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Synthesis, cure kinetics and thermal properties of the 2,7-dihydroxynaphthalene dicyanate

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Abstract

The novel dicyanate ester resin containing the naphthalene ring (DNCY) was synthesized from 2,7-dihydroxynaphthalene and cyanogen bromide by two-step method. The monomer of DNCY was characterized by FT-IR, ^{1}H NMR, ^{13}C NMR and elemental analyses (EA). The cure behavior of DNCY was studied by means of nonisothermal DSC, and the kinetics parameters were determined by the Kissinger method. The thermal properties of DNCY resin were studied by thermal degradation analysis at a heating rate of 10 °C min^{-1} both in N_2 (thermal stability) and in air (thermal-oxidative stability). The DNCY resin showed excellent thermal stability, compared with that of bisphenol A dicyanate (BACY) resin, which could be demonstrated by the extensional onset temperature (435.8 °C), the temperature of maximum weight loss rate (450.3 °C) and the percentage char yields at 700 °C (60.5%) in N_2, and thermal-oxidative stability, which could be demonstrated by the extensional onset temperature (435.4 °C), the first temperature of maximum weight loss rate (450.7 °C), the second temperature of maximum weight loss rate (580.0 °C) and the temperature of complete degradation (704.4 °C) in air. The DNCY resin exhibited higher T_g and thermal degradation temperature than BACY resin.

Keywords: Synthesis of the 2,7-dihydroxynaphthalene dicyanate; Cure kinetics; Thermal properties

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1. Introduction

Cyanate ester resins have attracted increasing attention due to their highly desirable chemical, electrical, and mechanical properties for several applications [1–3]. They have been widely applied at aspect of high-speed printed circuit boards because of the low dielectric constant, dissipation factor, and good adhesion to metal [4]. Their high glass transition temperature, fracture toughness, thermo-oxidative stability, and retention of mechanical properties at high temperature make them applied in aerospace structural composites [2]. With good processability in most applications, they surpass the performance of the state-of-the-art formulations in structural composites like epoxies and bismaleimides [2,5]. Owing to its good solubility in solvents and low moisture absorption compared with epoxies and bismaleimides, good miscibility and physicochemical characterization with the two systems, cyanate ester resins are also applied to blend with epoxies and bismaleimides for enhancing their thermal characteristics and fracture toughness [2,6–11].

Only bisphenol A dicyanate (BACY) is widely studied and applied at present, few concern cyanate ester resin containing a naphthalene structure (DNCY). Due to the introduction of the naphthalene ring in the structure, many properties of the dicyanate ester resin containing naphthalene may be changed. The thermoset cure of DNCY may be also different from that of BACY due to the electro-attracting difference between naphthalene and benzene. Therefore, it is necessary for us to study the thermoset cure kinetics and properties of DNCY resin.

In this paper, the dicyanate ester resin (DNCY) containing the naphthalene ring had been synthesized. The cure kinetics of different DNCY resin systems in the absence of catalysts and in the presence of catalysts were investigated by differential scanning calorimetry (DSC) used Kissinger method. The glass transition temperature (T_g) and thermal stability were evaluated by DSC and thermogravimetric analysis (TGA) in N_2 (thermal stability) and in air (thermal-oxidative stability).

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2. Experimental section

2.1. Materials

2,7-Dihydroxynaphthalene, bromine, potassium cyanide, triethylamine were used as received. Cobalt acetylacetonate was prepared by reacting cobaltous chloride with acetyl acetone. Technical grade nonylphenol (99%) was used. All solvents used were of regent grade.

2.2. Monomer synthesis

Synthesis of cyanogen bromide [12]. A 250-ml, three-necked, round-bottomed flask equipped with a mechanical stirrer, thermometer, and a pressure-equalizing dropping funnel with a stopper was charged with 80 g (25.45 ml, 0.5 mol) of bromine and 50 ml of water. The mixture was stirred rapidly while cooling in an ice–salt bath to −10 °C, and a water solution of 20% potassium cyanide was added dropwise until the color of the reaction mixture became white from reddish brown, while maintaining the temperature of the reaction mixture at −5 to 5 °C. The depleted quantity of potassium cyanide was 35.8 g (0.55 mol). The reaction apparatus was changed into distilling apparatus. The white cyanogens bromide was obtained by distillation.

