

아데닌기를 포함한 새로운 방향족 아민의 고성능 프탈로니트릴 경화반응 및 특성연구

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High Performance Phthalonitrile Cure Reaction and Property Research with a Novel Adenine-containing Aromatic Amine

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Abstract: An adenine-containing curing agent, 9,10-bis(4-aminophenyl) adenine (*p*-APA) was designed to decrease the volatility of curing agent. The exact structure of *p*-APA was confirmed by proton nuclear magnetic resonance (¹H NMR), infrared spectroscopy (IR) and elementary analyzer (EA). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were measured to compare volatility of *p*-APA with that of a traditional curing agent, 1,3-bis(4-aminophenoxy) benzene (4-APB), which indicated *p*-APA has better thermal stability and lower volatility. The thermal tests of different curing process of phthalonitriles showed good thermal and thermo-oxidative stabilities. The thermal property was improved along with increasing curing temperature and time and the glass-transition temperature (T_g) was not observed on DSC before 400 °C. The Fourier transform infrared spectroscopy (FTIR) showed that triazine and phthalocyanine rings were the dominant reaction products of the cured phthalonitriles. The dynamic mechanical analysis (DMA) of post-cured phthalonitriles showed a storage modulus of 1.3 GPa at 40 °C and T_g about 500 °C.

Keywords: thermosetting resins, thermal stability, adenine, aromatic curing agents, phthalonitrile composites.

Introduction

Phthalonitrile polymer is a class of high-temperature thermosetting polymers, which was first synthesized by Keller and coworkers.¹ Because of the outstanding physical and chemical properties, phthalonitrile polymers have been used for a wide range of applications, such as marine, aerospace and microelectronics.²⁻⁷ Normally the curing system of phthalonitrile resins is an curing additives/phthalonitriles binary system which favors the control of the ratio between the additives and phthalonitriles. The small molecular diamines, such as 1,3-bis(3-aminophenoxy)benzene (4-APB), were usually used as the curing additives of phthalonitriles in the earlier studies.^{2,12}

However, from the shortcoming of the small molecular cur-

ing additives are revealed. As is well known, the curing reaction of phthalonitrile is a high temperature process which happens at temperature higher than 250 °C and the phthalonitrile resins should be post-cured at 325 °C or higher. In this situation, the properties of the phthalonitrile resins, especially the phthalonitrile CNODPA with high melting point will be affected by the volatile property of the small molecular curing additives. Thus, the study on inhibiting the volatilization of small molecules becomes significant.² To solve this problem, researchers have done a lot of work. T. M. Keller and his coworkers have introduced two relatively high molecular weight diamines (*m*-BAPS and *p*-BAPS), which exhibit lower volatility and reactivity relative to *m*-APB, to improve the processability of phthalonitrile-based resins by replacing the small molecular diamines as the curing agent.² K. Zeng *et al.* offered a self-promoted system to inhibit the volatility of small molecular curing agents. They introduced the curing group into the phthalonitrile monomers (amino and hydroxyl-containing

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phthalonitriles), which showed a self-promoted curing behavior even in the system without curing additives.^{8,9,13-17}

As a continuation of the research on lowering the volatility of small molecular curing agents, this paper describes a novel binary curing agents/phthalonitrile system (*p*-APA/CNODPA), which possesses hydrogen bonds between their molecules. The systematic research showed that the adenine-containing curing agents possess higher melting point, thermal stability and lower volatility relative to 4-APB. Phthalonitriles cured by *p*-APA exhibit good thermal and thermo-oxidative stability and high glass transition temperature. This study may provide a probable direction in the design of curing agents especially for the phthalonitrile monomers contained aromatic ether, imide, sulfone, and other linkages,¹⁰ which possess high melting point and curing temperature.

