured polymers. The cure kinetics were studied by dynamic experiment at different heating rates and applied to the Kissinger method [21] given by the following equation:

$$\frac{\mathrm{d}\ln(\beta/T_p^2)}{\mathrm{d}(1/T_P)} = -\frac{E_a}{R} \tag{1}$$

where E_a is the activation energy, β is the heating rate, T_p is the peak exotherm temperature, and R is the gas constant. The E_a can be calculated from the slope of the plot. When Crane method [22] as depicted in Eq. (2) is applied, the cure reaction order can also be obtained:

$$\frac{\mathrm{d}\ln\beta}{\mathrm{d}(1/T_P)} = -\left(\frac{E_a}{nR} + 2T_p\right) \tag{2}$$

where n is reaction order.

The DSC traces of **3**/PN and **3**/DICY from dynamic scan at a heating rate of 5 °C/min were represented in Fig. 4. The cure reaction parameters of several epoxy systems were summarized in Table 2. Both DSC scans of **3**/DICY

Table 1
Characteristics of the synthesized epoxy resins

Sample	Feed ratio of 1-na/2-na	M_n	EEW
3	100:0	1690	295
4(80)	80:20	1410	302
4(60)	60:40	1150	300

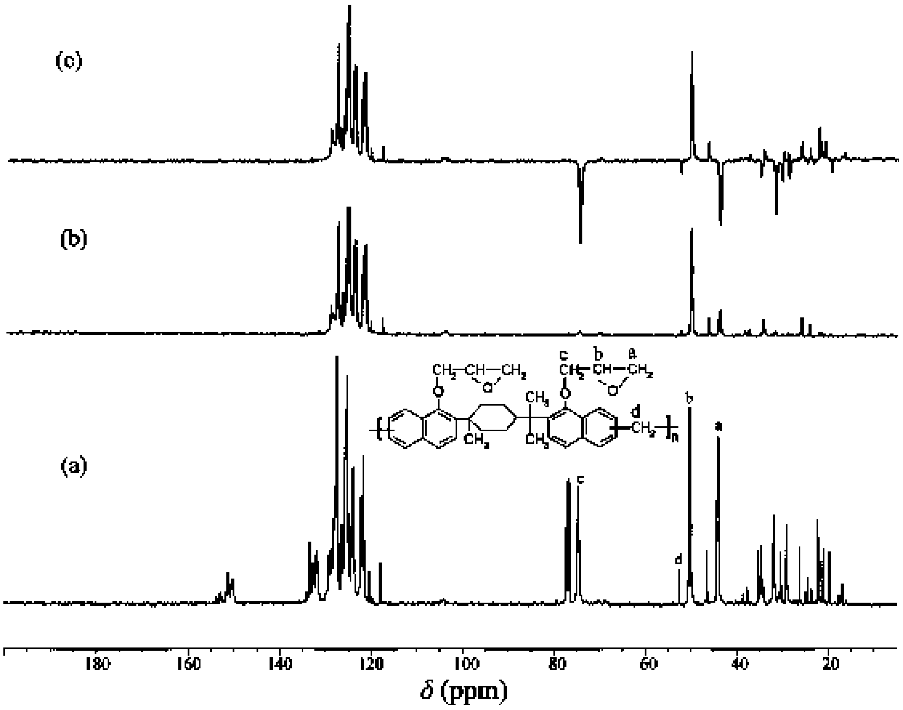


Fig. 2. ^{13}C NMR spectra of **3**: (a) broad-band decoupling NMR; (b) DEPT-90 NMR; (c) DEPT-135 NMR.

Table 2
Dynamic cure parameters of various epoxy systems

Sample	T_0[a] (°C)	T_m[a] (°C)	ΔH[a] (kJ/mol)	E_a (kJ/mol)	n
3/DICY	159.6	179.0	51.6	106.25	0.932
3/PN	129.9	151.7	29.1	74.91	0.911
3 + DGEBA/DICY[b]	150.9	165.6	46.9	97.33	0.929
3 + DGEBA/PN[b]	125.1	138.3	31.6	68.02	0.906
DGEBA/DICY	116.3	144.1	62.4	99.22	1.173

[a] At a heating rate of 5 °C/min and under nitrogen atmosphere.

