

Insights into Phthalonitrile/Epoxy Blends Modification System from Non-competitive Cure System Based on Alicyclic Anhydride*

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Abstract A series of polymer blends were prepared from 1,3-bis(3,4-dicyanophenoxy)benzene (3BOCN) and epoxy resin with methyl tetrahydrophthalic anhydride as curing agent. The curing behavior and curing kinetics of the blends were studied by differential scanning calorimetry. The apparent activation energy of the blends with various contents of 3BOCN was higher than that of the blends without 3BOCN. A model experiment suggested that there is no obvious reaction between phthalonitrile and epoxy. The thermal and mechanical properties of the polymer blends were evaluated. The polymer blends exhibit high storage modulus and char yield compared with the neat epoxy. The polymer blends show ductile fracture morphology by scanning electron microscopy (SEM) images.

Keywords Polymer blends; Phthalonitrile; Epoxy resin; Non-competitive

INTRODUCTION

Phthalonitriles resins (PN) are an attractive class of high temperature thermosetting polymers and have drawn great attention for their exceptional properties, such as outstanding thermal and thermo-oxidative stability, low water absorption, excellent mechanical properties, superior fire resistance and high glass transition temperature (T_g , above 450 °C)^[1–8]. These high-performance properties make the phthalonitriles possess plenty of applications, such as composite components^[3, 4], electronics industry^[5], and aerospace^[6]. However, the phthalonitriles have problems of high processing temperature, long curing time and narrow processing windows^[7, 9]. Therefore, many curing agents such as active hydrogen-containing heterocyclic structure, strong organic/amine salts and metallic salts have been used to initiate curing process and shorten the curing time of phthalonitriles^[1, 8, 10–12].

In our laboratory, previous investigations on hydroxy, amino or benzimidazole-containing PN derivatives (HPN, APN or BIPN) showed a self-promoted thermal polymerization even in the absence of curing additives which are required for conventional binary composition systems^[13–16]. The systematic investigation on the curing behavior of self-promoted PN indicated that polymerization proceeds with active-hydrogen source. Recently, our laboratory reported the cooperative curing effect between phthalonitrile and alkynyl and the thermal synergistic polymerization effect (TSP) between phthalonitrile and methyl tetrahydrophthalic anhydride end-capped imide compound^[17, 18]. We found that methyl tetrahydrophthalic anhydride end-capped imide compound promoted phthalonitrile possessed a wide processing window (~100 °C), excellent thermal and thermal oxidation

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stabilities. The reaction of phthalonitrile and alicyclic imide moiety showed a free radical process^[17, 18].

Epoxy resins are widely used in commerce as coatings, adhesives, electrical and electronic materials and aerospace composites due to their good mechanical, electrical and thermal properties^[19–21]. However, their application is limited by their low softening temperature, poor thermal and thermal-oxidative stabilities. Polymer blending technology is a well-established approach for designing new polymeric materials which has been widely explored. Some examples of various thermosetting resin systems that have been investigated include epoxy/benzoxazine, epoxy/bismaleimide, phthalonitrile/phthalonitrile and epoxy/phthalonitrile^[22–27].

It seems that epoxy-phthalonitrile is an attractive resin system due to the excellent thermal properties of PN. Currently, one of the strategies is to use aromatic amine as a co-curing agent of phthalonitrile-epoxy blends^[25–27]. Probably due to the competing reaction, large amounts of amine were in the first instance consumed by epoxy at relatively lower temperatures. Therefore, high temperature post-curing procedure is needed to induce the curing reaction of PN component. However, this procedure is undesirable because of the possible thermal degradation of epoxy^[28, 29]. Another potential alternative idea is proposed to directly induce the co-polymerization between epoxy and phthalonitrile, although the co-polymerization mechanism and feasibility have not been fully verified^[30, 31].

The investigation of curing reaction kinetics is important to understand the curing behavior and it is also an indirect proof that whether there is a reaction between phthalonitrile and epoxy. Differential scanning calorimetry (DSC) is a simple tool to analyze the curing kinetics through the calculation of the heat variation. In the present work, methyl tetrahydrophthalic anhydride was used as a non-competitive curing agent for epoxy-phthalonitrile system. The cure behavior and the activation energy of epoxy-phthalonitrile system were investigated by the non-isothermal curing kinetics using DSC analysis. The effect of the phthalonitrile addition on the thermal and mechanical properties of epoxy resin was assessed. A model experiment was initially designed to provide a basis for studying the effect of the phthalonitrile addition on curing reaction of epoxy resin by NMR technique. The results revealed that epoxy group was decomposed at high temperature. Phthalonitrile inhibited the decomposition of epoxy group and there was no new hydrogen shift peak in ¹H-NMR spectrum when the blend of phthalonitrile-epoxy was heated at high temperature. The thermal properties of the phthalonitrile-epoxy polymer blends were also studied by thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA) measurements. This study also showed that designing new non-competitive low-temperature curing agent of PN-epoxy is required to achieve a breakthrough for epoxy-phthalonitrile system.

EXPERIMENTAL

Materials

4-Nitrophthalonitrile (99%) was purchased from Jinan Weido Chemical Co. Ltd. 4-Phenylphenol (97%) was obtained from Adamas Reagent, Co., Ltd. Resorcinol (99.5%), potassium carbonate (99.0%), urea (99%), tetrabutylammonium hydrogen sulfate (IPC-TBA-HS, 98%), *N,N*-dimethylformamide (DMF) and dimethylsulfoxide (DMSO, AR) were supplied by Chengdu Kelong Chemical Reagent Co., Ltd. Epichlorohydrin and *o*-phthalic anhydride (99%) were purchased from Tianjin Bodi chemical Co., Ltd. Diglycidyl ether of bisphenol A epoxy resin E-51 was supplied by Yangnong Chemical Co., Ltd. Methyl tetrahydrophthalic anhydride was purchased from Jinan Sunny Chemical Co., Ltd. 2-Ehyl-4-methylimidazole (98%) was supplied by Adamas Reagent Co., Ltd.