Experimental

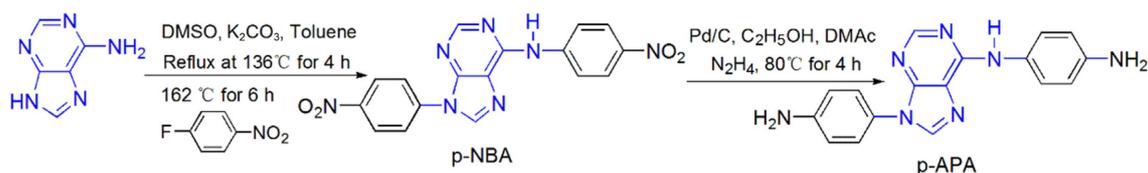
Materials. Adenine was purchased from Chengdu Best Reagent Co. Ltd.. 4-Fluoronitrobenzene was purchased from Shanghai Kefeng Chemical Reagent Co. Ltd.. Ethanol and methanol were purchased from Shanghai Fine Chemical Reagent Co. Ltd.. 4-APB was purchased from Aladdin Chemistry Co. Ltd and was used as received. 3-Aminophenol was purchased from Sinopharm Chemical Reagent Co. Ltd.. Dimethyl sulfoxide (DMSO), toluene, acetic acid, *N,N*-dimethylacetamide (DMAc), *N,N'*-dimethylformamide (DMF), tetrahydrofuran (THF), potassium carbonate, palladium on carbon (Pd/C, 5%), hydrazine hydrate and other chemicals were purchased from Chengdu Kelong Chemical Reagent Co. Ltd. and were all used as received.

Syntheses. The syntheses of *p*-APA (9,10-bis(4-aminophenyl) adenine) was according to the literature *Bio-based adenine-containing high performance polyimide (Submitted to Polymer)* (Scheme 1).

Synthesis of Compound 9,10-bis(4-nitrobenzene)adenine (*p*-NBA): To a 1000 mL, three-necked flask was added adenine (13.51 g), DMSO (480 mL), toluene (125 mL) and

K₂CO₃ (42.00 g). The reaction was performed at 135-145 °C for 4 h in DMSO in the presence of toluene (25 mL) to allow azeotropic distillation of the water formed as a by-product in the reaction. Then, steamed out of toluene by raising temperature and the 4-fluoronitrobenzene (29.61 g) was added when the reaction mixture was cooled to 60 °C, and then the temperature of the reaction was increased to 162 °C and held at this temperature for 6 h. After reaction system was cooled to room temperature, the system was poured into 5000 mL deionized water, the solution was filtered and the precipitation was washed three times with 3000 mL deionized water each time. The resulting filter cake, which including the mixture of compound *p*-NBA and 9-(4-nitrobenzene) adenine, was dried at 80 °C for 8 h under vacuum. We got rid of the 9-(4-nitrobenzene) adenine according to its solubility in *N,N*-dimethylformamide (DMF) which is 2.33 mg/mL, while the compound *p*-NBA is hardly soluble in DMF. The insoluble part, namely *p*-NBA, was leached with a small amount of alcohol after washed with DMF for several times, then the compound *p*-NBA was dried at 80 °C for 12 h under vacuum. Yield: 11.10 g, 29.4%.

Synthesis of 9,10-bis(4-aminophenyl) Adenine (*p*-APA): To a 250 mL, three-necked flask was added compound *p*-NBA (17.25 g), palladium-charcoal (Pd/C (5%), 1.725 g), ethanol (45.90 mL), and DMAc (as an auxiliary solvent, 69.00 mL). and then the solution of hydrazine hydrate (57.27 g) was added drop wise (3-5 sec per drop, as slowly as possible). The reaction mixture was heated at 80 °C for 4 h after the solution of hydrazine hydrate was completely added. Then the hot reaction mixture was filtered, and the filtrate into 1200 mL deionized water, then the solution of water was filtered again and the precipitation was washed with 1000 mL deionized water for three times. The resulting filter cake was dried at 80 °C for 12 h under vacuum. The crude product was purified by dry HCl gas into THF solution, producing hydrochloric acid salt precipitate, which was collected by filtration and then neutralized using saturated aqueous solution of Na₂CO₃. Yield: 79%; mp 254 °C; ¹H NMR (300 MHz, DMSO-*d*₆): 9.42 (H, s,



Scheme 1. Synthesis of *p*-APA.

NH), 8.26-8.42 (H, d, Ar H), 7.39-7.48 (H, m, Ar H), 6.69-6.72 (H, d, Ar H), 6.54-6.56 (H, d, Ar H), 5.38 (H, s, NH₂), 4.87 (H, s, NH₂), FTIR (KBr, cm⁻¹): 3414 (N-H stretching), 3310, 3210 (NH₂ stretching), 1630(C=N stretching), 1300(C-N stretching), 835(Ar-H stretching). Elemental analyses: found: C, 64.47; N, 28.15; H, 4.64. Calcd for C₁₇H₁₅N₇: C, 64.34; N, 30.90; H, 4.76%.