[b] Blend of **3** and DGEBA in weight ratio of 50:50.

and **3**/PN showed an exothermic peak and no endothermic peak, which implied that the cure reactions occurred prior to the melting of epoxy systems. In the case of **3**/DICY, the exothermic peak (T_p) centered at 179 °C corresponding to the cure reaction of **3** and the functional group of DICY. For the mixture of **3** and PN, T_p was observed at 151.7 °C, which was attributed to the cure reaction of epoxy group with phenyl hydroxy. The total heat of cure reaction (ΔH), which was calculated from the total area under the baseline and the weight of **3**, was 51.6 and 29.1 kJ/mol for **3**/DICY and **3**/PN, respectively. From the slope of Eq. (1), the activation energy for cure was calculated as 106.25 and 74.91 kJ/mol for the above two epoxy systems, respectively. By judging from the T_p, cure onset temperature (T_o) and E_a, it may be concluded that the phenolic functional curing agent PN, in spite of its larger size, displayed higher reactivity than DICY. This is known by considering the chemical reactivity of amine group and hydroxy. The hydroxy group of phenol may

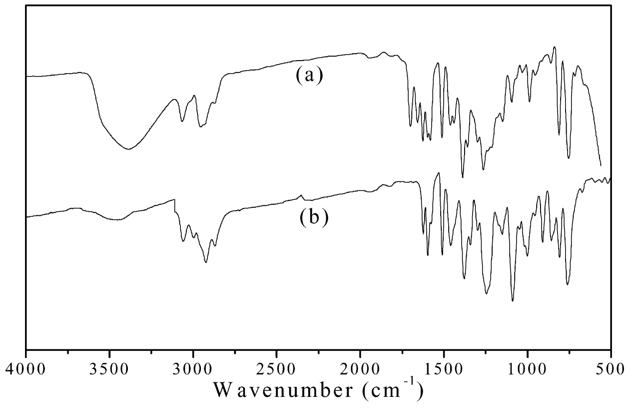


Fig. 3. FTIR spectra of (a) **2** and (b) **3**.

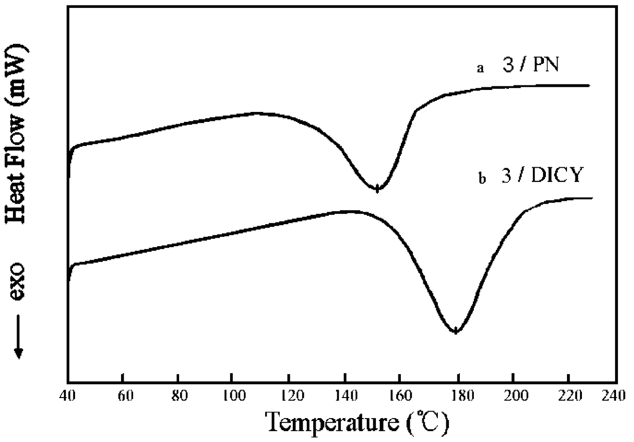


Fig. 4. Dynamic DSC thermograms of the cure of (a) **3**/PN and (b) **3**/DICY at a heating rate of 5 °C/min under nitrogen atmosphere.

possess higher nucleophilicity towards NL epoxy resin than amine in the presence of accelerator. There are significant differences in T_o, T_p and E_a values between **3**/DICY and DGEBA/DICY system, implying that they show different reactivity. **3** shows lower cure reactivity towards DICY than DGEBA. This result may be attributed to the steric hindrance based on the naphthalene structure and the stiff cycloaliphatic group in **3**, which reduce the molecular mobility and depress the reactivity of reactive site.