Monomer Synthesis

Synthesis of 1,3-bis(3,4-dicyanophenoxy)benzene (3BOCN, Scheme 1)

The phthalonitrile monomer 3BOCN was synthesized according to a reported literature^[1].

¹H-NMR (400 MHz, DMSO-d₆, δ , ppm): 8.11–8.14 (d, 2H, Ar–H), 7.91–7.92 (d, 2H, Ar–H), 7.60–7.63 (dd, 1H, Ar–H), 7.53–7.59 (dd, 2H, Ar–H), 7.13–7.14 (s, 2H, Ar–H), 7.12 (s, 1H, Ar–H).

Synthesis of phthalonitrile model compound (CN1, Scheme 1)

The phthalonitrile model compound CN1 was synthesized according to the reference reported previously^[18].

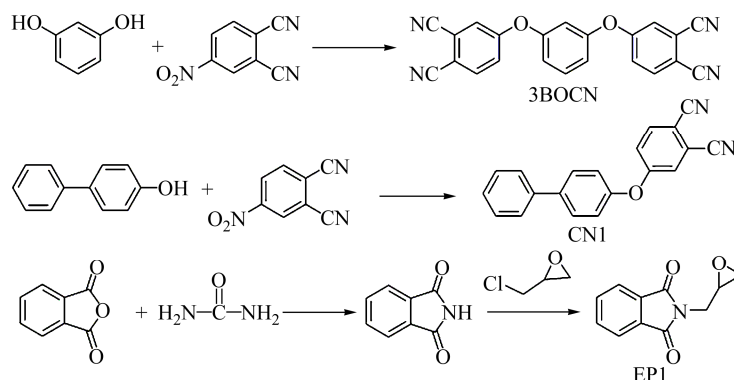
$^1\text{H-NMR}$ (400 MHz, DMSO-d_6 , δ , ppm): 8.13–8.10 (d, 1H, Ar–H), 7.86 (s, 1H, Ar–H), 7.80–7.78 (d, 2H, Ar–H), 7.70–7.68 (d, 2H, Ar–H), 7.50–7.43 (q, 3H, Ar–H), 7.39–7.36 (m, 1H, Ar–H), 7.30–7.28 (d, 2H, Ar–H).

Synthesis of epoxy model compound (EP1, Scheme 1)

Synthesis of phthalimide. To a 100 mL, three-necked flask were added *o*-phthalic anhydride (10.00 g, 67.5 mmol), urea (2.63 g, 43.87 mmol) and DMF (50 mL). While stirring, the mixture was heated at 140 °C for 3 h under an inert atmosphere. The reaction solution was washed with water and then filtered until the filtrate was neutral. The white solid was dried at 80 °C under reduced pressure for 12 h.

To a 100 mL, three-necked flask were added phthalimide (3.81 g, 25.9 mmol) and IPC-TBA-HS (0.875 g, 2.58 mmol). Epichlorohydrin (60.97 mL) was slowly dropped into the flask in a cold water bath and then was heated at 110 °C for 24 h. Most of epichlorohydrin was distilled under vacuum at 95 °C and then recrystallized from $\text{C}_2\text{H}_5\text{OH}$. The product was dried under vacuum at 65 °C for 10 h. The white solid was obtained in 61 wt% yield (3.15 g).

$^1\text{H-NMR}$ (400 MHz, DMSO-d_6 , δ , ppm): 7.99–7.76 (m, 4H, Ar–H), 3.88–3.70 (d, 2H, CH_2 –H), 3.27–3.11 (m, 1H, CH–H), 2.80–2.53 (m, 2H, CH_2 –H).



Scheme 1 Synthesis of 3BOCN and model compounds CN1 and EP1

Preparation of the Phthalonitrile-epoxy Blends, Polymer Blends and Model Blends of EP1/CN1 Reaction

The blends were prepared by stirring 3BOCN, methyl tetrahydrophthalic anhydride curing agent and 2-ethyl-4-methylimidazole curing accelerant into liquid epoxy under ambient conditions to form a homogeneous mixture. The 3BOCN-epoxy blends were formulated with 30:70, 20:80, 10:90 and 0:100, in which the numbers represent the weight ratios of 3BOCN and epoxy resin. The curing accelerant was added by 1 wt% of epoxy resin. Methyl tetrahydrophthalic anhydride curing agent was added equivalent stoichiometry of anhydride and epoxy functionalities. The curing schedule of the blends was as follows: 80, 100 and 130 °C for 1 h each, 160 °C for 3 h, 200 °C for 3 h, 230 °C for 2 h and 250 °C for 2 h, respectively. The polymer blends were cooled to room temperature and then removed from the molds.

The model blends in equimolar ratio of EP1/CN1 were stirred for 4 h at 230 °C with N_2 atmosphere and were investigated by $^1\text{H-NMR}$ characterization.

Measurements

Differential scanning calorimetry (DSC) was performed on a TA instrument Q200 differential scanning calorimeter under nitrogen atmosphere (50 mL/min). Thermogravimetric (TG) analysis was performed with a TA Instruments Q500 in nitrogen atmosphere (60 mL/min) at a heating rate of 10 K/min from 40 °C to 800 °C. Dynamic mechanical analysis (DMA) was performed using a TA Instruments Q800 to measure the storage modulus and damping factor ($\tan\delta$) of the material in nitrogen atmosphere. FTIR spectra of the mixture and cured samples were recorded on a Nicolet FTIR-460 Fourier transform infrared spectrometer in KBr pellets. The mechanical properties of the polymer blends were measured with a Shimadzu Corporation AGS-J

electromechanical universal testing machine and were gained as average values for each sample. $^1\text{H-NMR}$ spectra were recorded using a Bruker AV-400 nuclear magnetic resonance spectrometer with DMSO-d_6 as the solvents. The morphology of the cured samples was investigated using a JEOL JSM-7500F field-emission scanning electron microscope (SEM). The specimen was coated with Au prior to observation.

