

Plasticization of Poly(arylene ether nitrile) by the Melt Blending of Phthalonitrile Prepolymer: A Rheological, Mechanical, and Thermal Study

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ABSTRACT: Poly(arylene ether nitrile) (PEN)/phthalonitrile prepolymer (PNP) blends were prepared via a melt-mixing process. The melt flow properties, compatibility, and thermal and mechanical properties were characterized by dynamic rheological testing, dynamic mechanical analysis, tensile testing, thermal analysis, and fracture surface morphology observation. The melt-mixed PEN/PNP blends displayed excellent melt flow properties during processing. When the PNP content in PEN was increased, the viscosity of the blends decreased considerably. Compared with that of pure PEN, the dynamic complex viscosity of the PEN/PNP blend with an 11% addition of PNP dropped sharply from 7000 to 2000 Pa s at 350°C and a

frequency of 10 Hz. The dynamic mechanical analysis and differential scanning calorimetry results showed good compatibility between PEN and PNP. Observations of the morphology of the fractured surfaces revealed better component dispersion in which PNP was dissolved in the PEN matrix. Importantly for further commercial applications, the blending materials maintained the characteristic thermal and thermooxidative stability and mechanical properties of PEN. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 2668–2673, 2010

Key words: blending; compatibility; high performance polymers; processing; viscoelastic properties

INTRODUCTION

Poly(arylene ether nitrile)s (PENs) are well known for their outstanding properties; for example, their radiation resistance and high thermal and thermooxidative stability, good mechanical properties, and chemical inertia make them very attractive for composites used at elevated temperatures and in aggressive chemical environments, such as those encountered in aerospace, industrial, and automotive applications.^{1–5} Although it is well known that thermoplastic high-performance polymers such as aromatic poly(aryl ether ketone)s,^{6,7} aromatic poly(ether sulfone)s,⁸ and aromatic PENs^{1,9} have a lot of favorable properties from many perspectives and they have been commercially available for a long time, much research is still urgently needed to resolve problems such as poor solubility, high-temperature processing, and melt flowability.^{2,3}

Recently, a series of PENs with high molecular weights have been prepared in our laboratory, and the resins exhibited outstanding high-temperature stability and better mechanical properties.¹⁰ How-

ever, high molecular weights also bring problems to processing, especially when resins are being blended with glass fibers for industrial applications. Improving the processability of resins through a reduction of the melt viscosity is very strategic for both laboratory research and industrial applications. Blending high-performance polymers with low-melt-viscosity polymers or oligomers to improve the processability has been reported elsewhere.¹¹ As for the plasticizers commonly blended with PEN, although the processability of the blends has obviously been increased, because of their inherent disadvantages, such as poor compatibility and poor high-temperature resistance, there is a big gap for applications under tough conditions such as those encountered in the aerospace industry. From this viewpoint, phthalonitrile prepolymer (PNP), which has a high initial decomposition temperature (>450°C) and a low initial melt viscosity at 330°C (<0.1 Pa s),^{12–17} was first studied as a kind of plasticizer used to overcome the temperature resistance problem, and the blending materials maintained the high thermal and thermooxidative stability of PEN. As for the molecular structure, the bone structures of PEN and PNP have similar molecular structures, aromatic ether bonds, and cyano groups, and considerable compatibility between PEN and PNP would be expected. Morphological examinations in this work revealed that

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PEN/PNP has very good component dispersion, and this means that the blends could have very extensive industrial applications.

EXPERIMENTAL

Materials

N,N'-Dimethylformamide (DMF; >99%) and potassium carbonate (99%) were obtained from Tianjin Bodi Chemicals (Tianjin, China). Diphenyl diamine sulfoxide (DDS), 4,4'-biphenol, and 4-nitrophthalonitrile were purchased from Yangzhou Tianchen Meticulous Chemical Co., Ltd. (Yangzhou, China). All the chemicals and reagents were used without further purification. PEN was provided by the Union Laboratory of Special Polymers (University of Electronic Science and Technology of China/FEIYA, Chengdu, China). It is a copolymer derived from 2,6-difluorobenzonitrile with hydroquinone and resorcin and has an inherent viscosity of 1.22 dL/g (0.005 g/mL in *N*-methylpyrrolidone). The repeating unit of PEN is shown in Figure 1. PNP, shown in Figure 2, was prepared in our laboratory.