The dynamic DSC thermograms for the cure of blend of **3** + DGEBA towards DICY and PN were similar to that of single-component NL epoxy system. Compared with the cure reaction of **3**, the blend displayed relatively lower T_o and T_p, probably indicating that the cure reaction of NL epoxy resin is facilitated for the existence of DGEBA in the blend, matching the previous observation for the mixed biphenyl epoxy resins [23]. The E_a values for the blends towards DICY and PN fell in the range of values for DGEBA + amine systems (90–100 kJ/mol) [24–28], and for epoxy + phenolic resin systems (69–75 kJ/mol) [29], respectively. However, because the reaction order *n*s which were calculated from the slope of Crane relationship for NL epoxy systems were less than 1, the cure reaction may proceed complicatedly. Thus, further investigation should be carried out to characterize the cure kinetic model in later communications.

3.3. Mechanical and thermal properties

Dynamic mechanical thermal analysis, DMTA, was studied to track the viscoelastic responses of epoxy thermosets to the deformation, useful for understanding of the structure-property correlations and the occurrence of molecular mobility transitions such as main transition associated with glass transition and other relaxations [30, 31]. Fig. 5 shows the dependence of storage modulus and tan δ of **3**/DICY, **3**/PN and the common epoxy system DGEBA/DICY. The storage modulus (E') of **3**/DICY was higher than that of DGEBA/DICY both in the glassy and rubbery region characterized by the temperature corresponding to the maximum peak of tan δ (Fig. 5(a)). The cured **3**/DICY exhibited much higher T_g than that of the common phenyl-based epoxy system by about 70 °C. In general, the T_g of cured polymer depends strongly on the chemical structure. Therefore, this result may confirm that the T_g value of epoxy system can be elevated drastically by introducing some rigid group into the backbone of epoxy monomer. One possibility for this result might arise from the higher rigidity of naphthalene and cycloaliphatic skeleton in the molecular backbone, which would restrain the thermal movements and rotations of polymer chains. Another possible explanation could be the planar and bulky naphthalene structure, which would lead to better packing in the molecules in NL epoxy networks, compared to diphenyl-propane unit. By comparing the results of **3** cured with DICY and PN, a striking observation showed that **3**/DICY had higher E' values than **3**/PN in glassy region while at temperatures above T_g, the situation reversed. Higher retention of E' for **3**/PN at higher temperature indicate higher crosslinking density, according to the literatures [30,32]. And then, the network of **3**/PN shows higher T_g (206 °C) than **3**/DCIY ($T_g = 197$ °C). This tendency is also reasonably consistent with the different rigidity between DICY and PN.

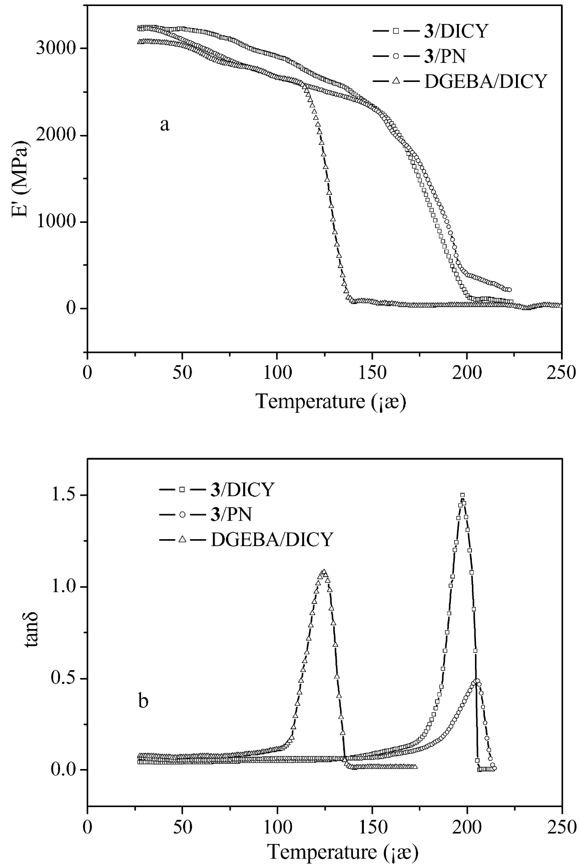


Fig. 5. Temperature dependences of storage modulus E' and tan δ for cured **3**/DICY, **3**/PN and DGEBA/DICY.

