

# Effect of Curing Behaviors on the Properties of Poly(arylene ether nitrile) End-Capped with Phthalonitrile

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**ABSTRACT:** Poly(arylene ether nitrile) (PEN) end-capped with phthalonitrile (PEN-n) was synthesized by incorporating phthalonitrile into the terminals of PEN. The as-prepared flexible PEN-n (after elevated temperature treatment) was characterized by infrared spectroscopy, nuclear magnetic resonance, gel permeation chromatography, and rheological measurements. In addition, the effects of curing behaviors on properties of PEN-n films were studied by thermal, dielectric and mechanical measurements. Differential scanning calorimetry analysis showed that glass transition temperature of PEN-n was improved from 176 to 232°C as the curing temperature and time increased. Thermal gravimetric analysis revealed that initial decomposition temperature of PEN-n cured at

320°C for 2 h was 570°C. Mechanical properties showed that tensile strength of PEN-n uncured and cured at 320°C for 3 h was 85 and 97 MPa, respectively. The dielectric properties showed that the dielectric constant of PEN-n film decreased from 4.0 to 3.1 as the curing time increased and dielectric loss of PEN-n was 0.01 at 100 kHz. This kind of PEN-n film may be used as a good candidate for high-performance polymeric materials. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** poly(arylene ether nitrile); phthalonitrile end-capped; phthalocyanine; thermal properties; dielectric properties; mechanical properties

## INTRODUCTION

Engineering thermoplastics are widely used in high-performance fields such as aerospace, automobile, electronic applications. In the past 30 years, poly(arylene ether nitrile) (PEN) has attracted attention for high engineering thermoplastic applications and became one of the most important branches of engineering thermoplastics families.<sup>1–7</sup> The presence of nitriles in PEN endows the polymers with strong polarizability, which promotes the adhesion of the polymers to many substrates. Moreover, the nitriles also serve as potential sites for the crosslinking reaction of PEN because the groups are likely to form thermally stable phthalocyanine rings.<sup>8</sup> For industry applications, it is essential to make polymeric materials possess high glass transition temperatures, good mechanical, and dielectric properties.

However, despite the advantages of the PEN, its poor thermal and mechanical properties limited its

usage and processability for high performance applications.<sup>9,10</sup> According to previous reports, 4-nitro-phthalonitriles possess good linkable groups, which are easy to react with hydroxyl groups or halogen elements.<sup>7,8</sup> Lots of polymers with nitriles as end or pendant groups have been proved to be crosslinked by phthalocyanine rings resulted from the crosslinking reaction among the nitriles.<sup>11–13</sup> The thermal stability of crosslinked polymers is enhanced by the strong resonance energy of phthalocyanine rings. To endow the better thermal, mechanical, and dielectric properties, PEN with linkable group on the terminal was synthesized.<sup>7,14–16</sup> We hoped to incorporate nitriles into the terminals of PEN for endowing with the crosslink and branch abilities to the resins, because high performances can be obtained by end-capped with proper terminal linkage groups.<sup>17–20</sup> The mechanical performances can be accelerated by incorporating terminal linkable groups as well.<sup>21</sup> Crosslinking structures from reaction of functional groups nitriles cured at elevated temperature have shown good mechanical and thermal stabilities.<sup>22–25</sup> In fact, crosslinking of polymers generally improves their physical properties, such as dimensional stability, resistance to thermal deformation and stress cracking, particularly at high temperature.

In this article, a novel linkable PEN end-capped with phthalonitrile (PEN-n) was synthesized. We have synthesized PEN end-capped with hydroxyl

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groups (PEN-OH) via extra biphenyl (BP) contents. Then, PEN-n films were synthesized via 4-nitrophthalonitrile reacting with hydroxyl groups on terminal of PEN-OH. The structure of PEN-n was characterized by infrared spectroscopy and nuclear magnetic resonance (NMR) spectroscopy. The effects of curing temperature and time on thermal properties, dynamic mechanical properties, mechanical properties, and dielectric properties of PEN-n were investigated. The topography photographs of different curing temperature were given by scanning electron microscope (SEM) measurement.

## EXPERIMENTAL

### Materials

*N*-Methyl-2-pyrrolidone (NMP) was purchased from Tianjin BODI chemicals, China. 4-Nitrophthalonitrile (99%) was obtained from Alpha Chemicals (Dezhou). Potassium carbonate ( $K_2CO_3$ ), BP, hydroquinone (HQ), 2,6-dihalobenzonitriles (DCBN), and methylbenzene were provided by different commercial sources. All the reagents were used without further purification.