Synthesis of 2,7-dihydroxynaphthalene dicyanate (DNCY) [12,13]. A four-necked, round-bottomed flask equipped with a mechanical stirrer, thermometer, and two pressure-equalizing dropping funnel with a stopper, charged with cyanogen bromide (0.15 mol) and acetone (100 ml), and was placed in a ice–salt bath to maintain at −5 to 5 °C. The acetone solution of 2,7-dihydroxynathphalene (0.05 mol) and that of triethylamine (0.11 mol) were added dropwise simultaneously into the flask within a 40–60 min period at such a rate that made temperature not to exceed 10 °C. After addition, the reaction was continued for 2 h while the reaction mixture temperature was not higher than 10 °C. At the end of reaction, the reaction mixture was poured slowly into a large amount of ice-water, the solid obtained by filtration, washed with distilled water and dried in vacuo.

2.3. Sample preparation

The required amount of catalyst ($Co(AcAc)_2$ at concentration of 0.11 mmol/mol ($Co(AcAc)_2$/dicyanate esters)) was predissolved in nonylphenol (nonylphenol at a concentration of 2% of the total resin weight) at 100 °C with continuous stirring until a homogeneous mixture was obtained and cooled to room temperature. The catalytic blend was added to the destined amount of the cyanate resins predissolved in solvent at 60 °C, stirred for 5 min, and evaporated the solvent under vacuum at room temperature. The mixture was pulverized to obtain a homogeneous mixture.

2.4. Measurement

Melting point (mp) was obtained on a polarizing microscope (X-4). VECTOR 22 FTIR spectrophotometer was used for studying the IR spectroscopy (400–4000 cm^{-1}) of the synthesized monomer. Solid KBr pellet was prepared for crystalline compound. ^{1}H NMR and ^{13}C NMR of the compound synthesized was run on the Avance DMX 500 (500 MHz) spectrometer at room temperature using $CDCl_3$ as a solvent. Elemental analyses (EA) were carried out with Flash EA1112 element analyzer. DSC measurements were performed with a Perkin–Elmer DSC-7 supported by a Perkin–Elmer computer for data acquisition. DSC was calibrated with a high purity indium, and experiments were conducted under a nitrogen flow of 20 $cm^3\ min^{-1}$. In nonisothermal DSC experiments, all the samples were subjected to a dynamic DSC scan from 50 to 400 °C at different heating rates ($\beta = 10, 20, 30, 40$ °C min^{-1}). The conversion of each sample (α) under nonisothermal conditions can be calculated from

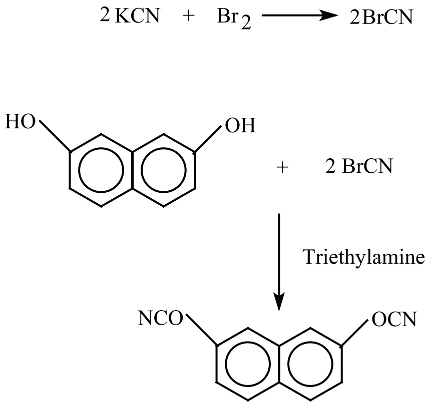
$$\alpha = \frac{(H_{\text{noniso}})_T}{H_{\text{noniso}}} \tag{1}$$

where $(\Delta H_{\text{noniso}})_T$ is the enthalpy of reaction at a temperature T calculated from the nonisothermal mode, and ΔH_{noniso} is the total enthalpy from the nonisothermal mode. The cured samples which required about 10–14 mg were tested at a heating rate of 10 °C min^{-1} from room temperature to 400 °C to test the glass transition temperature. TGA measurements were performed with a Perkin–Elmer Pyris 1 TGA to study the thermal degradation behavior of the cured resins. The cure resin samples (around 15 mg) were heated at a heating rate of 10 °C min^{-1} from room temperature to 900 °C. The tests were carried out both in purified N_2 and in air. The gas flow rates were set at 60 $cm^3\ min^{-1}$.