RESULTS AND DISCUSSION

Curing Behavior of Blends

The curing behavior of 3BOCN-epoxy blends was investigated by DSC measurement. The DSC curves from 40 °C to 200 °C of the 3BOCN-epoxy blends are presented in Fig. 1. The DSC thermogram of the 3BOCN-epoxy blends had one well-resolved exothermic transition at 153–156 °C. The exotherms are attributed to the reaction of the epoxy resin with the anhydride curing additive and imidazole curing accelerator and to the melting of the 3BOCN and/or the reaction of the 3BOCN with the alicyclic of methyl tetrahydrophthalic anhydride. The exotherm peak intensities and temperatures were dependent on the blend compositions. As the 3BOCN content of the blend increased after adding 3BOCN into cure system, the exotherm peak intensities decreased and the peak temperature increased. This may be attributed to the melting of more phthalonitrile.

The structure of the 3BOCN-epoxy polymer blends was investigated by FTIR spectroscopy shown in Fig. 2. The absorption peaks at 1180 and 1290 cm^{-1} were assigned to the epoxy groups^[27]. In addition, a new weak absorption peak at 1092 cm^{-1} was observed. It was attributed to the formation of isoindoline due to the polymerization of the phthalonitrile and alicyclic of methyl tetrahydrophthalic anhydride^[18]. Nitrile group absorption peak at around 2230 cm^{-1} could be observed in the FTIR spectrum for 3BOCN-epoxy polymer blends. It proved that the cyano group was not fully involved in the reaction.

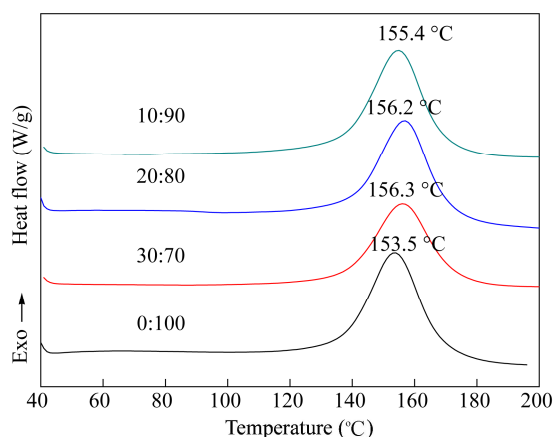


Fig. 1 DSC curves of the 3BOCN-epoxy blends

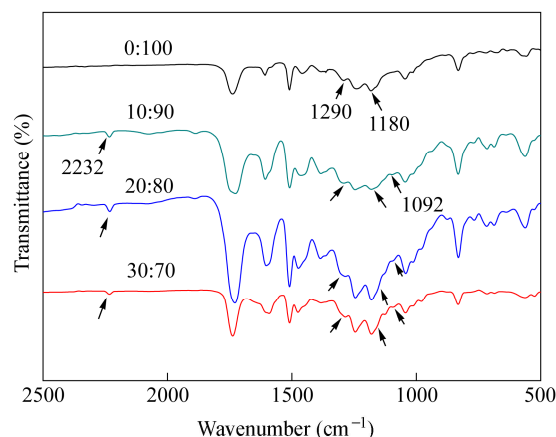


Fig. 2 FTIR spectra of the 3BOCN-epoxy polymer blends

Curing Kinetics

The dynamic kinetic analysis was performed using two established non-isothermal kinetic models: Kissinger and Flynn-Wall-Ozawa models^[32–34]. The blends of 3BOCN-epoxy were employed to study non-isothermal curing behavior by DSC at different heating rates. According to Kissinger method, the activation energy can be obtained from the peak exotherm temperatures in the DSC curves. The relation can be expressed as the following equation:

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

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 can 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 Ozawa method yields a simple relationship between the activation energy E_a , heating rate q , and the iso-conversion temperature T , giving the activation energy as:

$$E_a = \frac{-R}{1.052} \frac{\Delta \ln q}{\Delta(1/T)} \quad (2)$$

Table 1 summarizes the dynamic cure reaction parameters. The activation energies that were calculated based on the two models were in close agreement. From the result, it can be observed that the curing onset temperature (T_o) and the curing peak temperature (T_p) of different proportions are almost the same. The activation energy (E_a) of the blends without phthalonitrile (0:100) was lower than those of the other blends with various percentages of phthalonitrile (10:90, 20:80 and 30:70). It was probably attributed to the epoxy group becoming more stable and the ring-opening polymerization of epoxy group becoming difficult after adding phthalonitrile. The suggestion that epoxy group became stable after adding phthalonitrile was further verified by model reaction using NMR technology in Fig. 3. Compared with those of 10:90 and 20:80 curing systems, the reaction enthalpy (ΔH) of 30:70 system was relatively lower and the activation energy (E_a) was relatively higher, which may be attributed to the possibility that more phthalonitrile makes epoxy group more stable. The values of the activation energy (E_a) of phthalonitrile-epoxy with different ratios were almost the same as the other epoxy resins but much lower than those of phthalonitrile resins, as reported^[35–37]. The result showed that curing process of epoxy was not changed significantly after adding phthalonitrile.