Preparation of Two Curing Systems. CNODPA was synthesized according to a published literature.¹⁸ Yield: 95%; mp 245 °C; ¹H NMR(400 MHz, DMSO-*d*₆, δ): 8.17–8.14 (d, 2H; Ar H), 8.10–8.07 (d, 2H; Ar H), 7.91 (s, 2H; Ar H), 7.68–7.63 (t, 6H; Ar H), 7.51–7.47 (dd, 2H; Ar H), 7.43–7.40 (d, 2H; Ar H), 7.33–7.28 (m, 4H; Ar H); IR (KBr): ν = 2234 (w, C≡N), 1778 (s, C=O), 1721 (vs, C=O), 1372 (s, C–N), 745 cm⁻¹ (m, C=O). The *p*-APA/CNODPA and 4-APB/CNODPA curing systems were obtained by solution blending. Two curing agents (8% mole content) were co-blending with CNODPA in acetone solution respectively. The mixture was stirred for 4 h and dried at 60 °C in rotary evaporation for 3 h. Finally, the mixture was grinded in mortar to make sure evenly dispersed.

Characterization. The confirmation of *p*-APA conducted by ¹H NMR (300 MHz) was measured on a Bruker Avance-300 NMR spectrometer with DMSO-*d*₆ as the solvent and tetramethylsilane as the internal standard. FTIR spectra were traced by a Nicolet FTIR-380 Fourier transform infrared spectrometer with KBr pellet. Elemental analyses (EA) were tested on an Italy CARLO ERBA 1106 elemental analyzer. The thermal analysis on the diamines and cured phthalonitrile polymers were conducted on a TA instrument Q500 thermogravimetric analyzer and the thermal gravimetric analysis (TGA) tests were carried out from 40 to 800 °C at a flowing nitrogen rate of 60 mL min⁻¹ and a heating rate of 10 °C min⁻¹. Differential scanning calorimetry (DSC) was performed on a TA instrument Q200 differential scanning calorimeter at a flowing nitrogen rate of 50 mL min⁻¹ and a heating rate of 10 °C min⁻¹. Rheological experiments were conducted on a TA instruments AR-2000 rheometer in conjunction with an environmental testing chamber for temperature control. The measurements were made using a 25 mm diameter parallel plates at low strain values (2.5×10⁻⁴) and a frequency of 1 Hz. The sample specimen disks, 25 mm in diameter, were prepared by press-molding the mixture of *p*-APA/CNODPA powder (the molar ratio of *p*-APA is 8%, the sample is around 0.50 g) at room temperature. The compacted sample disk was subsequently loaded in the rheometer. Dynamic mechanical analysis (DMA) was carried through a TA Instruments Q800 dynamic mechanical analyzer

from 40 to 500 °C at a heating rate of 5 °C min⁻¹ and a frequency of 1 Hz.

Results and Discussion

Characterization of *p*-APA. The structures of diamine curing agents and phthalonitrile monomer were exhibited in Figure 1. The exact structure of *p*-APA was confirmed by ¹H NMR, FTIR and EA (as shown in Figure 2(a)). In FTIR spectra of *p*-APA, a small sharp peak corresponding to N-H was found at 3414 cm⁻¹ which became a broad peak ranging from 3476 to 3285 cm⁻¹ in FTIR spectra of *p*-APA/CNODPA (50 mol%) (as shown in Figure 2(b)). This is coincided with the characteristic in definition of the hydrogen bond (IUPAC Recommendations 2011)* and is also similar to the system of BPDA/DABA with a broad peak ranging from 3000 to 3500 cm⁻¹ reported by Yan Feng etc., which indicates the formation of hydrogen bond derived from N-H acceptor and donor groups.¹⁹⁻²¹ These interactions may be contributed to restrain the volatility of *p*-APA in *p*-APA/CNODPA system. The proposed intermolecular hydrogen bond between *p*-APA and CNODPA is shown in Figure 2(b).