3. Result and discussion

3.1. Monomer synthesis

The cyanate ester containing naphthalene, 2,7-dihydroxynaphthalene dicyanate (DNCY), was synthesized by two steps as shown in Scheme 1. The potassium cyanide was reacted with bromine in H_2O to give cyanogen bromide, and its yield was 86.7%. The 2,7-dihydroxynaphthalene was reacted with cyanogen bromide in acetone at −5 to 5 °C to give 2,7-dihydroxynaphthalene dicyanate. The yield of DNCY was 83.2%, mp: 138–139 °C. Elemental analysis calculated for $C_{12}H_6N_2O_2$: C, 68.57%; H, 2.86%; N, 13.33%; found C, 68.49%; H, 2.89%; N, 13.53%. The infrared spectrum of DNCY was shown in Fig. 1. As shown in Fig. 1, DNCY showed a strong absorption at 2266 cm^{-1}, assigned to the nitrile grouping stretching vibration; and it



Scheme 1. Synthesis of 2,7-dihydroxynaphthalene dicyanate (DNCY).

also lacked the absorption at 3500–3400 cm^{-1} associated with OH grouping stretching vibration of 2,7-dihydroxynaphthalene. The ^{1}H NMR spectrum of DNCY was shown in Fig. 2. The absence of hydroxy protons (9.54 ppm) of 2,7-dihydroxynaphthalene and the presence of three protons at 7.46–8.05 ppm corresponding to the naphthalene were observed from Fig. 2, and the area ratio of three hydrogen protons was 1.000:0.972:0.961 ($a:b:c$), which was about fit to 1:1:1 of the number ratio of three kinds of hydrogen proton in structure. The ^{13}C NMR spectrum of DNCY was shown in Fig. 3. There were carbons of the nitrile grouping (108.48 ppm) in the molecular structure of synthesized monomer besides six kinds of carbons of the naphthalene in Fig. 3, which accorded with kinds of carbon in the molecule structure of DNCY. Consequently, the synthesized monomer could be confirmed by means of these spectra.

3.2. Kinetics of cure

Typical DSC thermograms for the cure reactions of the neat resin and the catalyzed resin under different heating rates were shown in Figs. 4 and 5, respectively. The cure characteristics and the enthalpy of cure reaction (ΔH) under different conditions are given in Table 1.

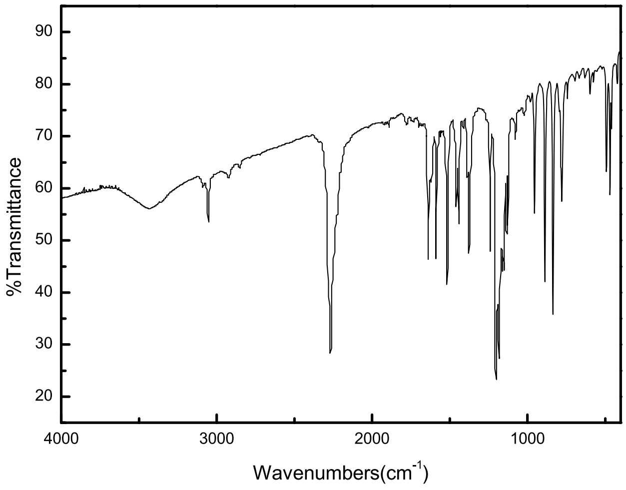


Fig. 1. The infrared spectrum of 2,7-dihydroxynaphthalene dicyanate.

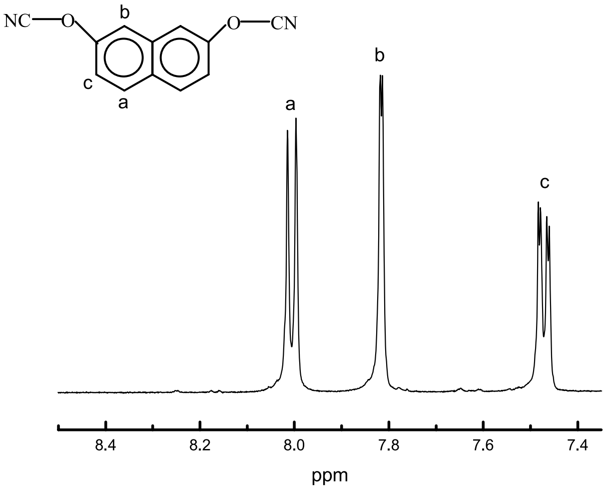


Fig. 2. The ^{1}H NMR spectrum of 2,7-dihydroxynaphthalene dicyanate.

It is known that no reaction occurs if absolutely pure dicyanate ester is heated, thereby the reaction is believed to be catalyzed by residual hydrogen-donating impurities such as phenol, moisture etc. present in the sample in the absence of catalysts externally added. Dicyanate ester resins could cure by thermal/catalytic cyclotrimerization to form triazine network, as show in Scheme 2. When the catalysts were added, the curing shifted to lower temperature as observed from a systematic drift in the cure characteristics, such as temperature of onset of cure (T_i), peak temperature in DSC (T_p), conversion at $T_p(\alpha_p)$, temperature corresponding to 50% conversion (T_{50}), and temperature corresponding to end of cure (T_f) to lower temperature, as shown in Table 1 and Fig. 5.