Table 1 Dynamic cure parameters of the 3BOCN-epoxy systems derived from the DSC thermograms at various heating rates

Weight ratio of 3BOCN-epoxy	Heating rate (K/min)	T_o (°C)	T_p (°C)	ΔH (J/g)	E_a (kJ/mol)	
					Kissinger	Ozawa
0:100	5	124.4	139.8	302.1	66.49	69.93
	10	137.0	153.5	307.3		
	15	144.6	162.0	302.3		
	20	150.9	168.4	295.0		
10:90	5	125.3	142.7	297.5	71.87	75.09
	10	137.5	155.4	292.4		
	15	145.4	163.7	310.3		
	20	150.7	169.5	314.9		
20:80	5	125.8	143.1	297.0	71.02	74.29
	10	138.7	156.2	297.6		
	15	146.1	164.2	305.7		
	20	151.8	170.4	313.3		
30:70	5	127.2	144.0	247.3	74.26	77.37
	10	138.3	156.3	261.2		
	15	145.7	164.3	272.5		
	20	150.8	170.2	278.3		

Model Compounds Reaction

In order to eliminate the possible decomposition of bisphenol A at high temperature, imide-containing epoxy (EP1) was designed and readily synthesized to test and verify the reaction between epoxy group and phthalonitrile. The phthalonitrile model monomer (CN1) was synthesized by a simple nucleophilic displacement of a labile nitro-substituent from 4-nitrophthalonitrile by the dialkaline salt of 4-phenylphenol in a polar aprotic solvent with the presence of either weak or strong bases. Two model compounds were mixed in the molar ratio of 5:5 and isothermally treated at 230 °C for 4 h in N_2 to observe the reaction between epoxy group and cyano group by ^1H -NMR. As a comparison, two model compounds were formulated by isothermal treatment at 230 °C for 4 h in N_2 atmosphere. ^1H -NMR spectra of CN1, EP1, the blends (5:5) and isothermal treatment at 230 °C for 4 h are presented in Fig. 3(A). Drawing of the partial enlargement are also shown in Figs. 3(B) and 3(C).

Earlier report showed that the mechanism of epoxies and phthalonitrile appeared to react resulting in oxazoline ring^[31]. However, there is insufficient evidence to prove the formation of oxazoline ring. Another

report simulated the minimal energy of forming oxazoline network structure by the reaction of epoxies and phthalonitrile and found oxazoline network at 1606 cm^{-1} was intensified in the FTIR spectrum^[30]. However, other types of heterocyclic rings like isoindoline also show obvious absorption at around 1600 cm^{-1} , which is not a strong evidence of the oxazoline formation. Therefore, we first investigated the reaction of epoxies and phthalonitrile using model reaction by NMR technique. As shown in Fig. 3, comparison of curves a and b showed no evident reaction of the cyano group during heated treatment at $230\text{ }^{\circ}\text{C}$ for 4 h. However, epoxy groups were decomposed at $230\text{ }^{\circ}\text{C}$ for 4 h from curves c and d. Aliphatic proton chemical shift of EP1 disappeared. New proton chemical shifts could not be seen when the blend of phthalonitrile and epoxy groups was heated at $230\text{ }^{\circ}\text{C}$ for 4 h as evidenced by curve e. Epoxy group became stable in the blends of phthalonitrile and epoxy at a high temperature. Therefore, the co-polymerization between epoxy groups and phthalonitrile cannot be tested by NMR. It indicated that there is no obvious reaction between epoxies and phthalonitrile at $230\text{ }^{\circ}\text{C}$ within the detection limit of ^1H -NMR technique. Therefore, a possible non-competitive reaction mechanism of alicyclic anhydride-promoted phthalonitrile-epoxy blends is depicted in Scheme 2.

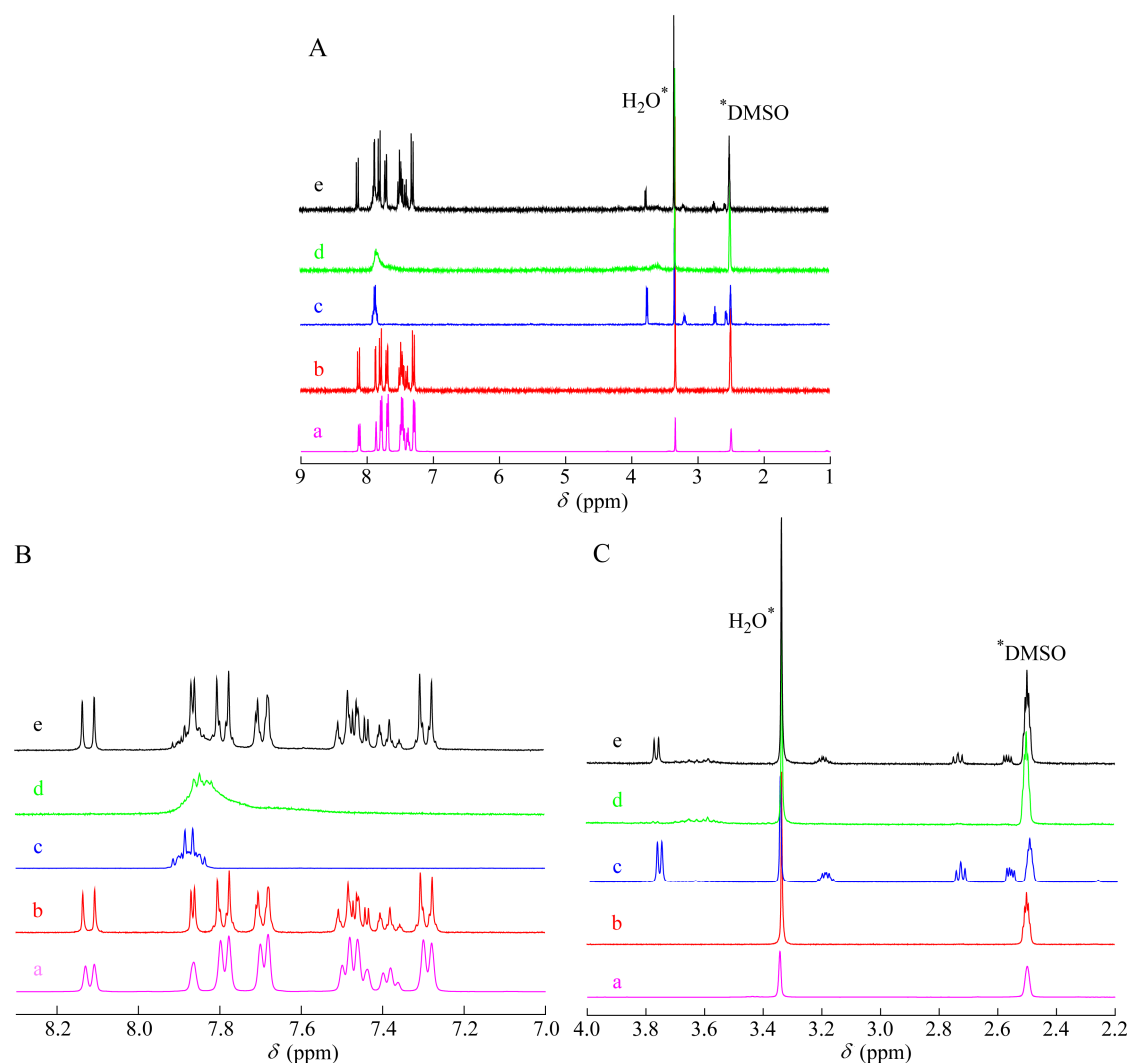
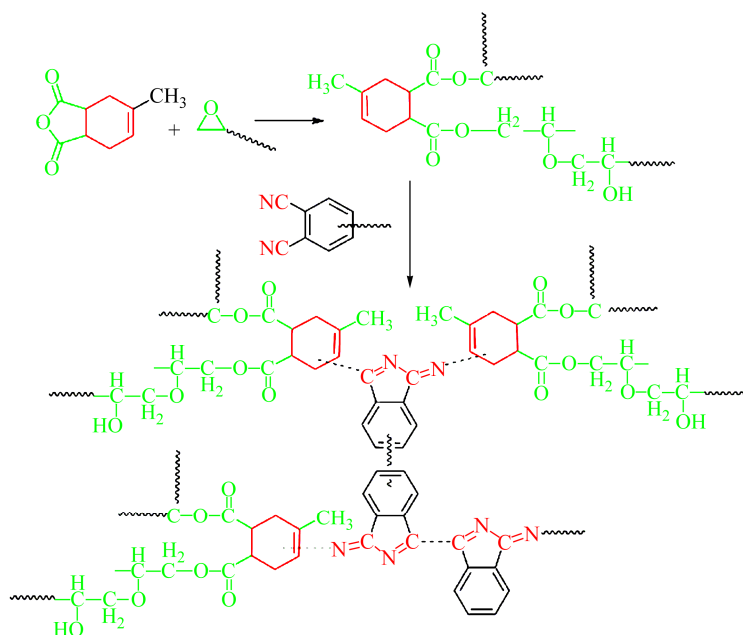


