

Crosslinking Behavior of Polyarylene Ether Nitrile Terminated with Phthalonitrile (PEN-*t*-Ph)/1,3,5-Tri-(3,4-dicyanophenoxy) Benzene (TPh) System and Its Enhanced Thermal Stability

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ABSTRACT: A novel polyarylene ether nitrile terminated with phthalonitrile (PEN-*t*-Ph) was synthesized by a simple solution polycondensation of biphenyl and hydroquinone with 2,6-dichlorobenzonitrile, followed by termination with 4-nitrophthalonitrile. The PEN-*t*-Ph/1,3,5-Tri-(3,4-dicyanophenoxy) benzene (TPh) system was prepared by cure treatment. The phthalonitrile on PEN-*t*-Ph were thermally crosslinked with TPh in the presence of diamino diphenyl sulfone through cure treatment up to 280–340°C, which led to the transformation from thermoplastic polymers to thermosetting polymers. This is because the phthalonitrile on the PEN-*t*-Ph can react with TPh by forming phthalocyanine ring. The glass transition temperatures of the PEN-*t*-Ph/TPh system increased from 152.4°C to 194.7°C, and the initial decomposition temperature (ranging from 475.3°C to 544.0°C) increased by 68°C after thermal curing. Therefore, their thermal properties can be greatly enhanced by crosslinking. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 1363–1368, 2013

KEYWORDS: crosslinking; thermal properties; morphology; glass transition; phase behavior

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INTRODUCTION

During the past decades, a mass of engineering polymers have been developed as matrices in advanced materials for structural applications in aerospace industry and commercial production. Among these, poly(arylene ether)s such as sulfone-containing poly(arylene ether)s or ketone functional polymers have been identified as excellent matrix resins for carbon reinforcement and have gained significant commercial importance.¹ In recent years, as a well-known type of engineering thermoplastic resin, polyarylene ether nitriles (PEN) have attracted considerable attention in the fields of aerospace, industrial, automotive, and electric application because of its outstanding properties such as excellent thermal and thermo-oxidative stability, good mechanical properties, superior chemical inertia, and radiation resistance.^{2–4} Because of these advantages, PEN have attracted much interest from industry to be used at elevated temperatures and in aggressive applications.

Due to the presence of nitrile groups, PENs have stronger polarizability than that of other poly(arylene ether)s, which appear to promote the adhesion of the polymers to a variety of substrates, possibly through polar interactions with functional

groups on the substrate.⁵ Moreover, the nitrile groups also serve as potential sites for the crosslinking reaction of PEN because the nitrile groups are likely to form thermally stable triazine rings.^{6–8} According to the previous reports,^{9–11} it was proved that the pendant or end nitriles groups on polymers can give rise to crosslinking reaction, thus the polymer chains could crosslink each other by forming phthalocyanine rings or triazine rings, which would improve the thermal stability and mechanical properties of the polymers.^{12–15} Moreover, after crosslinking, the physical properties of the polymers could be improved,¹⁶ such as dimensional stability, resistance to thermal deformation, and stress cracking, particularly at high temperature. Furthermore, addition of a catalyst is not required for the crosslinking of the nitrile end groups. Accordingly, the nitro groups on 4-nitrophthalonitriles, which can react with hydroxyl groups or halogen elements easily, have a good linkable property.^{17,18} Our laboratory synthesized crosslinkable PEN which terminated with phthalonitrile through structure modification to PEN. However, their poor processability and mechanical properties limited their use in high performance applications.

In this article, PEN terminated with phthalonitrile (PEN-*t*-Ph) was blended with TPh which played a novel crosslinking agent