The kinetics of uncatalyzed cure reaction of cyanate ester has been established to follow second-order autocatalytic model [14] as

$$\frac{d\alpha}{dt} = k_1(1-\alpha)^2 + k_2(1-\alpha)^2\alpha \quad (2)$$

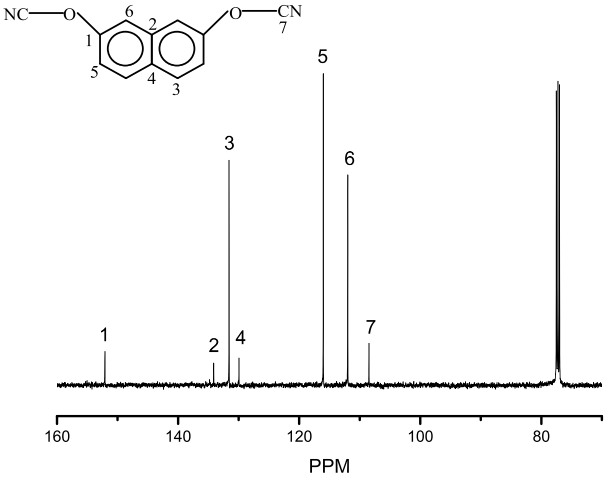


Fig. 3. The ^{13}C NMR spectrum of 2,7-dihydroxynaphthalene dicyanate.

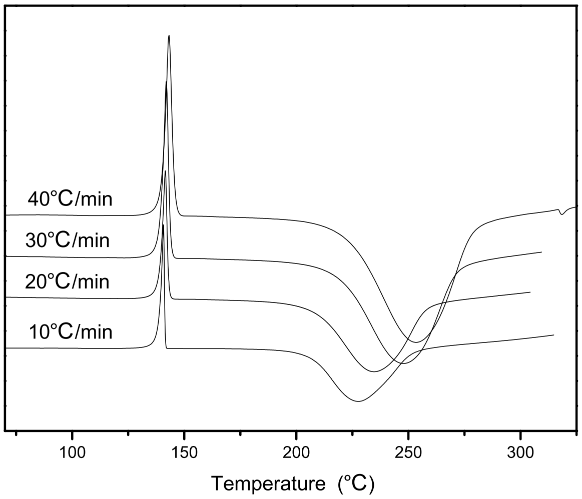


Fig. 4. DSC thermograms for cure reactions of the neat resin by different heating rates.

However, in some cases, for both catalyzed and uncatalyzed systems an *n*th order reaction has been found to satisfactorily explain the cure profile [15,16].

Under nonisothermal conditions, this rate expression takes the form

$$\frac{d\alpha}{dt} = \frac{A}{\beta}\exp\left(\frac{-E}{RT}\right)f(\alpha) \tag{3}$$

where $f(\alpha)$ is the mathematical expression of the kinetics model; β is the heating rate; E is the activation energy and A is the Arrhenius frequency factor.

Different methods are available in the literature for the calculation the activation energy values. Kissinger method is used in this paper.

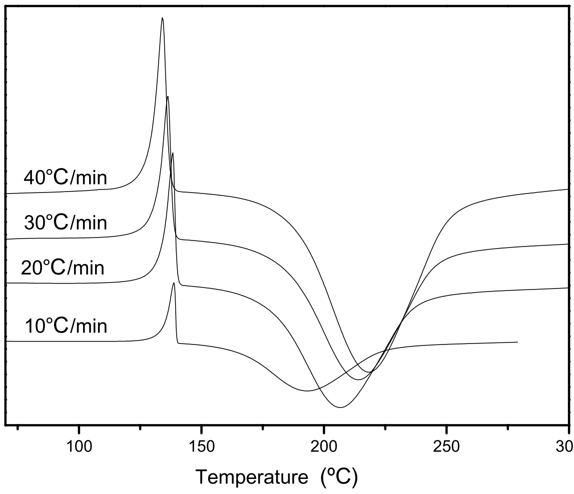


Fig. 5. DSC thermograms for cure reactions of the catalyzed resin by different heating rates.