Preparation of PNP

The phthalonitrile monomer was synthesized in our laboratory. The synthetic procedure and raw materials were previously reported.¹⁸ PNPs were made as follows: DDS was added at a weight ratio of 2% to the monomer melt (melting temperature = 234°C), the mixture was vigorously stirred for 5 min, and then the reaction was quenched at room temperature. PNPs were obtained, and the PNP structures are shown in Figure 2. The PNP weight-average molecular weight (1805) was determined by gel permeation chromatography with a Waters Breeze high-performance liquid chromatography system (USA).

Preparation of the blends

A series of PEN/PNP blends (95/5, 92/8, and 89/11 wt %) were melt-mixed in a TSSJ-2S corotating twin-screw extruder (China Bluestar Chengrand Chemical Co., Ltd., Chengdu, China). The temperature was maintained at 310, 320, 330, 330, 330, and 325°C from the hopper to the die, and the screw speed was about 120 rpm. Extruded strands of the molten blends were then pelletized and dried in a vacuum oven at 120°C for 24 h, and this was followed by

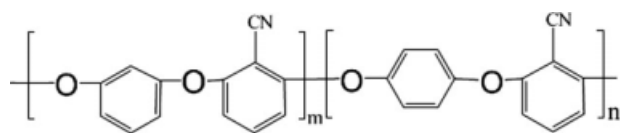


Figure 1 Repeating unit of PEN.

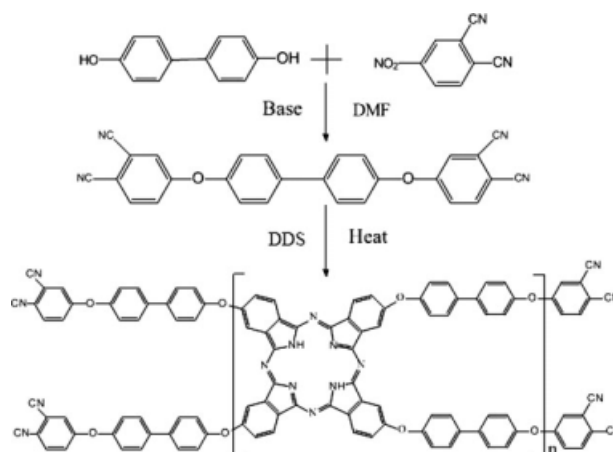


Figure 2 Synthesis of PNP.

injection molding to prepare standard samples for tensile, flexural, Izod impact strength, and thermal testing with an injection and molding machine. The injection-mold temperature was maintained at 340°C.

Characterization and apparatus

The tensile strength and flexural strength of the blends were tested with a SANS CMT6104 series desktop electromechanical universal testing machine (Shenzhen, China). The stretching direction of the sheets was the same as the tensile deformation direction. The moving speed of the crosshead was 5 mm/min, and the measurement temperature was about 25°C. The tensile strength and elongation at break were directly obtained from the stress-strain curves. The reported values were calculated as averages of five specimens for each composite.

The melting index of the blends was characterized with a Goettfert melting index instrument (Postfach, Germany) at 340°C with a weight of 10 kg.

A differential scanning calorimetry (DSC) analysis was performed on a TA Instruments (New Castle, DE) DSC-Q100 modulated thermal analyzer under a nitrogen purge of 50 cm³/min with heating to 350°C at a heating rate of 20°C/min, then cooling to 50°C at a cooling rate of 20°C/min, and finally heating to 350°C at a heating rate of 20°C/min again. Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA Q50 at a heating rate of 10°C/min under a nitrogen purge of 50 cm³/min.

TABLE I
Relationship Between the Composition and the Thermal and Mechanical Properties

PEN/PNP (w/w)	100 : 0	95 : 5	92 : 8	89 : 11
Tensile strength (MPa)	117.3	115.8	119.8	97.4
Flexural strength (MPa)	146.7	149.2	146.8	142.9
HDT (°C)	144.8	142.1	140.8	138.9

TABLE II
Melting Indices with Different PNP Contents

PEN/PNP (w/w)	100 : 0	95 : 5	92 : 8	89 : 11
Melting index at 340°C and 10 kg (g/min)	0	1.31	3.88	4.11

The heat deformation temperature (HDT) of the blends was measured according to ASTM D 648-2007 with a ZWK computer-controlled HDT Vikar tester (Shenzhen New Sans Materials Testing Machine Co., Shenzhen, China).

Scanning electron microscopy (SEM) was carried out on a JEOL JSM-5900LV instrument (North Billerica, MA). The specimens were fractured in liquid nitrogen, and the fractured surfaces were coated with a thin layer of gold before examinations.