Thermal Property of *p*-APA and the Mixture. The thermal property of two kinds of diamine were carried out by TGA and DSC. The TGA of 4-APB and *p*-APA are shown in Figure 3. Compared to 4-APB, the *p*-APA shows excellent stability almost without weight loss up to 320 °C, while the 4-APB begins to lose weight from 250 °C. The molecular weight of *p*-

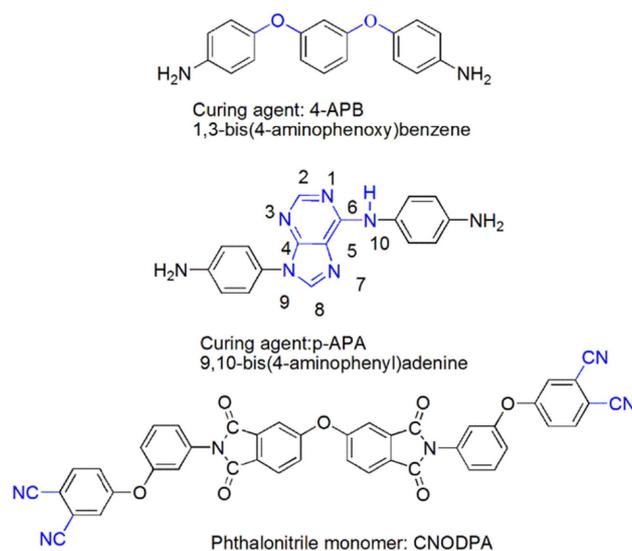


Figure 1. Structures of diamine curing agents and phthalonitrile monomer.

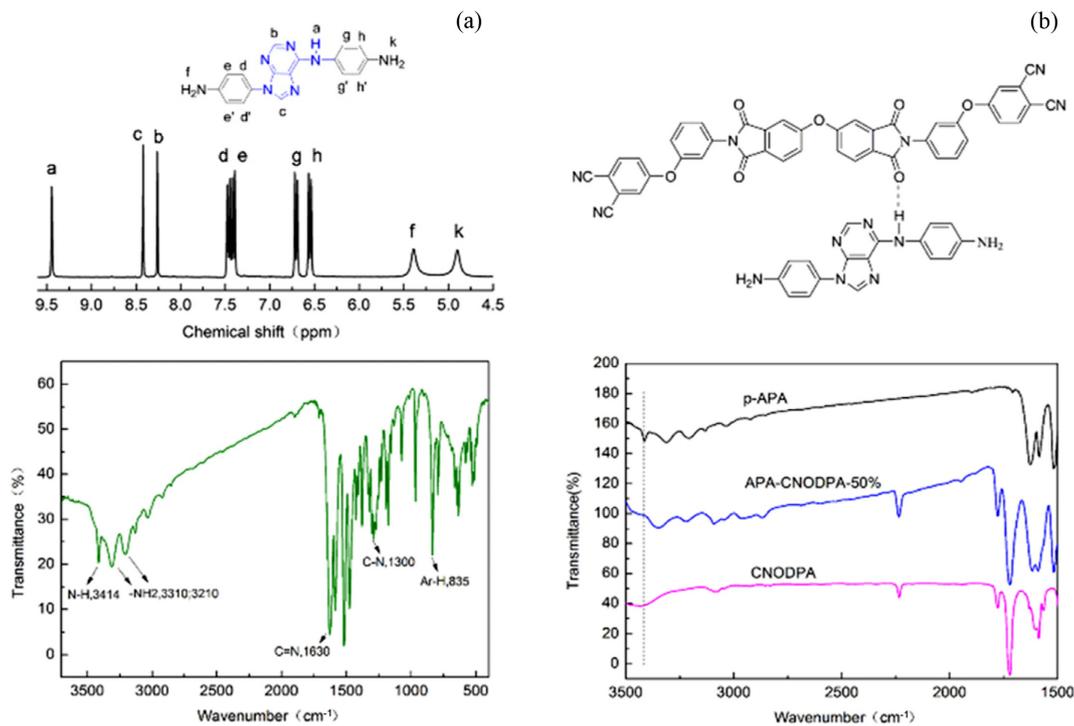


Figure 2. (a) ^1H NMR and FTIR spectrum of *p*-APA; (b) FTIR of *p*-APA, CNODPA and the mixture (*p*-APA)/CNODPA (mole content is 50%) and the proposed intermolecular hydrogen bond between *p*-APA and CNODPA.