Table 1
Thermal cure characteristics of DNCY

	β (°C/min)	T_i (°C)	T_p (°C)	α_p (%)	T_{50} (°C)	T_f (°C)	ΔH (J/g)
Neat system	10	196.4	227.8	48.0	218.3	254.4	−794.7
	20	208.5	234.7	52.1	234.0	274.1	−805.4
	30	218.7	247.8	53.8	246.6	287.3	−848.3
	40	222.4	253.4	53.0	252.6	296.9	−836.2
Catalyzed system	10	164.2	193.0	48.6	193.7	249.5	−734.7
	20	177.4	206.3	49.0	207.2	261.0	−804.9
	30	183.7	213.8	52.5	214.1	271.1	−785.6
	40	186.9	218.4	50.4	218.9	277.5	−816.7

Kissinger method is based on the equation derived from the condition for the maximum rate [15,17–20]. Kissinger thought that the thermogram peak of the cure reactions coincided with the maximum reaction rate. By setting the derivative of Eq. (3) equal to zero, as shown in Eq. (4):

$$\frac{\beta}{T_p^2} = \left[\frac{AR}{E}n(1-\alpha_p)^{n-1}\right]\exp\left(\frac{-E}{RT_p}\right) \tag{4}$$

Assuming that $n(1-\alpha_p)^{n-1}$ is independent of heating rate, a plot of $\ln(\beta/T_p^2)$ vs. T_p^{-1} will have a slope of $-E/R$. It was shown as

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left[\frac{AR}{E}n(1-\alpha_p)^{n-1}\right] - \frac{E}{RT_p} \tag{5}$$

Furthermore, Kissinger argued that

$$n(1-\alpha_p)^{n-1} = 1 + (n-1)\frac{2RT_p}{E} \approx 1 \tag{6}$$

Which means that the frequency factor A can also be obtained from the variation of peak temperature with heating rate.

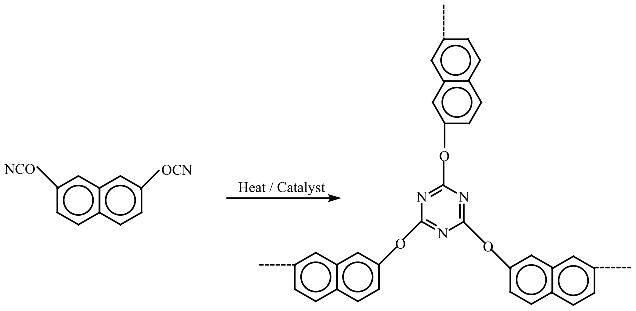
Taking the logarithms form of Eq. (4) gives:

$$\ln\beta = \ln\left(\frac{nAR}{E}\right) + (n-1)\ln(1-\alpha) + 2\ln T_p - E/RT_p \tag{7}$$

On differentiating:

$$\frac{d(\ln\beta)}{d(1/T_p)} = \left[\frac{(1-n)T_p}{1-\alpha}\right]\left(\frac{d\alpha}{dT}\right) - 2T_p - E/R \tag{8}$$

When $d^2H_p/dT^2 = 0$ at the peak exotherm, viz. $T = T_p$, the



Scheme 2. Polymerization of 2,7-dihydroxynaphthalene dicyanate ester resin.

rate expression takes the form

$$\frac{d\alpha}{dt} = \left[\frac{(1-\alpha)}{n}\right]\left(\frac{E}{RT_p^2}\right) \tag{9}$$

Then, Eq. (10) is obtained from Eqs. (8) and (9):

$$\frac{d(\ln \beta)}{d(1/T_p)} = -[E/nR + 2T_p] \tag{10}$$

The Crane equation was obtained under condition of $E/nR \gg 2T_p$.

$$\frac{d(\ln \beta)}{d(1/T_p)} \approx -E/nR \tag{11}$$

The n value could be obtained by the Crane equation.