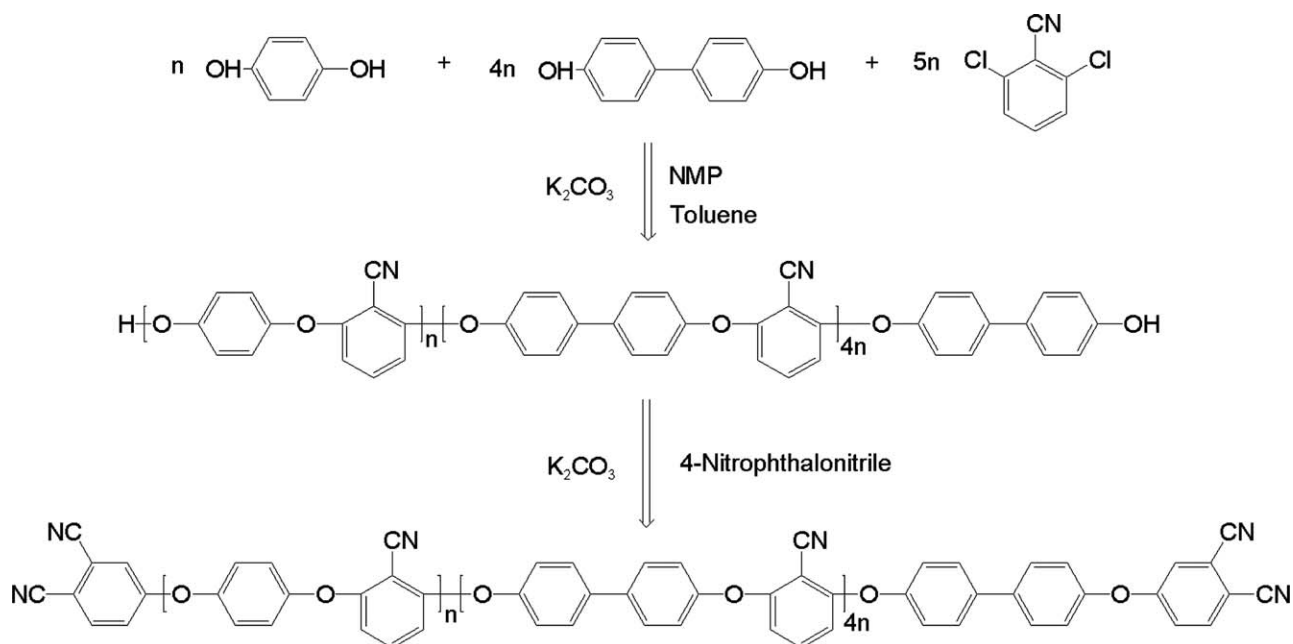


Figure 1. Synthetic route of polyarylene ether nitrile terminated with phthalonitrile.

to prepare the crosslinkable PEN-*t*-Ph/TPh films by cure treatment with different procedures. The mechanism of crosslinking reaction of PEN-*t*-Ph/TPh and the effect of crosslinking on the morphological, mechanical, and thermal properties were investigated in detail by Fourier transform infrared spectrum (FTIR), scanning electron microscope (SEM), thermal gravimetric analyses (TGA), differential scanning calorimetry (DSC), and so on.

EXPERIMENTAL

Materials

N-Methyl-2-pyrrolidone (NMP) was supplied by Tianjin BODI chemicals, Tianjin, China. 4-Nitrophthalonitrile (99%) was purchased from Alpha chemicals (Dezhou) Co., Dezhou, China. 1,3,5-Tri-(3,4-dicyanophenoxy) benzene (TPh) was prepared in our laboratory through phloroglucinol reacted with 4-nitrophthalonitrile, and purified by methanol before use. Biphenyl (BP), hydroquinone (HQ), 2,6-dichlorobenzonitrile (DCBN), potassium carbonate (K_2CO_3), toluene, and diamino diphenyl sulfone (DDS) were commercially available and used without further purification.

Synthesis of Polyarylene Ether Nitrile Terminated with Phthalonitrile

Polyarylene ether nitrile terminated with phthalonitrile was synthesized via nucleophilic aromatic substitution polymerization according to a modified method reported before,¹⁹ as depicted in Figure 1. BP (0.336 mol, 63.2 g), HQ (0.08 mol, 8.8 g), and DCBN (0.4 mol, 68.8 g) were mixed in a 500-mL three-necked round-bottom flask equipped with a Dean Stark trap, a condenser, and a mechanical stirrer with 150 mL NMP and 50 mL toluene. During the course of the reaction, K_2CO_3 (0.8 mol, 66 g) was added into three-necked round-bottom flask for several times. After the water-toluene azeotrope distilled off, the reaction mixture was heated to 200°C for about 2 h. When the mixture cooled to about 80°C, 4-nitrophthalonitrile (0.04 mol, 6.92

g), K_2CO_3 (0.072 mol, 10 g), and NMP (50 mL) were added into the three-necked flask. The mixture was heated at about 80°C for 5 h. After cooling to room temperature, the mixture was poured into 1000 mL of dilute HCl solution in order to purify the PEN product, and then rinsed by alcohol till the solvent and monomers were washed out completely. After filtration, it was dried at 120°C overnight.