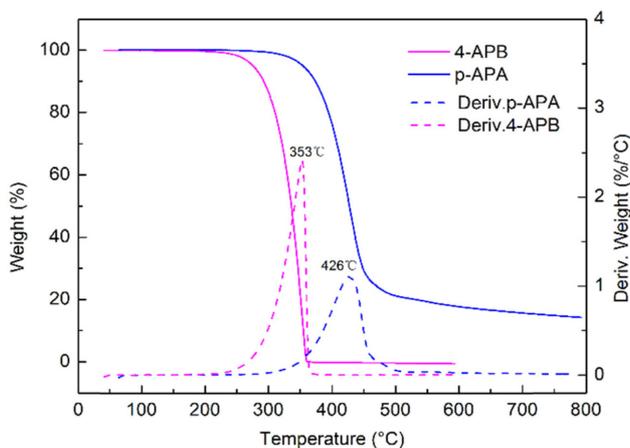


Figure 3. TGA and DTG spectra of *p*-APA and 4-APB in nitrogen.

APA is 317.14 which is close to 4-APB (292.12). The $T_{50\%}$ of *p*-APA is 354 °C, which is 79 °C higher than 4-APB and the residual weight retention at 600 °C of *p*-APA is 17.7% under nitrogen atmosphere. The DTG curves of *p*-APA and 4-APB show that the rapidest weight loss temperature appear at 426 and 353 °C, respectively. The peak of *p*-APA DTG curve is a broad peak related to the sharp peak of 4-APB. The peak of *p*-APA DTG curve increased and decreased gently and the peak

of 4-APB DTG curve increased rapidly and decreased vertically. This obviously suggests that the *p*-APA possesses lower volatility than 4-APB.

The TGA of *p*-APA, CNODPA and the mixture (*p*-APA)/CNODPA are shown in Figure 4(a). The char yield of the mixture is 50% more than the fitted curve which was simulated by *p*-APA and CNODPA monomer, illustrating that the polymerization occurred during in the heating process. This is coincident to the corresponding DSC curve (as shown in Figure 4(b)), where a very clear exothermic peak at 260 °C attributed to the reaction of the diamine with the phthalonitrile units.²² This also provides a guide to choose 260 °C as the initial curing temperature for rheological tests. The *p*-APA and CNODPA exhibit an endothermic peak at approximately 254 and 245 °C due to melting, respectively.

As reported, the adenine as building blocks of DNA is easy to form intermolecular hydrogen bond interactions. The DNA double helix structure are constructed with the four purines so where is the H-bond.²³ The hydrogen bond interactions also exist in adenine and thymine or adenine self-association.²⁴ Thus, the molecule interactions are likely to the reason of outstanding thermal performance of adenine-containing agent *p*-APA and the mixture.

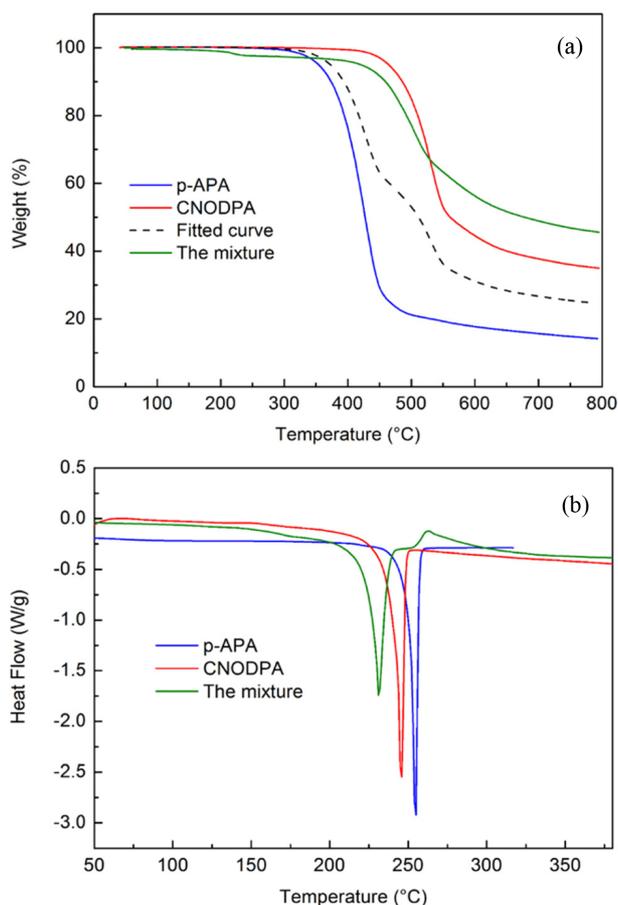


Figure 4. (a) TGA; (b) DSC of *p*-APA, CNODPA and the mixture (*p*-APA)/CNODPA.