Fig. 3 ^1H -NMR spectra of EP1 and CN1 in isothermal condition

(B) and (C) are the enlarged drawing of (A). The samples are as follows: (a) CN1, (b) CN1 $230\text{ }^{\circ}\text{C}$ -4 h, (c) EP1, (d) EP1 $230\text{ }^{\circ}\text{C}$ -4 h and (e) 5:5 CN1/EP1 $230\text{ }^{\circ}\text{C}$ -4 h.



Scheme 2 Possible non-competitive reaction mechanism of alicyclic anhydride-epoxy-phthalonitrile blends

Thermal Properties of 3BOCN-epoxy Polymer Blends

TGA of 3BOCN-epoxy polymer blends

3BOCN-epoxy polymer blends with different ratios of 3BOCN and epoxy were cured following the schedule already discussed. The thermal stability of polymer blends obtained using TGA is shown in Fig. 4. The effect of different weight percentage of 3BOCN-epoxy was analyzed from 40 °C to 800 °C and the thermal parameters are summarized in Table 2. The degradation temperature at which the 5% weight loss ($T_{5\%}$) occurs was found to be in the range of 311.7–342.0 °C. The polymer blends' char yield improved with increasing 3BOCN content from 5.24% to 19.87% at 600 °C in nitrogen. According to the results, it can be noted that the thermal decomposition temperature of the polymer blends was almost the same. The slight decrease of $T_{5\%}$ may be because there was no obvious reaction between epoxy and phthalonitrile. The same phenomenon can also be visualized from the $^1\text{H-NMR}$ of model experiment. Besides, the reaction extent between phthalonitrile and the alicyclic of methyl tetrahydrophthalic anhydride was not high and there still was some unreacted cyano group. Fortunately, the reaction between phthalonitrile and alicyclic still improved the char yield of the polymer blends due to the outstanding thermal and thermo-oxidative property of phthalonitrile. With more phthalonitrile existence, more aromatic heterocyclic structures (isoindoline) may be formed leading to higher char yield.

Dynamic mechanical analysis

The dynamic mechanical properties (storage modulus and damping factor ($\tan\delta$)) for the 3BOCN-epoxy polymer blends as a function of temperature were investigated under nitrogen atmosphere. Plots of the storage modulus (G') and damping factor ($\tan\delta$) are presented in Figs. 5(a) and 5(b), respectively. The G' values for 0 wt%, 10 wt%, 20 wt% and 30 wt% of 3BOCN-epoxy polymer blends were 2.60, 3.67, 3.21 and 3.10 GPa at 50 °C, respectively. Compared with the sample without phthalonitrile, it can be seen that the storage modulus shifts to higher values in the presence of phthalonitrile. It may be attributed to the reaction between phthalonitrile and alicyclic anhydride forming aromatic heterocyclic structure which increased the rigidity of molecular chain. The storage modulus (G') of the 10:90 curing system was higher than those of 20:80 and 30:70 curing systems. This phenomenon might be caused by the formation of more aromatic heterocyclic structure which plays a role of oligomeric plasticizer after adding more phthalonitrile.