Preparation of PEN-*t*-Ph/TPh Crosslinking Films

The PEN-*t*-Ph, TPh (10 wt %), and DDS (0.2 wt %) were added into a three-necked flask and dissolved in the medium of NMP at 200°C for 2 h with stirring. Then, the reaction mixture was filtered and cast on six clean glass plates to obtain films. Afterwards, the films were dried in an oven according to the procedure of 80°C, 100°C, 120°C, 140°C, 160°C, 180°C, and 200°C for 1 h, respectively. Then the film a without cure treatment was obtained, and the curing procedures of the other five films are described in Table I. All the films were cooled to room temperature naturally.

Characterization

The FTIR spectra of the PEN-*t*-Ph/TPh films were recorded on NICOLET MX-1E Fourier transform infrared spectrometer in

Table I. The Curing Procedure of the PEN-*t*-Ph/TPh System

Samples	Time and temperature
A	Without cure treatment
B	280°C and 4 h
C	280°C and 4 h; 300°C and 4 h
D	280°C and 4 h; 300°C and 4 h; 320°C and 4 h
E	280°C and 4 h; 300°C and 4 h; 320°C and 4 h; 340°C and 4 h
F	280°C and 4 h; 300°C and 4 h; 320°C and 4 h; 340°C and 4 h; 360°C and 4 h