Rheological Behavior of *p*-APA/CNODPA System. The isothermal rheological tests of *p*-APA/CNODPA were carried out to monitor the viscosity change accompanied by the curing reaction as shown in Figure 5. The *p*-APA curing system exhibited a wide processing time window and the viscosity increased gradually at 260 °C with an extended period of cure time. The viscosity of *p*-APA phthalonitriles (isothermal cured 300 min) reached 7300 Pa·s and the gel point emerged after 280 min of curing as revealed by inset. The rheological testing sample was obtained via solution blend. This is different from the research of Keller's group about *m*-BAPS and *p*-BAPS curing systems which were pre-cured before rheological test as reported previously.² The 4-APB/CNODPA curing system was also conducted as comparison with *p*-APA/CNODPA system. However, unlike the *p*-APA curing system, lots of bubbles were obviously observed in 4-APB curing system during the period of rheological test which was probably caused by the volatility of 4-APB with the temperature increasing duration

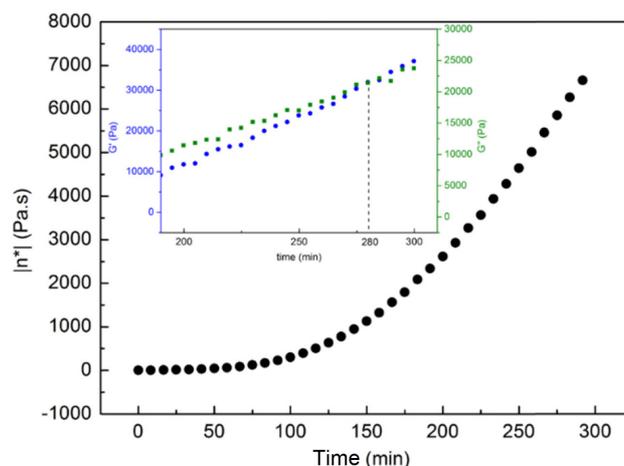


Figure 5. Viscosity vs. time plots at 260 °C for *p*-APA/CNODPA system.

times at 260 °C. The different behaviors of two curing systems demonstrate that the *p*-APA has lower volatility and this probably can be attributed to the hydrogen bond interactions, which can also restrain the volatilization of *p*-APA in *p*-APA/CNODPA system. This rheological research manifests that the *p*-APA is a good choice for curing the phthalonitriles. Especially the phthalonitrile monomers contained aromatic ether, imide, sulfone, and other linkages,² which possess high melting point and curing temperature.

Thermal Behavior of Phthalonitriles. The DSC scans of the phthalonitriles with different curing process are shown in Figure 6(b). For the analysis, the sample b was obtained by curing at 260 °C for 5 h, c was cured at 260 °C for 5 h, 280 °C for 5 h, d was cured at 260 °C for 5 h, 280 °C for 5 h, 300 °C for 5 h, and the post-cured sample e was cured at 260 °C for 5 h, 280 °C for 5 h, 300 °C for 5 h, 325 °C for 5 h, 350 °C for 5 h, 375 °C for 5 h. The DSC curves of the sample b, c, d and e with different curing process did not exhibit any glass transition up to 400 °C, indicating that the cured phthalonitriles exhibit excellent thermal performance.

The TGA tests of phthalonitriles with different curing degree are shown in Figure 6(a). The samples b, c, d and e exhibit high performance with $T_{5\%}$ appearing at 443, 452, 457 and 500 °C, and $T_{10\%}$ appearing at 472, 482, 489 and 530 °C respectively. The residual weight retention at 800 °C of b, c, d and e are 53.38, 61.35, 64.44 and 69.57% under N₂ atmosphere respectively. The thermal stability improved with the increased curing temperature and curing time.