### Synthesis

BP (63.17 g, 0.336 mol), HQ (8.8 g, 0.08 mol), DCBN (68.8 g, 0.4 mol), and 50 mL of methylbenzene and 150 mL of NMP were added into a 500-mL three-necked flask. During the course of the reaction, the  $K_2CO_3$  were added in several portions. Then, 4-nitrophthalonitrile and 50 mL NMP were added into three-necked flask after reaction for 5 h. The mixture was heated at 80–90°C for 5–6 h. After cooling to room temperature, the product mixture was poured into 1000 mL of dilute HCl solution to remove  $K_2CO_3$ . Then, PEN-n product was purified by alcohol till monomers were washed out. Afterward, the PEN-n was dissolved by a certain amount of NMP in a three-necked flask and heated at 160°C for 1.5 h. Then, the mixture was filtrated by gauze and cast onto a clean glass plate to obtain films. Molten mixtures transferred to the glass plated were heat treated at 80, 100, 120, 160, and 200°C for 2 h, respectively. Then, the glass plates were heated at 250°C for 2 h, and the samples were slowly cooled to room temperature; thus, the samples cured at 250°C for 2 h were obtained. The procedures of samples cured at 270°C for 2 h, 300°C for 2 h, and 320°C for 1 h, 320°C for 2 h, 320°C for 3 h, and 320°C for 4 h were carried out as same as that of samples cured at 250°C for 2 h.

### Characterizations

The polymer structure was analyzed by Fourier transform infrared spectroscopy (FTIR) spectra

recorded on a Nicolet 200 SXV spectrophotometer in transmission mode. The typical FTIR characteristic data: 3440  $cm^{-1}$  (stretch, —OH), 2230  $cm^{-1}$  (stretch, —CN), 1600  $cm^{-1}$  (stretch, —NH), 1490  $cm^{-1}$  (stretch, —C=N), and 1247  $cm^{-1}$  (stretch, Ar—O—Ar) and 885, 834, 782, and 722  $cm^{-1}$  (stretch, benzene).

The  $^1H$ -NMR spectra was recorded on a Bruker DPX-300 NMR spectrometer at a proton frequency of 300 MHz with dimethylsulfoxide- $d_6$  as the solvent.

Gel permeation chromatography (GPC) analysis was conducted with a PL-GPC220 system using polystyrene as standard and tetrahydrofuran as the eluent.

The microscopic homogeneity of the PEN films was observed with SEM (JEOL JSM-5900LV). The SEM samples were coated with a thin layer of gold before examinations.

Dynamical rheological measurements were carried out on a rheometer (TA Instruments Rheometer AR-G2) equipped with a parallel plate geometry (25 mm diameter). Samples for rheometric measurements were prepared as a thickness of 1.0 mm and diameter of 25 mm round piece. Time ramp sweep was measured at 1 Hz, and temperatures were fixed at 320°C.

Differential scanning calorimetry (DSC) analyses of films were performed on TA Instrument DSC Q100 modulated thermal analyzer under a nitrogen purge of 50  $cm^3 min^{-1}$  at a heating rate 10°C  $min^{-1}$  from room temperature to 350°C. Thermal gravimetric analyses (TGA) and derivative thermogravimetric analysis (DTG) of the films were performed on a TA Instruments TGA Q50 at a heating rate of 20°C  $min^{-1}$  from room temperature to 800°C under nitrogen purge of 50  $cm^3 min^{-1}$ .

The mechanical properties of the films were measured on SANS CMT6104 Series Desktop Electromechanical Universal Testing Machine, with the sample size as 10 × 100  $mm^2$ , and gained as average value for every three samples.

Dielectric measurements for sample films were performed by using a dielectric analyzer (DEA 2970, TA Instruments). The films of PEN-OH, PEN-n, and cured PEN-n were cut into small pieces of 10 × 10 mm and covered with conductive silver paste on both surfaces. The dielectric properties experiments were performed at different frequency fields from 20 Hz to 200 KHz at 20°C with 40% humidity.