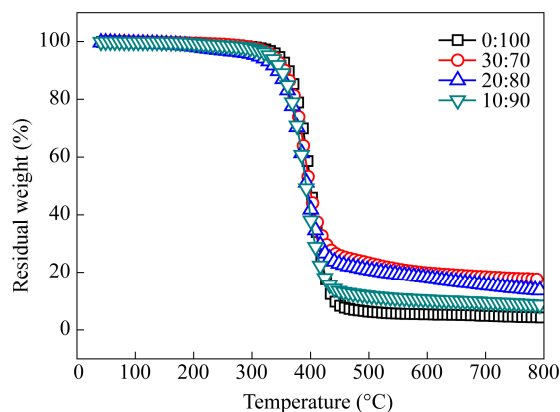


Fig. 4 TGA thermograms of the 3BOCN-epoxy polymer blends

Table 2 TGA data, DMA data and cross-link density values of 3BOCN-epoxy polymer blends

Weight ratio of 3BOCN-epoxy	DMA			TGA	
	G' at 50 °C (GPa)	T_g (°C)	V_e at 50 °C ($\times 10^5$ mol/m ³)	$T_{5\%}$ (°C)	Char yield at 600 °C (%)
0:100	2.60	178.02	3.23	342.0	5.24
10:90	3.67	170.55	4.55	330.2	10.51
20:80	3.21	169.94	3.98	311.7	17.99
30:70	3.10	164.66	3.85	335.9	19.87

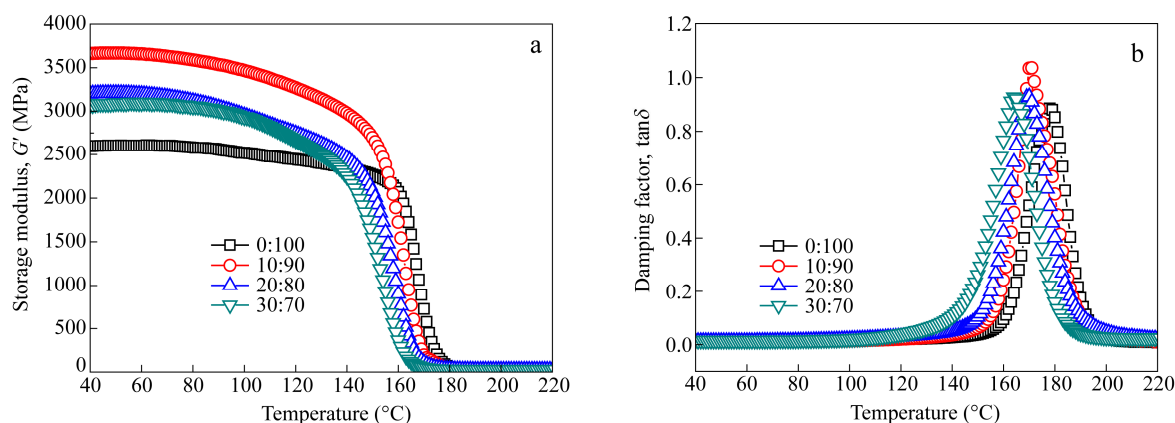


Fig. 5 (a) Storage modulus (G') and (b) damping factor ($\tan\delta$) as a function of temperature for different ratio 3BOCN-epoxy polymer blends

The peak value of temperature in the $\tan\delta$ curve is taken as the glass transition temperature (T_g). The single $\tan\delta$ peak proves a favorable compatibility between phthalonitrile and epoxy resin. The segmental motion of the polymer chains in polymer blends is indicated by T_g values. With the increase in 3BOCN content, the T_g values of the polymer blends had a marginal decline from 178.0 °C to 164.6 °C. This phenomenon might be due to the effect of oligomeric plasticizer resulting from relatively low reaction extent of phthalonitrile. The T_g of the specific molecular weight oligomeric structure was 175 °C^[18]. Relatively low glass transition temperature of the oligomeric structure might result in the slight decrease in T_g of phthalonitrile-epoxy polymer blends.

Cross-link density

Cross-link density is defined as the number of cross-link points per unit volume. For a typical rubber material, the values of the cross-link points may be in order of 10^{-3} – 10^{-5} mol/cm³ and these correspond to 15–1500 monomers between the cross-links. The cross-link density (V_e) of highly cross-linked thermosets can be

calculated using the following equation^[38, 39]:

$$V_e = \frac{G'}{3RT} \quad (3)$$

where G' is the tensile storage modulus, T is the temperature in K corresponding to the storage modulus and R is the gas constant.

With decrease in the percentage of 3BOCN, the V_e of the polymer blends increases and it is higher than the neat epoxy because of cross-link density reduction effect. The cross-link density values of the polymer blends at 50 °C are presented in Table 2.

Flexural Strength and Morphological Studies

Flexural strength

Figure 6 shows the close relationship between the flexural strength and 3BOCN content. The results indicate that the flexural strength decreased with the addition of 3BOCN. The flexural strength reached 86.6 MPa and was reduced by 40.1 MPa in comparison with those of epoxy resin. It is probably due to the effect of oligomeric plasticizer resulting from relatively low reaction extent of phthalonitrile, which became weak spots in the material structure.

Stress-strain curves of the 3BOCN-epoxy polymer blends are shown in Fig. 7 which indicated that the flexural modulus of 3BOCN-epoxy polymer blends increased compared with that of the polymer blends without 3BOCN. It can be attributed to the reaction of phthalonitrile and alicyclic of methyl tetrahydrophthalic anhydride that increased the rigidity of molecular chain derived from aromatic heterocyclic cross-linking sites (Scheme 2), which resulted in the increase of cross-link density. The increase of char yield can also be reasonably explained by this view. The flexural modulus of the 10:90 polymer blend was higher than those of 20:80 and 30:70 polymer blends. This phenomenon may be due to the low extent reaction of phthalonitrile. It formed some oligomer structures which play a role of an oligomeric plasticizer, leading to interface stress between epoxy matrix and oligomer. The different interface stress might be caused by the difference in oligomer content when various contents of phthalonitrile were added.