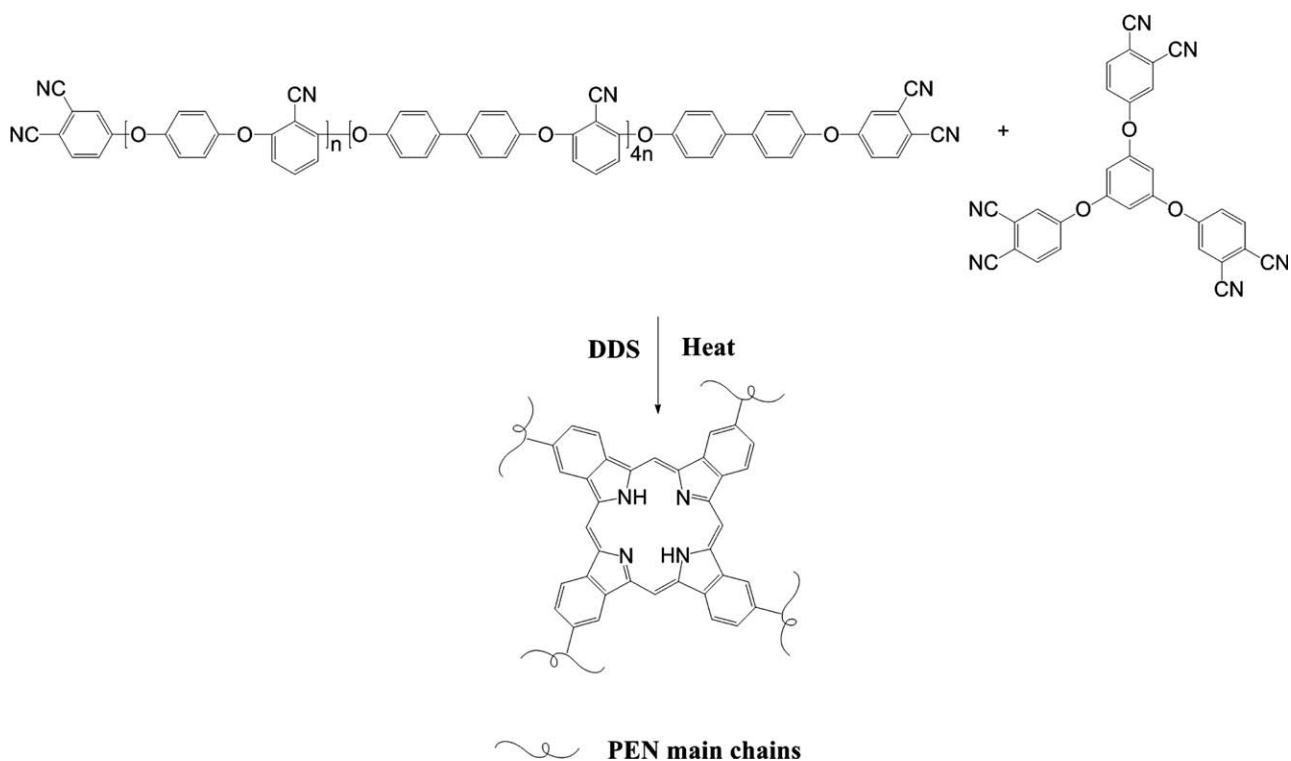


Figure 2. The mechanism of crosslinking reaction between PEN-*t*-Ph and TPh.

KBr pellets between 4000 and 400 cm^{-1} . The cross-sectional morphologies of the PEN-*t*-Ph/TPh films were observed with SEM (JEOL JSM-5900LV) operating at 20 kV. The thermal curing behavior of the PEN-*t*-Ph/TPh system was performed on TA Instrument DSC-Q100 with a heating rate of 10°C/min from room temperature to 350°C and a nitrogen flow rate of 50 mL/min. Thermal gravimetric analysis of the PEN-*t*-Ph/TPh system was obtained with a TA Instruments TGA-Q50 at a heating rate of 20°C/min from room temperature to 800°C under nitrogen atmosphere. The mechanical properties of the PEN-*t*-Ph/TPh films were investigated by SANS CMT6104 Series Desktop Electromechanical Universal Testing Machine. Before measured, the films were cut into samples of 10 mm × 100 mm, then gained the average value of the three samples.

RESULTS AND DISCUSSIONS

Crosslinking

Polymers with pendant nitrile or terminated nitrile groups can be crosslinked to form thermally stable triazine rings generally by a catalytic trimerization of the nitrile groups.²⁰ Phthalocyanine ring can be formed through crosslinking of the phthalonitrile according to the previous literatures.^{18,21} The mechanism of crosslinking reaction of PEN-*t*-Ph/TPh is described in Figure 2. As shown in Figure 2, PEN-*t*-Ph crosslinked with the TPh under the catalytic action of DDS, and formed the phthalocyanine ring.

The FTIR spectra of the PEN-*t*-Ph/TPh films are shown in Figure 3. As can be seen, two characteristic stretching bands which emerged at 830 cm^{-1} and 738 cm^{-1} were assigned to benzene rings, and the other two sharp and strong characteristic

absorption bands at 1490 cm^{-1} and 1460 cm^{-1} were also assigned to skeleton vibration of benzene rings. The absorption band at 1242 cm^{-1} was clearly observed, which is attributed to skeleton vibration of ether. These results suggest the existence of aryl ether (Ar—O—Ar). Besides, the characteristic stretching band appeared at around 2230 cm^{-1} suggesting that the nitrile groups existed in the system. Moreover, the particular characteristic absorption band at 1010 cm^{-1} was assigned to the stretching vibration of phthalocyanine ring, which provided supports for crosslinking reaction of phthalonitrile.^{22,23}

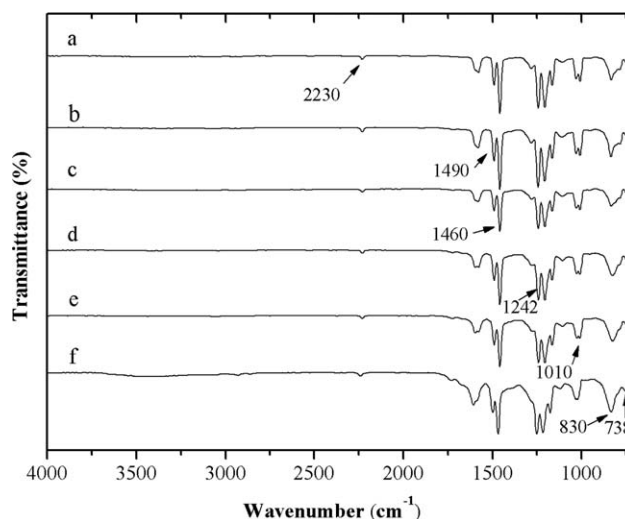


Figure 3. FTIR spectra of the PEN-*t*-Ph/TPh system with different curing procedures.