The properties evaluations of the cured polymers were performed by various means, and the results were summarized in Table 3. It was shown that T_gs of polymers cured with DICY increase linearly with increasing 2-naphthol content in the range of 0–40 replacement percent in NL epoxy monomers, for instance, **4**(60)/DICY have highest T_g despite its lowest molecular weight (see Table 1). This may be related to the different steric hindrance associated with the cycloaliphatic or methylene on the ring of 2-naphthol and 1-naphthol. When the alkylation reaction takes place, substitution might proceed mainly at 1 position, i.e. the *ortho* position of hydroxy group, of 2-naphthol for its higher reactivity according to the resonance theory. The C–C linkage at 1 position of 2-naphthol, especially the linkage of bulky limonene, would show more hindrance effect and make the alkylate structure more stiff with the present *ortho* substituent from another aromatic

Table 3
Properties of the cured polymers

Sample	CTE[a] (ppm/°C)	ε	W.A.[b] (%)	T_g[c] (°C)	T_{10}[d] (°C)	T_{max}[d] (°C)	Char yield at 600 °C (%)	
							N_2	Air
3/DICY	36	3.8	0.14	171	332	371	29	40
3/PN	43	4.0	0.26	182	343	385	21	32
4(80)/DICY	39	3.8	0.15	179	336	377	27	38
4(60)/DICY	35	3.7	0.13	186	339	381	30	41
DGEBA/DICY	59	4.8	0.35	136	307	336	8	17

[a] By TMA method in glassy region.

[b] W.A., water absorption; cut specimens were exposed to water for 2 h at 120 °C.

[c] By DSC method.

[d] T_{10}, temperature of 10% weight loss; T_{max}, temperature of maximum rate of weight loss under air atmosphere.

ring, compared with that in the case of 1-naphthol. Polymers derived from NL epoxy monomers were observed to exhibit significantly lower CTE values than common DGEBA thermoset below temperatures of T_g (i.e. glassy state). Since the network thermal motion in glassy state is believed to involve the vibration of side groups and the motion of crosslink segment, the bulky naphthyl and cycloaliphatic group in network may restrict these motions and improve the dimensional stability of the cured polymers. **3**/PN displayed higher CTE than **3**/DICY, presumably due to the higher crosslinking density of **3**/PN, while **3**/DICY showed remarkably lower water absorption value than **3**/PN. Comparing to phenyl thermoset, the cured polymers in this work exhibited higher moisture resistance. This result seems to depend partly on the different hydrophobic nature of benzene, naphthalene and cycloaliphatic group. Li and Guo have reported that the partition coefficient that is used to characterize the hydrophobicity for naphthalene and cycloaliphatic group was higher than that for benzene [33, 34]. This may suggest the incorporation of naphthalene and limonene in NL polymer could effectively depress the water absorption. As an important observation, it was found that the polymers resulted from NL epoxy resins had noteworthily lower dielectric constant values than conventional thermoset from DGEBA. It can be speculated that the combination of naphthyl and cycloaliphatic moiety having low polarizability in polymer backbone advances the dielectric stability.

Fig. 6 presents the TGA and DTG traces of **3**/DCIY. While the TGA curve involved one-stage weight loss, two peaks appeared in the DTG curve, implying that the complicated thermal degradation may experience two consecutive steps at least. As depicted in Table 3, by comparing the T_{10} and T_{max}, **3** and **4** cured polymers demonstrated better resistance to thermally oxidative degradation than DGEBA polymer. The content of 2-naphthol had slight influence on the thermal stability of cured polymers. The percent char yield for NL thermosets at 600 °C was much higher than that of DGEBA. This may be proposed that, because of the presence of cycloaliphatic and condensed aromatic moieties, the formation of char is facilitated. And more interestingly, the char yield under air atmosphere was higher than that under nitrogen atmosphere. This information may mean that the thermosets obtained from aromatic epoxy resins experience different degradation mechanism under different conditions; they are probably prone to forming char layer under oxidative atmosphere, and the formed char may act as a physical barrier preventing further degradation of the polymer medium.