Using Kissinger method, the apparent activation energy (E) and Arrhenius frequency factor (A) can be estimated through the dependence of the activation energy on the heating rate (β) and the peak temperature (T_p). The plots of $\ln(\beta/T_p^2)$ vs. reciprocal peak temperature ($1/T_p$) were given in Fig. 6. The reaction order (n) can be obtained by the Crane method. The plots of $\ln(\beta)$ vs. $1/T_p$ were given Fig. 7. The calculated results of E, A, and n were given in Table 2. The apparent activation energy of the neat system was 109.4 kJ/mol, and the apparent activation energy of the catalyzed system was 95.0 kJ/mol that was lower than that of the neat system due to the addition of catalysts. The apparent activation energy of DNCY for neat system was evidently enhanced due to the introduction of naphthalene in the structure, compared with that of BACY for neat system (the activation energy value of BACY calculated by Kissinger method was 60.95 kJ/mol by Reghunadhan Nair [15]). This illuminates that the existence of naphthalene in structure increase E value, of which electro-attracting ability is stronger than that of benzene and affects the cure reaction activity of dicyanate ester. The Arrhenius frequency factors of two system were within the range of $10^{10}-10^{11}$. The reaction order of two system were 1.0033 and 0.9234, respectively and close to 1, which indicated that the catalysts have little effect on the reaction mechanism and only decrease the apparent activation energy by charging the reaction approach.

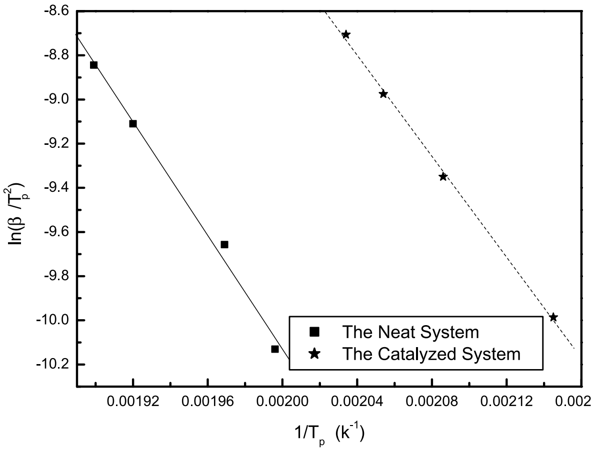


Fig. 6. The plots of $\ln(\beta/T_p^2)$ vs. $1/T_p$ for different systems.

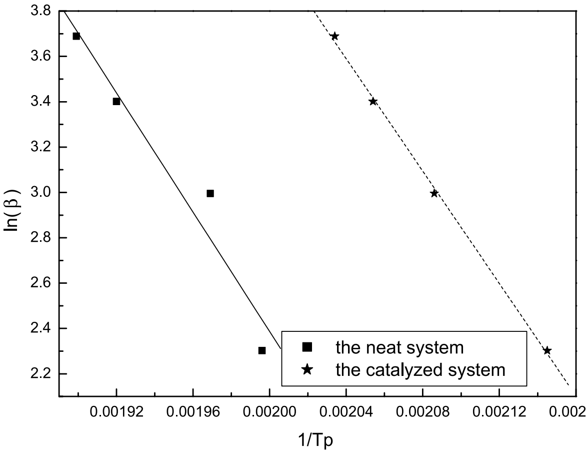


Fig. 7. The plots of $\ln(\beta/T_p^2)$ vs. $1/T_p$ for different systems.

Using Kissinger method, we can avoid a computational problem of simultaneously evaluating parameters E, A, the reaction order, and also needn't know the reaction kinetics to compute the activation energy values. Therefore, this method is also called 'single-point model-free method'.

3.3. Thermal properties of 2,7-dihydroxynaphthalene dicyanate resin for the catalyzed system

The thermal behaviors of 2,7-dihydroxynaphthalene dicyanate resin including $Co(AcAc)_2$ (0.11 mmol/mol ($Co(AcAc)_2$/dicyanate esters)) and nonylphenol (2% of the total resin weight) was evaluated by means of DSC (T_g) and TG both in N_2 (thermal stability) and in air (thermal-oxidative stability).

The glass transition temperature (T_g) of DNCY resin was showed in Table 3. The T_g of DNCY and BACY were 245.5 and 225.1 °C, respectively. Obviously, the T_g of dicyanate ester resin was enhanced due to the existence of naphthalene in the structure of resin networks. Figs. 8 and 9 show the overlay curves of weight loss as a function of temperature for different resin systems in nitrogen and in air respectively, both from room temperature to 800 °C at a heating rate of 10 °C min^{-1}. The result of the cured BACY resin including $Co(AcAc)_2$ (0.11 mmol/mol ($Co(AcAc)_2$/dicyanate esters)) and nonylphenol (2% of the

Table 2
Kinetic parameters obtained by Kissinger method

	E_a (kJ/mol)	A (S^{-1})	The values of n^a
The neat system	109.4	7.9479×10^{10}	1.0033
The catalyzed system	95.0	2.3163×10^{10}	0.9234

[a] Calculated by Crane method.