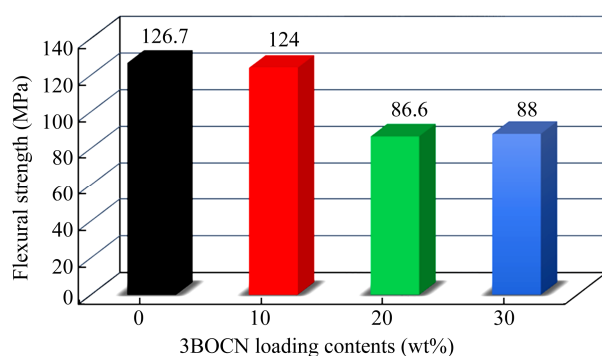


Fig. 6 Influence of the 3BOCN content on the mechanical properties of the polymer blends

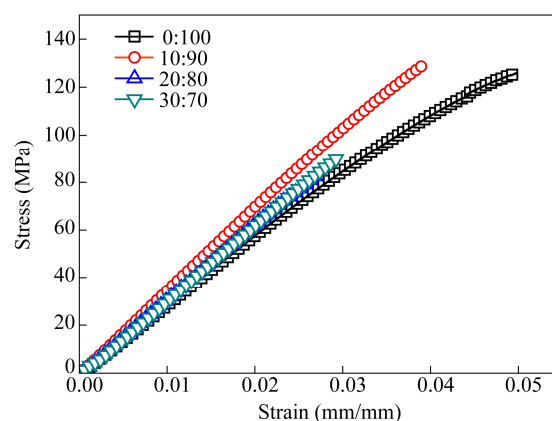


Fig. 7 Stress-strain curves of the 3BOCN-epoxy polymer blends

Morphological studies

The fracture morphologies of 3BOCN-epoxy polymer blends with different ratios were investigated by SEM. The fractured cross section morphologies of the samples are shown in Fig. 8. A typical characteristic of brittle failure is seen in the fracture surface of the pure epoxy resin from the Fig. 8(a). The fracture surface is flat and smooth without interrupted crack propagation path. The fractured morphologies of the 3BOCN-epoxy polymer

blends are relatively rough. The crack area has decreased with increasing 3BOCN content in the epoxy systems. The 3BOCN-epoxy polymer blends with 20:80 and 30:70 ratios showed a smaller flexural strength and an irregular fracture texture. Micro holes and protrusions can be seen from the 30:70 ratio of 3BOCN-epoxy in Fig. 8(d). The fracture surface was a typical ductile dimple fracture pattern. Further, the fractured morphologies showed a homogenous mixture with no phase separation for polymer blends.

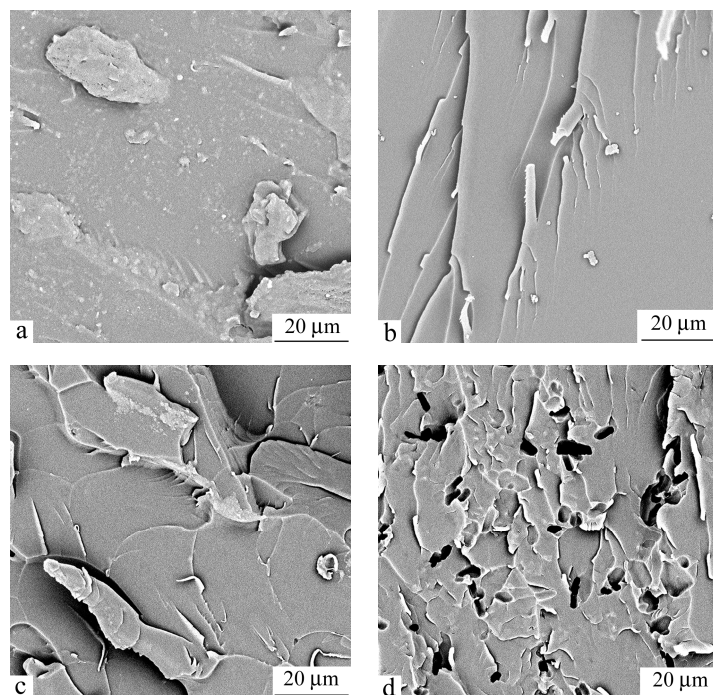


Fig. 8 SEM images of the fracture surface of 3BOCN-epoxy polymer blends: (a) 0:100, (b) 10:90, (c) 20:80 and (d) 30:70

CONCLUSIONS

The phthalonitrile-epoxy polymer blends were prepared from 3BOCN and epoxy resins with alicyclic anhydride as a curing agent. The thermal properties and structure of the polymer blends were investigated by DSC, TGA, DMA, and FTIR spectroscopy. The model compound reaction of EP1, CN1 and their blends revealed that the epoxy group could not react with phthalonitrile and epoxy group became stable after adding phthalonitrile. The curing kinetics of 3BOCN-epoxy blends were studied by non-isothermal DSC experiments. The storage modulus of the polymer blends was found to be increased compared with that of the neat epoxy polymer. The 3BOCN-epoxy polymer blends existed with higher char yield. SEM images of the polymer blends indicated a ductile fracture morphology.

Similar to amine competitive-curing system of epoxy-phthalonitrile polymer blends, alicyclic anhydride could not obviously promote phthalonitrile component at the curing temperature of epoxies although it is not a competing reaction. Therefore, the thermal properties of the alicyclic anhydride-promoted phthalonitrile/epoxy polymer blends were not improved remarkably. It is contradictory between the high temperature post-curing procedure of PN resin and the thermal degradation of epoxy. Resolving the contradiction is the key issue to develop an epoxy-phthalonitrile resin system. Designing a new non-competitive low-temperature curing agent of epoxy-phthalonitrile is a promising direction.