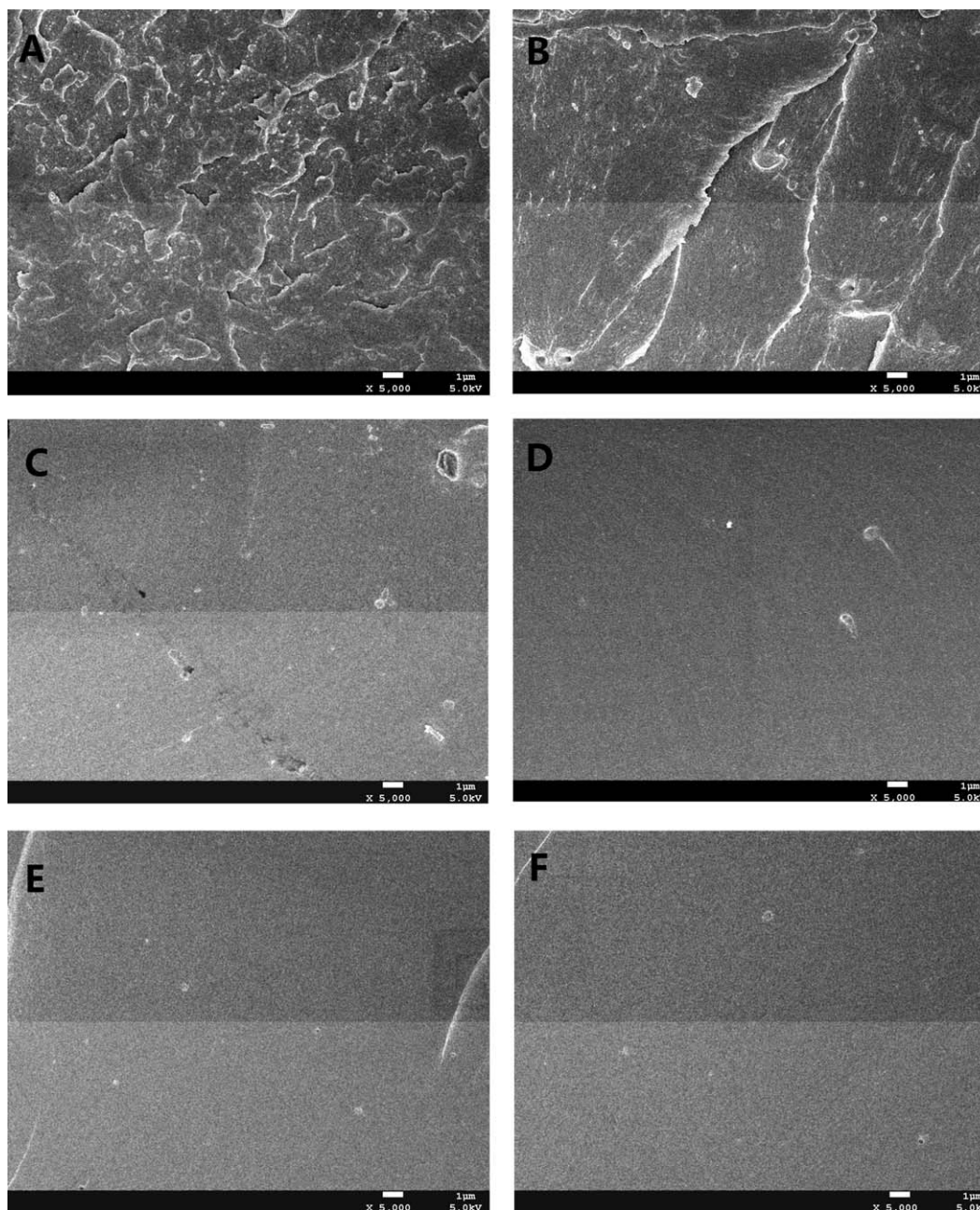


Figure 4. Effect of crosslinking on the morphology of PEN-*t*-Ph/TPh system: (A) sample a without heat crosslinking; (B–F) samples b–f with heat crosslinking by different procedure.