Table 3
T_g and thermal degradation results of different dicyanate ester resin systems (in N_2)

Resin systems	T_g (°C)	T_i (°C)	T_{max} (°C)	Y_C (%)
BACY	225.1	432.2	463.1	36.8
DNCY	245.5	435.8	450.3	60.5

total resin weight) is also depicted as a comparison in respective graphs.

The extensional onset temperature (T_i) was considered as the onset temperature for degradation of different cured resin systems for comparative purposes. The relative thermal stabilities of different cured resin systems were compared by the extensional onset temperature (T_i). The Thermal degradation results of different dicyanate ester resin systems were listed in Table 3 (in N_2) and Table 4 (in air). T_{max} was the temperature of maximum weight loss rate, and Y_C was the percentage char yields at 700 °C.

Cyanate ester resins were well known for its good thermal stability due to their aromatic ring and triazine ring, which formed by thermal/catalytic cyclotrimerization during curing [5,21]. As expected, the dicyanate ester resin systems showed good thermal and thermal-oxidative stability, as shown in Figs. 8 and 9. Thermal degradation results of different dicyanate ester resin systems in N_2 and in air were shown in Tables 3 and 4. Obviously shown in Tables 3 and 4, the thermal and thermal-oxidative stability of dicyanate ester resin has been enhanced due to the introduction of the naphthalene in structure resin networks, especially the anaerobic char yield of DNCY has been heightened over 20% at 700 °C than that of BACY. The T_i and T_{max} of BACY resin in air were lower than those in N_2, while those of DNCY in N_2 were nearly same as those in air, and especially the second thermal degradation rate was obviously decreased due to the effect of naphthalene in network structure. It illustrated that naphthalene ring played a more important role towards the thermal-oxidative stability than the thermal stability. The derivative weight loss (DTG) curves were shown in Figs. 10 and 11. The DTG curves of dicyanate ester resins showed one stage of weight loss in N_2, while the DTG curves showed two stages of weight loss in air. It illuminated that the thermal degradation mechanisms in N_2 were quite different from those in air. It was generally accepted that the degradation mechanism of dicyanate ester resins proceeded in several stages, involving reaction of unconverted cyanate ester with airborne moisture to form an iminocarbonate intermediate before the rapid rearrangement to a carbamate [22,23].

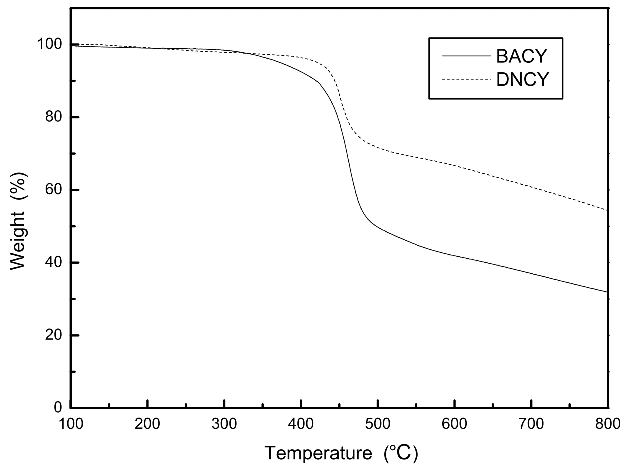


Fig. 8. TGA thermograms of different dicyanate esters resins systems in N_2 at a heating rate of 10 °C min^{-1}.

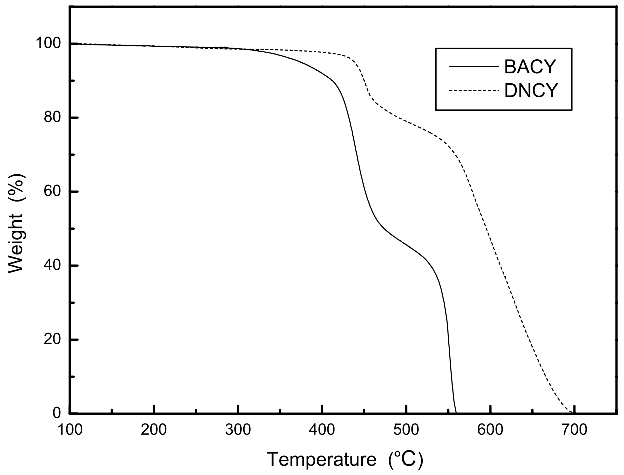


Fig. 9. TGA thermograms of different dicyanate esters resin systems in air at a heating of 10 °C min^{-1}.