### Gel content

The gel content of the powdered crosslinked sample was determined through Soxhlet extraction, using NMP as solvent. Samples were refluxed in NMP for at least 48 h, until the sample attained a constant weight. The residue after extraction was taken as the

**TABLE I**  
Gel Content of PEN-n Cured at 250, 270, 300, and 320°C for 2 h

Samples	PEN-n cured at 250°C	PEN-n cured at 270°C	PEN-n cured at 300°C	PEN-n cured at 320°C
Gel content (%)	34	59	70	100

gel component, and the gel content was calculated according to eq. (1).

$$\text{Gel content (\%)} = W_1/W_2 \times 100 \quad (1)$$

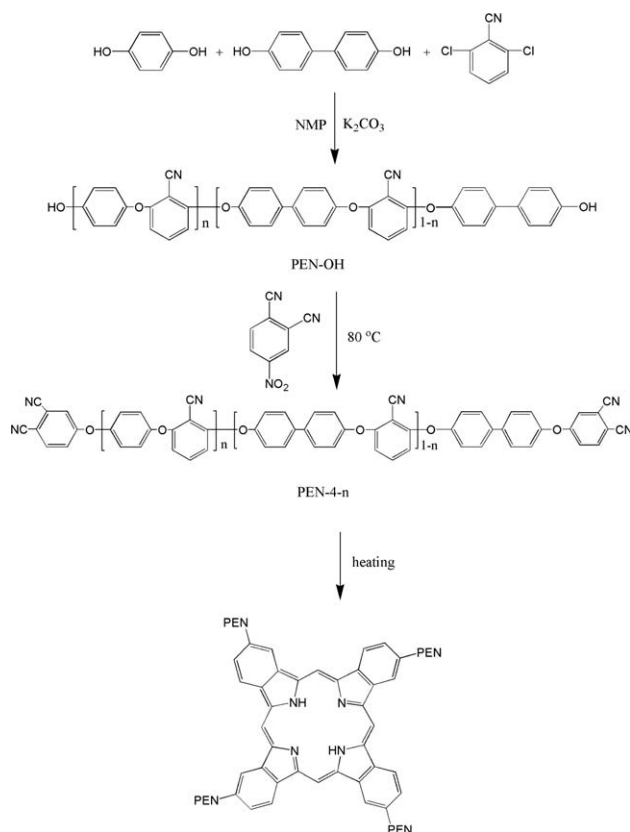
where  $W_1$  and  $W_2$  are the weights of the samples before and after refluxed in NMP for 48 h, respectively.

## RESULTS AND DISCUSSION

### Gel content and $^1\text{H-NMR}$ analysis of PEN-n

As shown in Table I, the gel contents of a cured PEN-n at 250, 270, 300, and 320°C were 34, 59, 70, and 100%, respectively. It was well accepted that the gel content was affected by a number of its inherent properties.

The structure of PEN-n shown in Scheme 1 was verified by  $^1\text{H-NMR}$  spectra (Fig. 1). In  $^1\text{H-NMR}$ , the

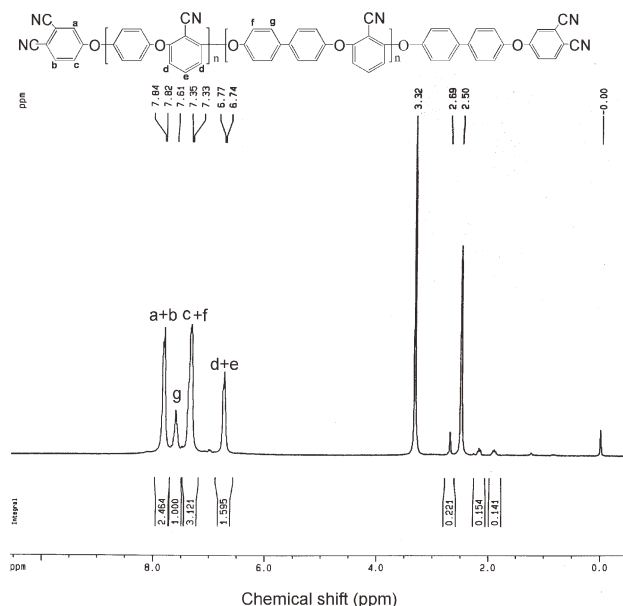


**Scheme 1** Synthesis route of PEN-n and the scheme of thermal curing reaction of PEN-n.

prominent resonances at 6.74–7.84 ppm in the aromatic frequency correspond to the hydrogen in the benzene ring. The resonance appearing at 7.61, 7.82, and 7.84 ppm confirmed that the phthalonitrile was incorporated at the polymer chain terminal. Thus, it indicated that the target polymer PEN-n was obtained.