REFERENCES

- 1 Keller, T.M. and Dominguez, D.D., *Polymer*, 2005, 46(13): 4614
- 2 Laskoski, M., Dominguez, D.D. and Keller, T.M., *J. Polym. Sci., Part A: Polym. Chem.*, 2005, 43(18): 4136
- 3 Sastri, S.B., Armistead, J.P. and Keller, T.M., *Polym. Compos.*, 1996, 17(17): 816
- 4 Zeng, K. and Yang, G., "Wiley Encyclopedia of Composites", Published Online, 2012, p.1
- 5 Keller, T.M., *Chemtech*, 1988, 18(10): 635
- 6 Keller, T.M. and Roland, C.M., 1993, U.S. Pat., 5,427,55A
- 7 Dominguez, D.D., Jones, H.N. and Keller, T.M., *Polym. Compos.*, 2004, 25(5): 554
- 8 Burchill, P.J., *J. Polym. Sci., Part A: Polym. Chem.*, 1994, 32(1): 1
- 9 Wang, Z.C., Yang, X.L., Xu, M.Z., Wei, J.J. and Liu, X.B., *J. Mater. Sci.: Mater. Electron*, 2013, 24(7): 2610
- 10 Laskoski, M., Schear, M.B., Neal, A., Dominguez, D.D., Ricks-Laskoski, H.L., Hervey, J. and Keller, T.M., *Polymer*, 2015, 67: 185
- 11 Laskoski, M., Dominguez, D.D. and Keller, T.M., *J. Polym. Sci., Part A: Polym. Chem.*, 2013, 51(22): 4774
- 12 Zhao, F.H., Liu, R.J., Kang, C., Yu, X.Y., Naito, K., Qu, X.W. and Zhang, Q.X., *RSC Adv.*, 2014, 4(16): 8383
- 13 Zeng, K., Zhou, K., Tang, W.R., Tang, Y., Zhou H.F., Liu T., Wang, Y.P., Zhou H.B. and Gang, Y., *Chin. Chem. Lett.*, 2007, 18(5): 523
- 14 Zhou, S.H., Hong, H.B., Zeng, K., Miao, P.K., Zhou, H.F., Wang, Y.P., Liu, T., Zhao, C.E, Xu, G.L. and Yang, G., *Polym. Bull.*, 2009, 62(5): 581
- 15 Zeng, K., Zhou, K., Zhou, S.H., Hong, H.B., Zhou, H.F., Wang, Y.P., Miao, P.K. and Yang, G., *Eur. Polym. J.*, 2009, 45(4): 1328
- 16 Wu, D.M., Zhao, Y.C., Zeng, K. and Yang, G., *J. Polym. Sci., Part A: Polym. Chem.*, 2015, 50(23): 4977
- 17 Ji, S.C., Yuan, P., Hu, J.H., Sun, R., Zeng, K. and Yang, G., *Polymer*, 2016, 84: 365
- 18 Yuan, P., Ji, S.C., Hu, J.H., Hu, X.P., Zeng, K. and Yang, G., *Polymer*, 2016, 102: 266
- 19 Perrin, F.X., Nguyen, M.H. and Vernet, J.L., *Eur. Polym. J.*, 2009, 45(5): 1524
- 20 Meng, Y., Zhang, X.H., Du, B.Y., Zhou, B.X., Zhou, X. and Qi, G.R., *Polymer*, 2011, 52(2): 391
- 21 Pihtili, H., *Eur. Polym. J.*, 2009, 45(1): 149
- 22 Ishida, H. and Ohba, S., *J. Appl. Polym. Sci.*, 2006, 101(3): 1670
- 23 Woo, E.M., Chen, L.B. and Seferis, J.C., *J. Mater. Sci.*, 1987, 22(10): 3665
- 24 Laskoski, M., Dominguez, D.D. and Keller, T.M., *Polymer*, 2007, 48(21): 6234
- 25 Dominguez, D.D. and Keller, T.M., *J. Appl. Polym. Sci.*, 2010, 110(4): 2504
- 26 Guo, H., Zou, Y.K., Chen, Z.R., Zhang, J.D., Zhan, Y.Q., Yang, J. and Liu, X.B., *High Perform. Polym.*, 2012, 24(7): 571
- 27 Zhao, X., Lei, Y.J., Zhao, R., Zhong, J.C. and Liu, X.B., *J. Appl. Polym. Sci.*, 2011, 123(6): 3580
- 28 Grassie, N., Guy, M.I. and Tennent, N.H., *Polym. Degrad. Stab.*, 1985, 12(1): 65
- 29 Grassie, N., Guy, M.I. and Tennent, N.H., *Polym. Degrad. Stab.*, 1985, 13(1): 11
- 30 Augustine, D., Vijayalakshmi, K.P., Sadhana, R., Mathew, D. and Nair, C.P.R., *Polymer*, 2014, 55(23): 6006
- 31 Keller, T.M., 1999, U.S. Pat., 5,939,508
- 32 Kissinger, H.E., *J. Res. Natl. Bur. Stand.*, 1956, 57(4): 217
- 33 Kissinger, H.E., *Anal. Chem.*, 1957, 29(11): 1702
- 34 Ozawa, T.J., *Therm. Anal.*, 1970, 2: 301
- 35 Teo, J.K.H., Teo, K.C., Pan, B., Yang, X. and Lu, X., *Polymer*, 2007, 48(19): 5671
- 36 Ren, H., Tang, S.C., Syed, J.A. and Meng, X.K., *High Perform. Polym.*, 2012, 24(7): 580
- 37 Zhang, T., Wang, J., Derradji, M., Ramdani, N., Wang, H., Lin, Z.W. and Liu, W.B., *Thermochim. Acta*, 2015, 602: 22
- 38 Thirukumaran, P., Parveen, A.S. and Sarojadevi, M., *ACS Sustain. Chem. Eng.*, 2014, 2(12): 2709
- 39 Thirukumaran, P., Parveen, A.S. and Sarojadevi, M., *Polym. Compos.*, 2014, 36(11): 1973