The TGA curve of post-cured sample e (as shown in Figure 7) in air shows a $T_{5\%}$ at 465 °C and the maximum decom-

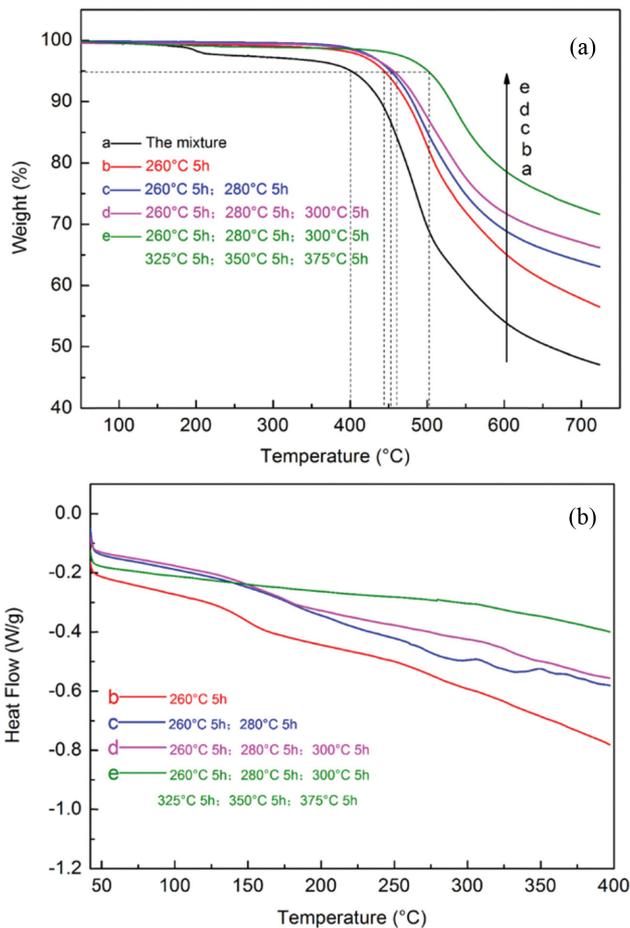


Figure 6. (a) TGA; (b) DSC of phthalonitriles with different curing process in nitrogen.

position temperature (T_{dmax}) at 536 °C in nitrogen, while at 530, 634, 679 and 744 °C in air. The rapid weight loss at high temperature was mainly caused by oxidation reaction. According to van Krevelen,²⁵ there is a linear relationship between LOI (limiting oxygen index) and CR (char yield) for halogen-free polymers, as shown below,

$$LOI = 17.5 + 0.4[CR] \quad (1)$$

LOI is defined as the minimum fraction of oxygen in an oxygen-nitrogen mixture that is just sufficient to sustain combustion of the specimen after ignition,²⁶ and CR is the char residue in weight percent in nitrogen. At 800 °C, the CR of the post cured sample e is 69.57% and the LOI is 45.33, and the LOI of the sample b, c and d are 39.35, 42.04, and 43.28 respectively. LOI value of 26 or higher is rated as a flame-retardant material.²⁶ Some specific parameters of the TGA

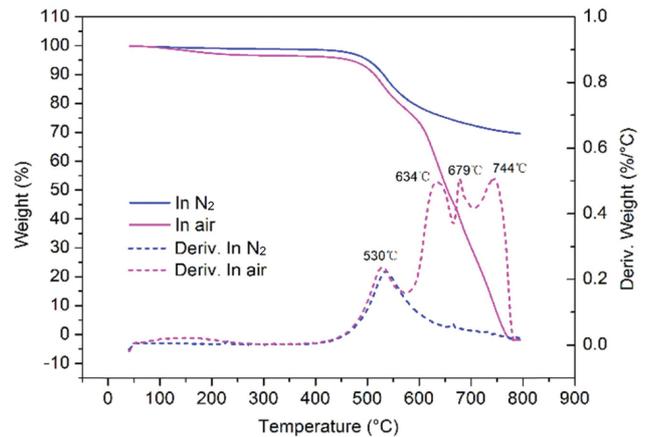


Figure 7. TGA and DTG of post-cured phthalonitriles in air and nitrogen.

Table 1. TGA Data of Different Cure Degree of Phthalonitrile

Samples	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	Char yield (%)	LOI
b(in nitrogen)	443	472	53.38	39.25
c(in nitrogen)	452	482	61.35	42.04
d(in nitrogen)	457	489	64.44	43.28
e(in nitrogen)	500	530	69.57	45.33
e(in air)	465	512	0	

were collected in Table 1. The results manifest that the cured phthalonitriles exhibit good thermal and thermo-oxidative stability and flame resistance. These thermal properties of cured phthalonitriles are attributed to the formation of triazine rings, phthalocyanine rings and imides as revealed by FTIR.