Dynamic mechanical analysis (DMA) data were obtained with dynamic viscoelasticity equipment (model DMA983, DuPont, New Castle, DE) with the bending mode at the frequency of 1 Hz.

Dynamic rheological measurements were carried out on a TA Instruments AR-G2 rheometer equipped with a parallel-plate geometry and 25-mm-diameter plates. The 1-mm-thick sheet samples were melted at a predetermined temperature for 5 min to eliminate the residual thermal history, and then experiments were carried out immediately.

RESULTS AND DISCUSSION

Mechanical and thermal properties

Table I presents the relationship between the composition ratio and the thermal and mechanical properties. The incorporation of PNP made the movement of the PEN chains easier at an elevated temperature. Pure PEN has a higher HDT value than the blends, and blending PNP reduced the HDT of the blends linearly. Mechanical data in Table I show that there

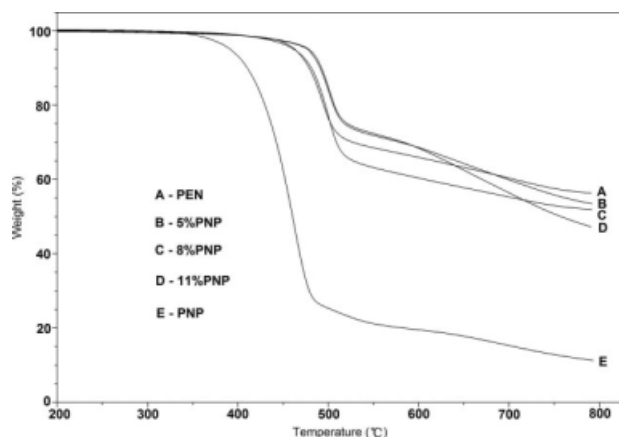


Figure 3 TGA traces for different PNP contents.

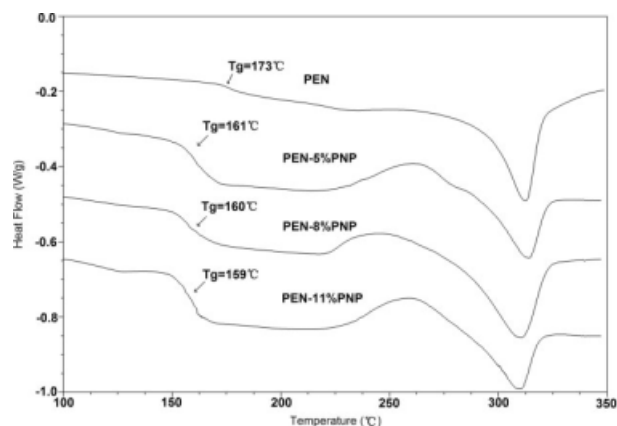


Figure 4 DSC thermograms of samples with various blending ratios.

were only very small differences between the blends with different PNP loadings. The tensile strength of the blends decreased sharply when the mass fraction of PNP was 11%. These results indicate that strong interfacial interaction layers formed between PEN and PNP.

The melting indices of PEN and its polymeric blends were characterized and are listed in Table II. The melt flowability of the blends was much better than that of PEN, and the fluidity of the blends increased as the PNP concentration increased. These results indicate that PNP acted as a plasticizer or lubricant: it reduced intermolecular friction and in this way increased the processing deformability of PEN.

TGA traces of PEN, PNP, and their polymeric blends in nitrogen are shown in Figure 3. The initial decomposition temperature of pure PEN and the PEN/PNP blends was approximately 500°C, and the initial decomposition temperature of PNP was about 400°C. The initial decomposition temperature of

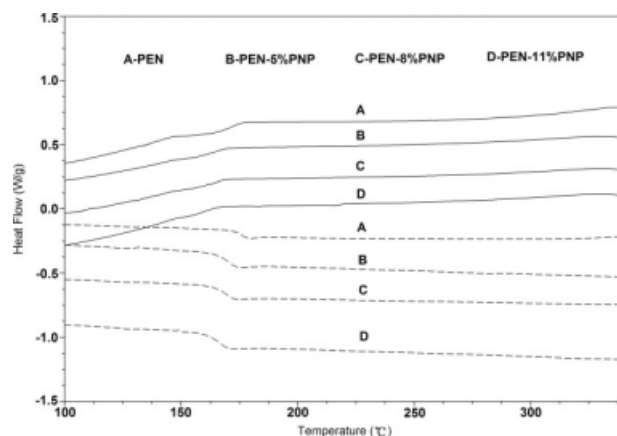


Figure 5 Second-run DSC thermograms. The solid lines represent cooling from 350 to 100°C, and the dashed lines represent heating from 100 to 350°C.