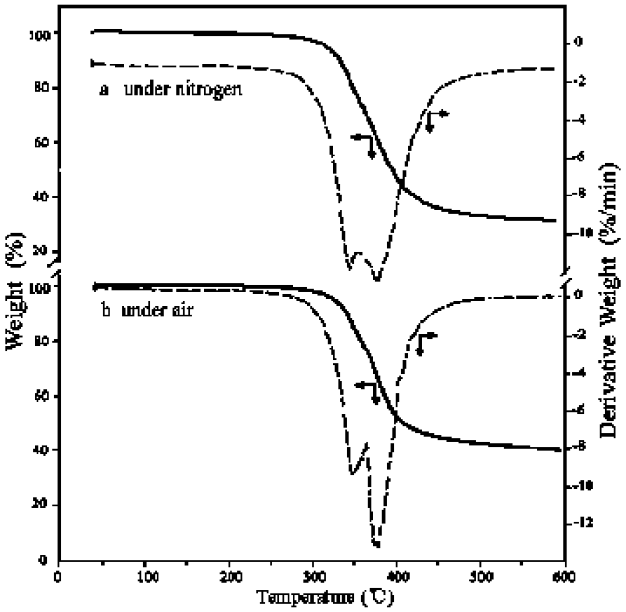


Fig. 6. TGA and DTG traces of **3**/DICY: (a) under nitrogen flow and (b) under air flow.

3.4. Wide-angle X-ray diffraction patterns

Fig. 7 showed the X-ray diffraction diagrams of various

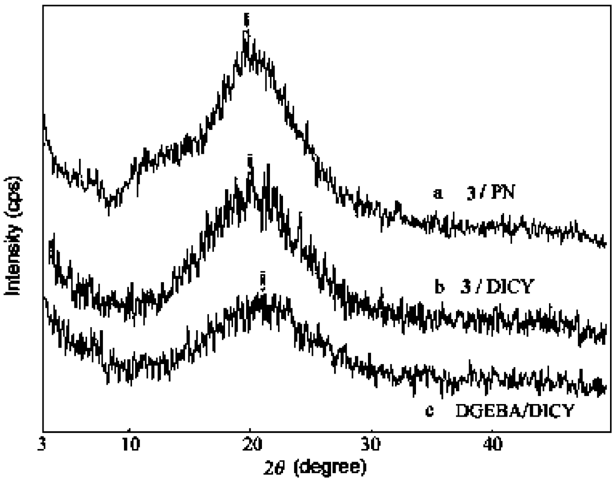


Fig. 7. WAXD patterns for cured epoxy systems.

cured polymers at room temperature. As can be seen in the diffractograms, the absence of noticeable diffractions primarily indicated that these cured polymers were amorphous materials. On the other hand, the greatly broad peak, centered on 19.7°, was observed, suggesting that for these epoxy system, layered structure with interlayer distance about 4.5 Å would be formed partly during cure reaction. The relative intensity for **3** was greater than that of DGEBA. This implied that the tendency towards layered structure for the NL epoxy systems prevail over that of phenyl thermoset. Thus, WAXD pattern can be used as a subsidiary evidence for convincing the dense packing in the resulting polymer of **3** that was proposed in DMTA analyses.

4. Conclusions

With the introduction of cycloaliphatic and naphthyl moiety into the backbone, NL epoxy resins were successfully designed and prepared by simple synthetic methods using inexpensive and readily available starting materials. The structural characterizations revealed that obtained epoxy monomers were in fact mixtures of stereoisomers and geometric isomers. The results of cure kinetics investigation showed that the NL epoxy resin had lower reactivity than conventional DGEBA, and DGEBA in the blend could facilitate the cure reaction. The resulting polymers from NL epoxy resins exhibited much higher glass transition temperatures, lower thermal expansion coefficient, lower water absorption, better resistance to thermally oxidative degradation, and, especially, lower dielectric constants compared to that of DGEBA. WAXD patterns provided a subsidiary evidence for convincing the dense packing in molecules of the cured polymers. These good overall performances make it a promising candidate as composite matrix and packaging material.

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