Morphological Properties

Figure 4 displays the SEM images of the PEN-*t*-Ph/TPh system to investigate the microscopic network structures of phthalocyanine rings formed by crosslinking between phthalonitrile at high temperature. As shown in Figure 4(A), the PEN-*t*-Ph/TPh film a without heat treatment exhibited microscopic phase-separation. However, as demonstrated in Figure 4(D–F), the PEN-*t*-Ph/TPh films with heat treatment exhibited homogeneous phase, and the fracture surface was smooth and compact, which is caused by the crosslinking reaction between PEN-*t*-Ph and TPh at high temperature. Obviously, this PEN-*t*-Ph/TPh system transformed gradually from two-phase separation to

completely single-phase. These results revealed that the cured PEN-*t*-Ph/TPh system formed continuous network after curing treatment. The SEM images showed that the microscopic network structures of PEN-*t*-Ph/TPh system had been transformed from phase-separation to homogeneous phase through the procedure of cure treatment, which is beneficial to improve the performance of the system.

Mechanical and Thermal Properties

The data of mechanical properties including elongation at break, tensile strength, and elastic modulus of the PEN-*t*-Ph/TPh films are listed in Table II. It was found that samples a, b

Table II. Mechanical Properties of PEN-*t*-Ph/TPH Films with Different Curing Procedures

Samples	Elongation at break (%)	Tensile strength (MPa)	Elastic modulus (MPa)
A	– ^a	–	–
B	–	–	–
C	3.57	57.71	2041.89
D	3.64	53.45	1909.69
E	2.95	45.83	2028.03
F	1.59	27.85	1817.05

^aThe detail parameter can not be measured due to their fragileness.

cannot be tested because of their fragileness caused by little crosslinking between phthalonitrile. When curing temperature increased to 300°C, the mechanical properties improved dramatically. Sample **c** possessed the best mechanical properties with tensile strength of 57.71 MPa and elastic modulus of 2041.9 MPa. However, the mechanical properties weakened when curing temperature goes up to 360°C. This may be due to high degree of crosslinking, thus results in the brittleness. These results showed that the mechanical properties of the films were improved greatly through the proper cure treatment method.

Thermally induced phase transition behavior of the PEN-*t*-Ph/TPH system was investigated by DSC under a nitrogen atmosphere. From the DSC curve of sample **a**, it was found that the crosslinking reaction occurs from ~220°C. As can be seen in Figure 5, the glass transition temperature (T_g) of sample **a** without cure treatment was 148.6°C and that of samples **b**, **c**, **d**, and **e** was 176.5°C, 194.7°C, 232.3°C, 236.7°C, respectively. The sample **f** had no evident glass transition behavior in the range of 200°C to 350°C. It was clear that the temperature for long-term use was improved with the curing temperature increasing. This is because the formed phthalocyanine rings via thermal

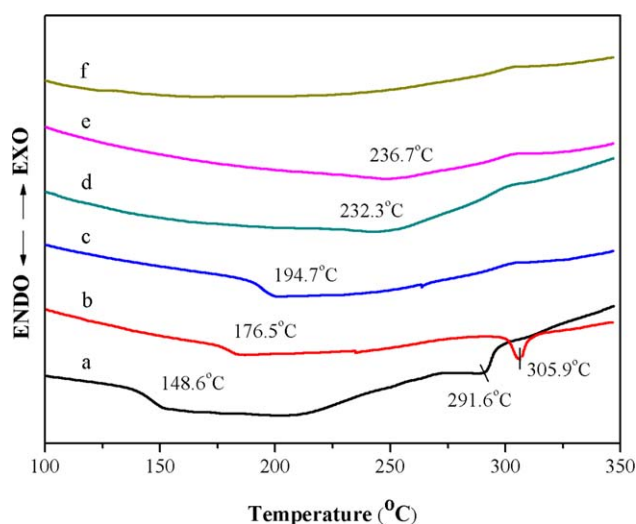


Figure 5. DSC curves of PEN-*t*-Ph/TPH system with different curing procedures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

crosslinking reaction between phthalonitrile enhanced the stability of polymer structure, and hampered the movement of polymer chains. In addition, both samples **a** and **b** had a melting peak which was attributed to the melting of TPH, and samples **c**, **d**, **e**, and **f** had no melting peaks but exothermic peaks in the range of 290–320°C. Furthermore, the intensity of the exothermic peaks weakened as the curing temperature increases. These results proved that the thermal properties of the PEN-*t*-Ph/TPH system were improved by cure treatment with high temperature.