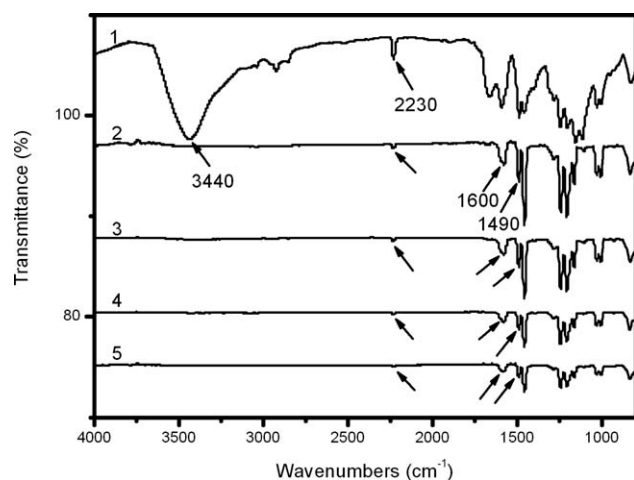
### Curing behavior studies on PEN-n

The FTIR spectra of PEN-OH, PEN-n before, and after cured treatment were shown in Figure 2. PEN-OH shows a characteristic stretching band occurring at  $3440\text{ cm}^{-1}$  ( $-\text{OH}$ ) and  $2230\text{ cm}^{-1}$  ( $-\text{CN}$ ), which provided supports for the structure of PEN-OH in the Scheme 1. After end-capping with 4-nitrophenalitrile, absorption peak of  $-\text{OH}$  disappeared and another two absorption bands emerged at 1600 and  $1490\text{ cm}^{-1}$ , which were assigned to  $-\text{NH}-$  and  $-\text{C}=\text{N}-$ , respectively. The results demonstrated that 4-nitrophenalitrile reacted with  $-\text{OH}$  on the terminal of PEN to form PEN-n. In addition, the appearances of  $-\text{NH}-$  and  $-\text{C}=\text{N}-$  are the characters of phthalocyanine. It was indicated that the phthalocyanine was formed at  $200^\circ\text{C}$ , which was consistent in previous reported.<sup>26</sup> These results could be attributed to formation of more phthalocyanines after curing reaction. In addition, these results