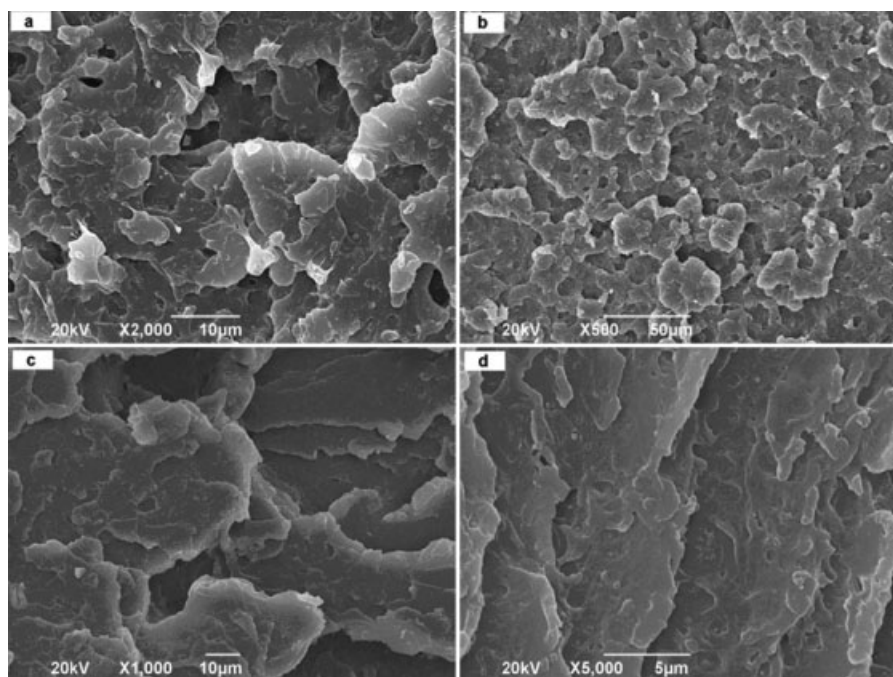


Figure 6 SEM images of PEN/PNP samples with various blending ratios: (a) 100 : 0, (b) 95 : 5, (c) 92 : 8, and (d) 89 : 11 (w/w).

PNP was lower than that of PEN, which did not reduce the initial decomposition temperature of the blends. This was mainly due to further polymerization of PNP while PNP and PEN were being melt-mixed in a corotating, twin-screw extruder at a high processing temperature. This result was confirmed by the DSC thermograms of the blends shown in Figure 4; the exothermic peak at 250–270°C in the DSC curves contributed to the polymerization of PNP.¹⁹ The char yield of the PEN/PNP blends decreased with increasing PNP content at 800°C. TGA studies proved that PNP would not be harmful to the thermooxidative stability of PEN.

DSC thermograms of PEN and its polymeric blends are shown in Figure 4. The results show

that the glass-transition temperature (T_g) of the blends decreased with increases in the PNP content; this happened because PNP promotes the chain mobility of PEN and improves the processing flowability of PEN in the melted state. The single T_g transition of the blends indicates favorable compatibility between PEN and PNP. The endothermic peak at 312°C on the DSC curves shows that PEN is a semicrystalline polymer,⁹ and the crystallinity of the blends was not reduced by the addition of PNP. However, in the second run of DSC (Fig. 5), the endothermic peak on the DSC curves disappeared because the low cooling rate of the blends did not meet the requirements of crystallization undercooling.