TGA curves of the PEN-*t*-Ph/TPH films are shown in Figure 6(A) to investigate the thermal stability of the PEN-*t*-Ph/TPH system, and the detail data are listed in Table III. With the increase of curing temperature, the temperatures corresponding to the weight loss of 5 wt % ($T_{5\%}$) rise from 475.3°C to 544.0°C, and the temperatures corresponding to the weight loss of 10 wt % ($T_{10\%}$) increased from 534.9°C to 576.7°C, and the char yield at the temperature of 800°C increased from 60.6% to 71.3%. In addition, samples **a**, **b**, **c** exhibited two peaks in their derivative thermogravimetry (DTG) curves, as shown in Figure 6(B), which is consistent with the fact that the samples **a**, **b** and **c** exhibited microscopic phase-separation. However, samples **e** and **f** had only one peak which is in agreement with the fact that their micro-morphologies exhibited homogeneous phase.

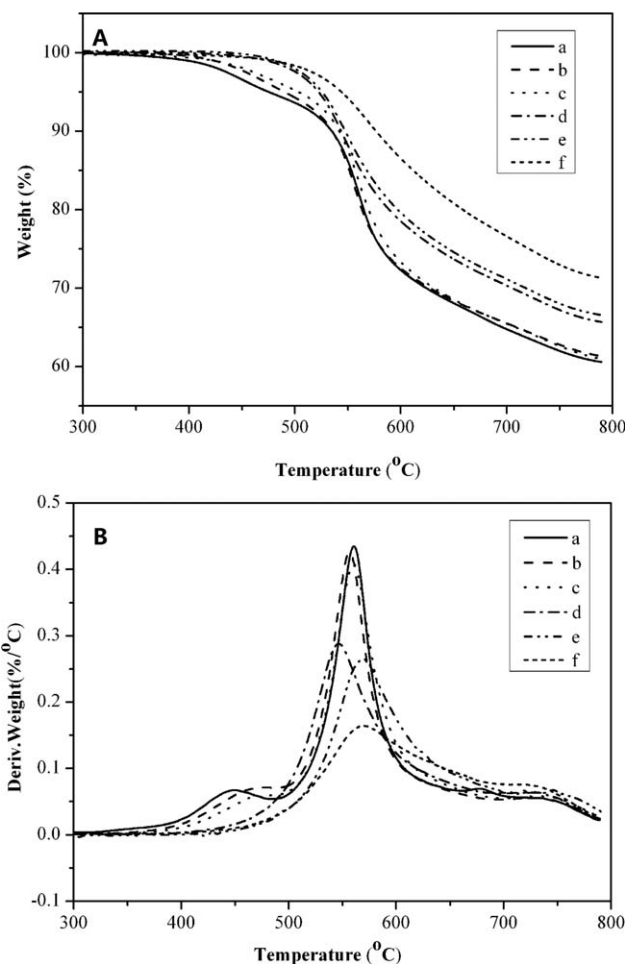


Figure 6. (A) TGA and (B) DTG curves of PEN-*t*-Ph/TPH system with different curing procedures.

Table III. Thermal Properties of the PEN-*t*-Ph/TPh Films with Different Curing Procedures

Samples	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	Char yield (%) at 800°C
A	475.34	534.93	60.61
B	490.09	535.31	61.32
C	504.56	542.26	60.99
D	522.39	543.78	65.67
E	525.68	547.59	66.54
F	543.96	576.70	71.29

Therefore, these results were consistent with the DSC and SEM analysis results. Furthermore, TGA and DTG results exhibited that the thermal properties of the PEN-*t*-Ph/TPh system were greatly enhanced by curing treatment, and increased with the increase of cure treatment temperature, due to the increasing degree of crosslinking.

CONCLUSIONS

In this work, the PEN-*t*-Ph/TPh films were successfully prepared by solution casting method and their curing behavior was investigated. FTIR results exhibited that phthalocyanine rings were formed through the crosslinking reaction between nitrile groups. It was found that the microscopic structures of PEN-*t*-Ph/TPh system had been transformed from phase-separation to homogeneous phase through the procedure of curing treatment. Thermal analysis results show that the thermal properties were greatly enhanced and increased with the increasing curing temperature. The PEN-*t*-Ph/TPh system will have potential application as high-temperature resistant materials in many fields.

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