**Figure 1**  $^1\text{H-NMR}$  spectra of PEN-n.

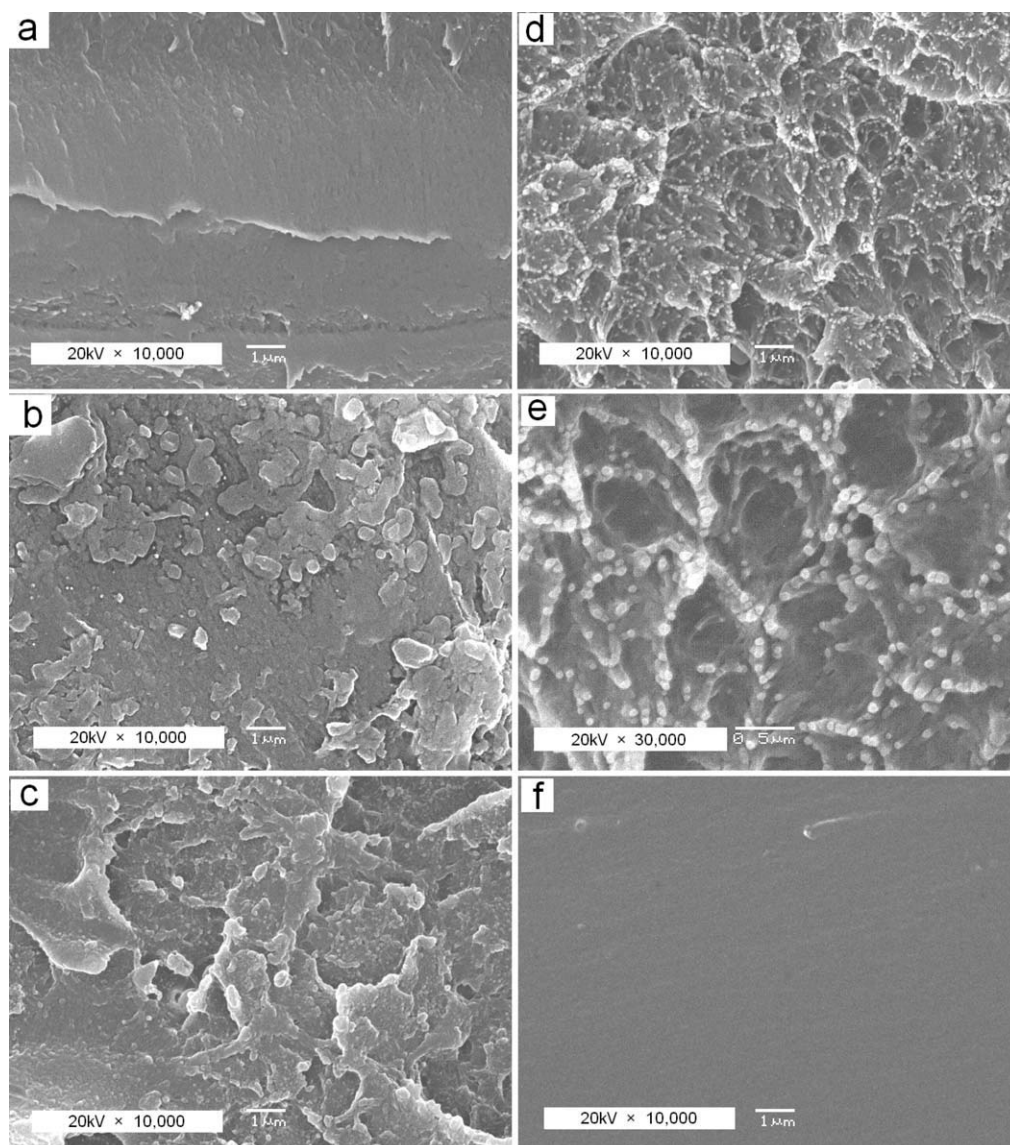




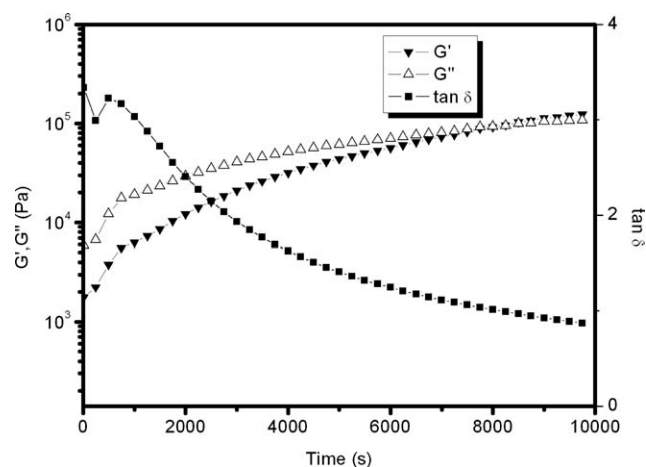
**Figure 2** FTIR spectra of PEN-OH (1), PEN-n (2), PEN-n-250°C cured (3), PEN-n-270°C cured (4), and PEN-n-300°C cured (5).

confirmed the curing reaction between  $\text{—CN}$  groups end-capped in the terminal of PEN.

SEM was performed to investigate the microscopic network structures of cured PEN-n films. The SEM micrographs were shown in Figure 3. According to the GPC results, the number-average molecular weight of PEN-n was in the range of 16,000–56,000. Thus, there was no difference between Figure 3(a) and other reported PENs. As shown in Figure 3(b,c), PEN-n films changed after heat treatment at 250 and 270°C, which was caused by gel particles. The gel particles were formed by crosslinking of phthalonitrile, which can be confirmed by measurement of gel content. With the heat-treatment temperature increasing, gel particles were increased and uniform dispersed in polymer. The gel particles were clearly seen from the polymer in Figure 3(d,e), which showed different amplification factors of PEN-n



**Figure 3** SEM images of the PEN-n films (a) uncured, (b) cured at 250°C, (c) cured at 270°C, and (d) cured at 300°C.



**Figure 4** Plots of the storage modulus ( $G'$ ), loss modulus ( $G''$ ), and damping factor ( $\tan \delta$ ) by time sweeping at  $320^\circ\text{C}$ .

cured at  $300^\circ\text{C}$  for 2 h. As can be seen from Figure 3(f), gel particles were dissolved after heat treatment at  $320^\circ\text{C}$ , because the polymer melted in this temperature and phthalonitrile crosslinking reacted quickly and sufficiently with the mobility of polymer increased. The SEM micrographs showed morphology changes from heterogeneous to homogeneous phase.