FTIR spectroscopy was used to monitor the polymerization reaction of the nitrile groups and the formation of cured phthalonitriles. The FTIR data (as shown in Figure 8) revealed that the characteristic absorption peak of the nitrile band at 2230 cm^{-1} gradually decreased with increasing of curing temperature and time, which corresponds to improvement of nitrile group's curing degree. It was consistent with a typical feature displayed from polymerization of phthalonitrile polymers.^{27,28} In addition, the emergence of peaks around 1720, 1778, 1520, and 1010 cm^{-1} corresponds to formation of imides structure, triazine rings, and phthalocyanine rings, respectively.^{9,29,30}

Dynamic Mechanical Properties of Post Cured Phthalonitriles. The DMA measurement (as shown in Figure 9) was carried out to confirm the storage modulus and the $\tan\delta$ of the post-cured phthalonitriles. The storage modulus is about

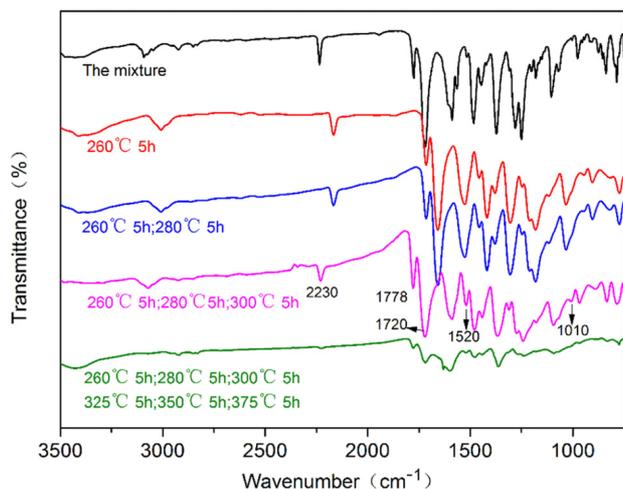


Figure 8. FTIR of phthalonitriles with different curing process in nitrogen.

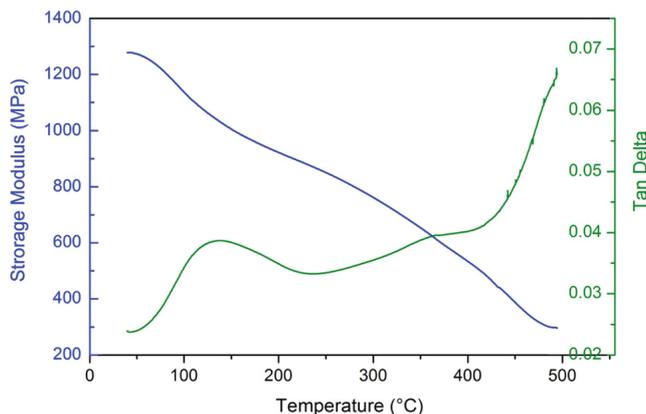


Figure 9. Dynamic mechanical analysis (DMA) of post-cured phthalonitrile.

1.3 GPa at 40 °C and decreased gradually with increasing temperature, which is due to the stress relaxation of the polymer network. The maximum damping factor ($\tan\delta$) represents the glass transition temperature (T_g) of the sample which is a particularly important parameter for polymer materials that generally determines the upper limit of the application temperature.¹⁶ The T_g of the post-cured phthalonitriles is over 500 °C. A small peak at about 140 °C, may correspond to the secondary transition of ether bond.

Conclusions

A novel adenine-containing curing agent *p*-APA was designed with lower volatility. The *p*-APA/CNODPA system with hydrogen bond interactions was prepared via solution

blend and exhibited good thermal processability with a wide processing time window at 260 °C. The *p*-APA cured phthalonitriles with different curing process displayed elevated thermal performance. The phthalonitriles post-cured at 375 °C demonstrated a good thermo-oxidative stability and a high glass transition temperature (over 500 °C). We find a novel agent/phthalonitrile system that restrains the volatility of curing agents, and the obtained phthalonitriles exhibited good property. This may provide a probable novel direction in designing of curing agents for phthalonitrile, especially for the phthalonitrile monomers that contains aromatic ether, imide, sulfone, and other linkages with high melting point and curing temperature.

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