4. Conclusions

The novel dicyanate ester resin containing the naphthalene ring was synthesized and characterized by FT-IR, ^1H NMR, ^{13}C NMR and EA. The yield of DNCY was 83.2%, mp: 138–139 °C. Elemental analysis calculated for $C_{12}H_6N_2O_2$: C, 68.57%; H, 2.86%; N, 13.33%; found C, 68.49%; H, 2.89%; N, 13.53%. DNCY was confirmed by means of infrared, ^1H NMR and ^{13}C NMR spectra. The cure behavior of DNCY was studied by means of nonisothermal DSC, and the kinetics parameters were determined by the Kissinger method. The apparent activation energy of the neat system was 109.4, and the apparent activation energy

Table 4
Thermal degradation results of different dicyanate eser resin systems (in air)

Resin systems	T_i (°C)	T_{max1} (°C)	T_{max2} (°C)	$T_{YC=0}$
BACY	415.1	438.7	551.3	563.1
DNCY	435.4	450.7	580.0	704.4

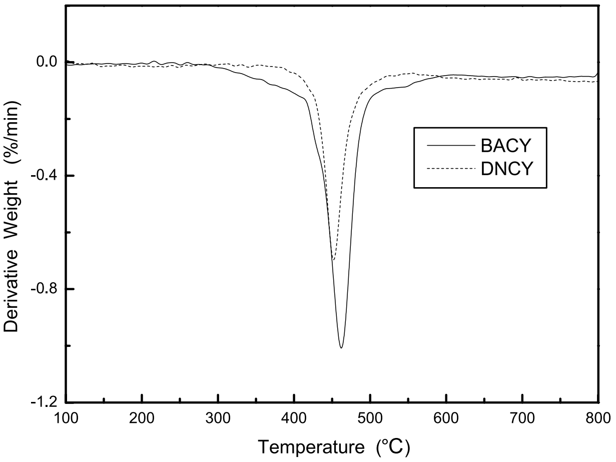


Fig. 10. DTG thermograms of different dicyanate estet resin systems in N_2 at a heating rate of 10 °C min^{-1}.

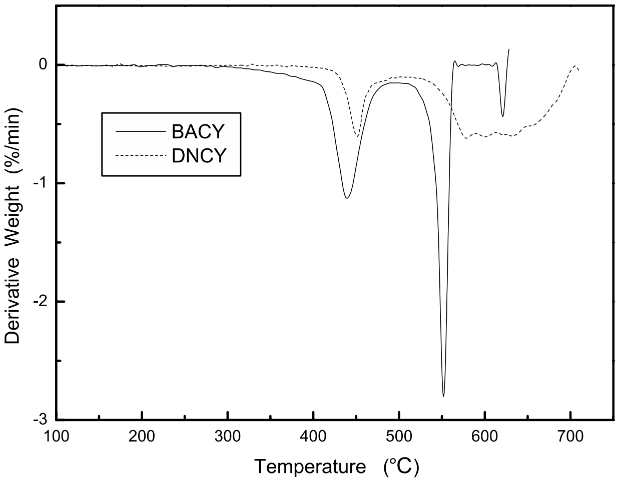


Fig. 11. DTG thermograms of different dicyanate ester resin systems in air at a heating rate of 10 °C min^{-1}.

of the catalyzed system was 95.0 kJ/mol. The Arrhenius frequency factors of two system were within the range of $10^{10}-10^{11}$. The reaction order of two system were 1.0033 and 0.9234, respectively and close to 1, as illuminated that the addition of catalysts had no effect on the reaction mechanism, and only changed the reaction approach. The T_g of dicyanate ester resin containing naphthalene ring was 245.5 °C, which was heightened compared with the T_g of BACY (225.1 °C). The DNCY and BACY resins exhibit good thermal and thermal-oxidative stability, because the extensional onset temperature (T_i) of DNCY and BACY were 435.8 and 432.2 °C in N_2 respectively, while that of DNCY and BACY were 435.4 and 415.1 °C in air, respectively. As shown in the DTG curves, the thermal degradation mechanism in N_2 was quite different from that in air. The DNCY resin exhibited higher T_g and better thermal degradation properties due to the influence of naphthalene on the rigidity and symmetry of resin network structure.

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