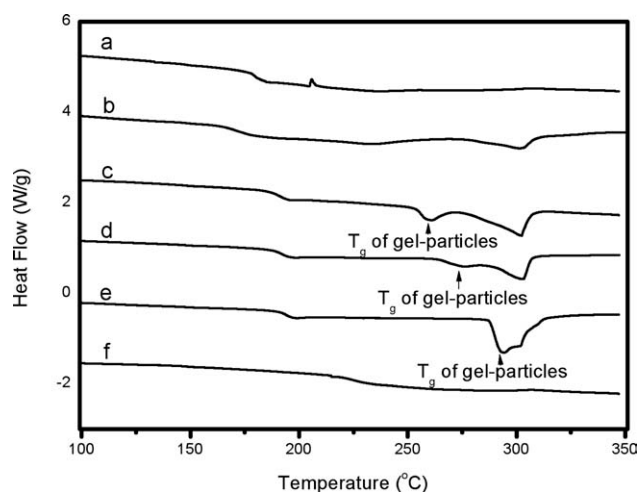
Rheological measurement could further prove the curing reactions of PEN-n at  $320^\circ\text{C}$ . Plots of the storage modulus ( $G'$ ), loss modulus ( $G''$ ), and damping factor ( $\tan \delta$ ) were presented in Figure 4. It was evident that the modulus of the PEN-n increased signally as the increasing of curing time, which indicated that PEN-n had been transferred from viscosity flow state to solid state and the  $\tan \delta$  decreased as well.  $G'$ ,  $G''$ , and  $\tan \delta$  changed slightly after  $G$  cross-over point, which was attributed to the reduc-

tion of segmental mobility. These results exhibited good processability and thermally activated polymerization, which were very useful to the processability and application.

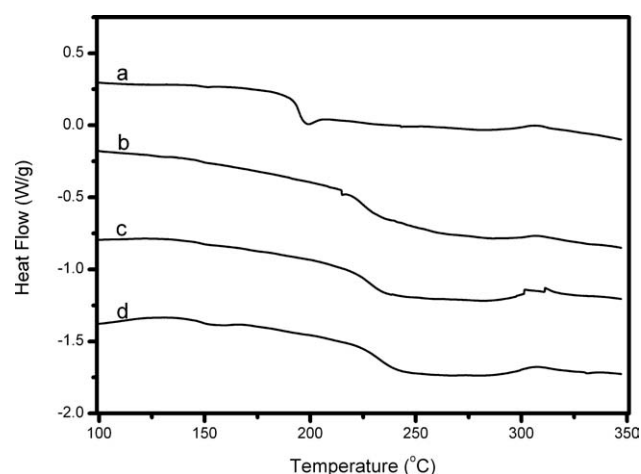
### Thermal analysis on curing reaction

DSC curves of films were shown in Figure 5. The curve of PEN-OH showed that the glass transition temperature ( $T_g$ ) was  $176^\circ\text{C}$ . It can be noticed that there was a slight change for  $T_g$  from the curve of uncured PEN-n compared with that of PEN-OH. A melting peak appears at  $300^\circ\text{C}$  and a curing peak appears at the range from  $230$  to  $300^\circ\text{C}$ . There were two heat absorption peaks in the curves of PEN-n undergo heat treatment. These results can be explained that the gel particles were separated from PEN-n resin, and they had their own  $T_{gs}$ s, respectively. In addition, it can be seen that the  $T_{gs}$  increased from  $170$  to  $230^\circ\text{C}$  when the heat-processing temperature reached  $320^\circ\text{C}$ . The reason of dramatic change could be attributed to the gelation transition of resins. These results exhibited the heat-resistant property was increased obviously after heat treatment.

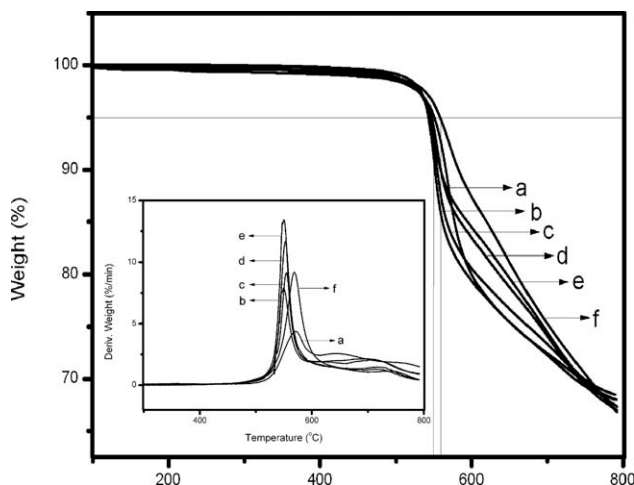
DSC curves of different curing times for PEN-n at  $320^\circ\text{C}$  were shown in Figure 6. As can be seen,  $T_g$  was enhanced from  $195$  to  $232^\circ\text{C}$  as the curing time increased, which reflected that a long curing time was needed to complete the phthalonitrile cure. Along with the long period of high-temperature processing, gel particles react with PEN-n adequately. This result indicated that the enhancement of  $T_g$  was due to the high curing temperature and long curing time by the increase of gel content. These results exhibited that the heat-resistant



**Figure 5** DSC curves of PEN-OH (a), PEN-n uncured (b), and PEN-n cured at  $250^\circ\text{C}$  (c),  $270^\circ\text{C}$  (d),  $300^\circ\text{C}$  (e), and  $320^\circ\text{C}$  (f) for 2 h, respectively.



**Figure 6** DSC curves of PEN-n cured at  $340^\circ\text{C}$  for (a) 1 h, (b) 2 h, (c) 3 h, and (d) 4 h.



**Figure 7** TGA and DTG curves of PEN-OH (a), PEN-n uncured (b), and PEN-n cured at 250°C (c), 270°C (d), 300°C (e), and 320°C (f) for 2 h, respectively.

property of PEN-n was increased obviously after elevated temperature treatment.

Figure 7 showed TGA and DTG curves of PEN-OH, PEN-n, and cured PEN-n, respectively. The initial decomposition temperature of PEN-n films cured at 320°C for 2 h increase by about 10°C, compared with that of PEN-OH and other PEN-n films. One possible mechanism was proposed to explain this phenomenon. The crosslinking structure efficiently improved the thermal stability of polymer. This indicated that the heat-resistance properties were improved obviously after elevated temperature treatment and modification. From derivative thermogravimetric curves, one can see the maximum rate of degradation ( $T_{max}$ ) of PEN-OH was nearly as the same as the modified polymers curing at 320°C, while other modified polymers uncured or cured were low. It may be explained that the gel particles like filler in matrix PEN-n broken the globality of resins, which further accelerated the rate of decomposition of polymer. Gel particles dissolved when cured at 320°C, which make PEN-n convert to complete crosslinking structure. It was obvious that the thermal stabilities of PEN-n increased with the curing temperature. This indicated that the extent of curing reaction and gel content increased with the increasing of temperature of heat treatment. The initial decomposition temperature increased as the curing temperature increased. These results indicated that the thermal properties of PEN-n increased as the curing temperature increased.

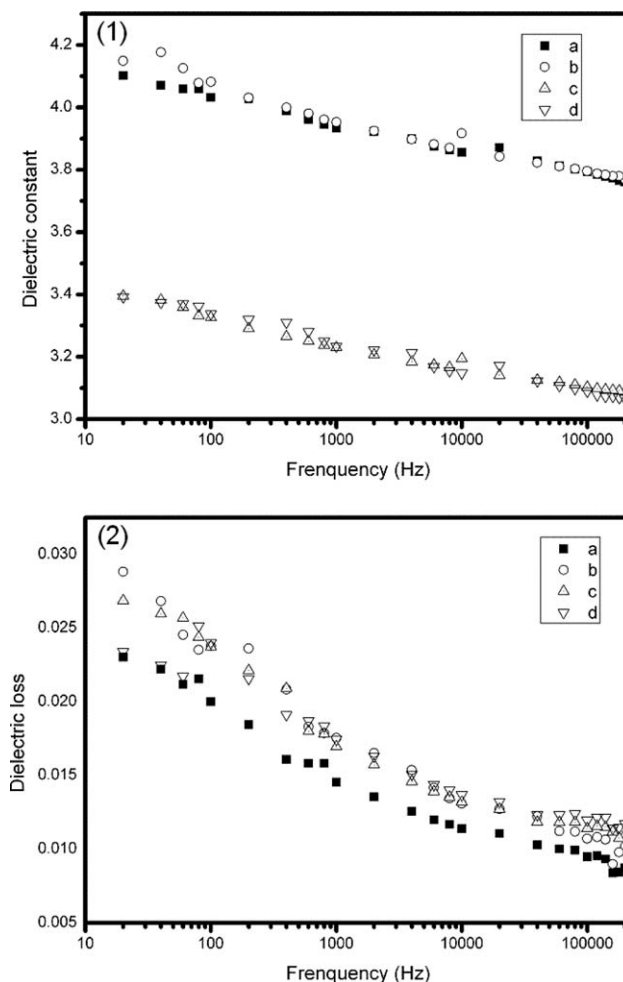
### Effects on dielectric properties

Figure 8 showed the results of dielectric constant ( $\epsilon$ ) and dielectric loss ( $\tan \delta$ ) of the films before and after heat treatment. It was obvious that the dielectric

constants of PEN-n changed a lot. The dielectric constants of PEN-n cured at 320°C for 3 and 4 h were lower than that of samples cured for 1 and 2 h. This may be attributed to the curing degrees of PEN-n increased with the increasing of curing time. Elevated temperature and long-time curing reaction reduced nitriles of polymer and further led to the reduction of dielectric constant. One can see that the dielectric loss did not change much. This result reflected that PEN-n matrix had formed stable framework after heat treatment at 320°C. The dielectric properties exhibited that the dielectric constant of PEN-n film cured at 320°C for 3 h was 3.1, and dielectric loss of PEN-n film was 0.01 at 100 kHz. This behavior was very useful for microelectronic application.

### Effects on mechanical properties

The mechanical properties of the films were listed in Table II. It was obvious that elongation at break and tensile strength increased with the increasing of



**Figure 8** (1) The dielectric constants and (2) dielectric losses of the PEN-n films.



**TABLE II**  
**Mechanical Properties of PEN and PEN-n Films**

Samples	Elongation at break (%)	Tensile strength (MPa)	Elastic modulus (MPa)
PEN-OH	6.13	71	2049
PEN-4-n	4.73	83	2366
PEN-4-n-250°C cured	7.13	85	2278
PEN-4-n-270°C cured	4.28	80	2322
PEN-4-n-300°C cured	4.25	81	2334
PEN-4-n-320°C cured for 1 h	6.22	82	2103
PEN-4-n-320°C cured for 2 h	10.89	90	2219
PEN-4-n-320°C cured for 3 h	11.65	97	2369
PEN-4-n-320°C cured for 4 h	8.1	89	1619

curing temperature. The PEN-n cured at 320°C for 3 h, the values of elongation at break attained 11.65%, and tensile strength was 97 MPa, was the best. Incomplete cured samples (for 1 and 2 h) possessed low elongation at break and tensile strength. When curing time reached to 4 h, elongation at break and tensile strength decreased, which was explained by oxidation or side reaction due to the excess curing time. These results revealed that the mechanical properties of complete cure were higher than that of uncompleted cure and excess cure. This may be explained that the excess increment in processing time and heating temperature will make the PEN-n films processed in an oven oxidation and side reaction, leading to the elastic modulus decreasing. These results showed that the mechanical properties were improved greatly cured at 320°C, and PEN-n possesses good mechanical properties for high-temperature applications.

## CONCLUSIONS

Novel PEN-n films were successfully synthesized from 4-nitrophthalonitrile, DCBN, BP, and HQ via solution reaction. Effects of curing reaction on the thermal, dielectric, mechanical, and rheological properties of PEN-n films were studied. The FTIR and <sup>1</sup>H-NMR spectra have exhibited that the phthalonitrile was incorporated on the polymer chain terminal, and the absorption peak of —CN group weaken with the increasing of the curing temperature, which can demonstrate that phthalocyanines were formed via curing reaction. SEM macrographs showed that the increase of gel particles was due to increase of heat-treatment temperatures. The thermal properties showed that the glass transition temperature ( $T_g$ ) of cured PEN-n improved 46°C and the initial decomposition temperatures ( $T_{id}$ ) of PEN-n films were

570°C. The dielectric measurements exhibited that the films of PEN-n possessed good dielectric properties for microelectronic application. In addition, the values of tensile strength of PEN-n cured at 320°C for 3 h attained 97 MPa and elastic modulus improved. The cured PEN-n films exhibited excellent thermal, dielectric, and mechanical properties, which were due to the crosslinking of PEN-n.

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