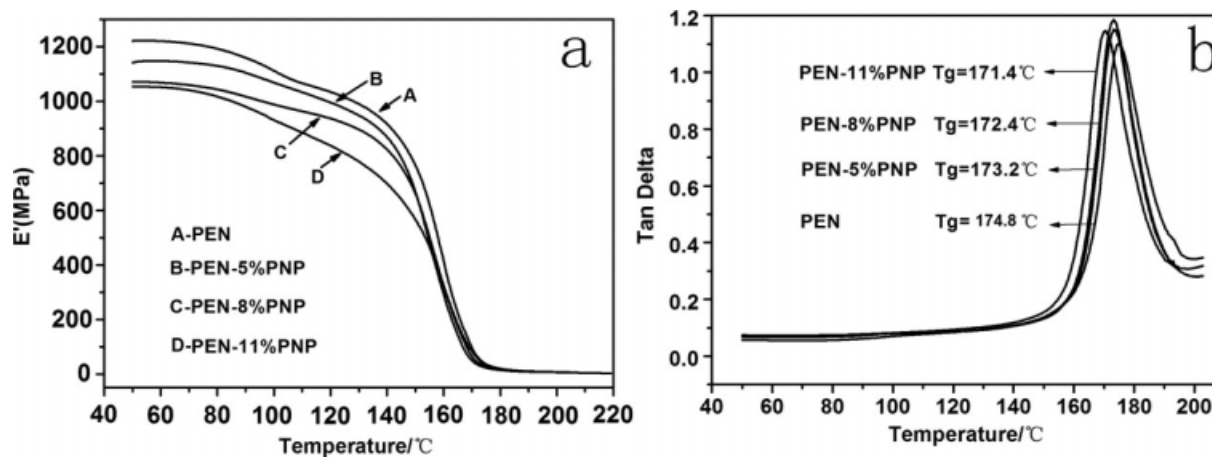


Figure 7 Temperature dependence of (a) E' and (b) $\tan \delta$ of PEN/PNP.

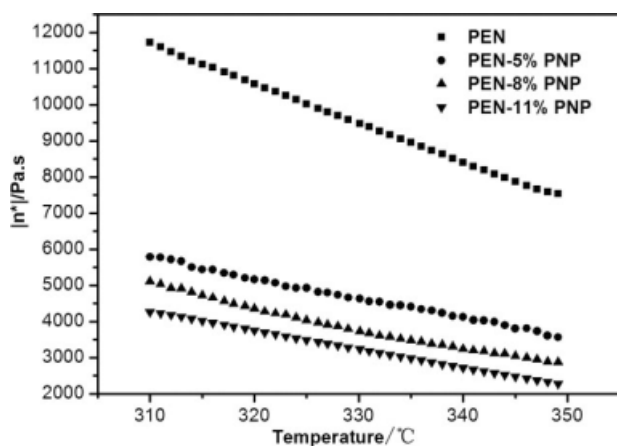


Figure 8 Complex viscosity (η^*) of pure PEN and its blends versus the temperature at 10 Hz.

SEM observations

SEM provided additional information on the morphology and phase adhesion. Figure 6 shows a high degree of phase adhesion in heterogeneous blends of various compositions; no phase separation was observed. At high and low PNP composition levels, the cryofractured specimens showed a homogeneous solid surface.²⁰ Moreover, the fractured surfaces of PEN and its blends were all toughness-fractured, and this suggests that PEN and PNP have favorable compatibility.

DMA

Figure 7(a,b) presents the storage modulus (E') and loss factor ($\tan \delta$) of pure PEN and its blends, respectively. Pure PEN presented higher E' values than all the blend samples, and E' decreased as the content of PNP increased. These results are in agreement with the HDT analysis. Similarly, T_g of the blends decreased in contrast to that of pure PEN, and the blends with a single T_g transition again

proved favorable compatibility between PEN and PNP.

Rheological measurements

The rheological properties of pure PEN and its blends were also studied in this work. Figure 8 presents the relationship between the complex viscosity and temperature for pure PEN and its blends. Generally, polymers with rigid molecular chains have higher viscoelastic flow activation energies and are sensitive to temperature variations.²¹ The complex viscosity of PEN and its blends decreased as the temperature increased linearly, but the variation of the complex viscosity that resulted from the blending of different amounts of PNP was more obvious than the variation that resulted from the temperature. These results reveal that PNP is an effective plasticizer for reducing the melt viscosity of PEN/PNP blends.

The dynamic storage modulus (G') and loss modulus (G'') data resulting from the dynamic frequency sweep measurements at 350°C for PEN/PNP blends with various PNP contents are compared in Figure 9(a,b), respectively. Obviously, the presence of the low-viscosity component PNP reduced G' and G'' of PEN, and this was attributed to the fact that PNP could reduce intermolecular friction and increase the deformability of PEN. In addition, G' and G'' of pure PEN and its blends increased sharply at a low frequency and exhibited a plateau at a high frequency.

CONCLUSIONS

PEN/PNP blends were prepared by melt mixing. The blending of PNP enhanced the fluidity of the PEN/PNP blends by reducing its viscosity, and this was beneficial for the processability of PEN. The blends possessed both excellent thermal stability and mechanical properties. DMA and DSC analyses showed that all the blends with various PNP

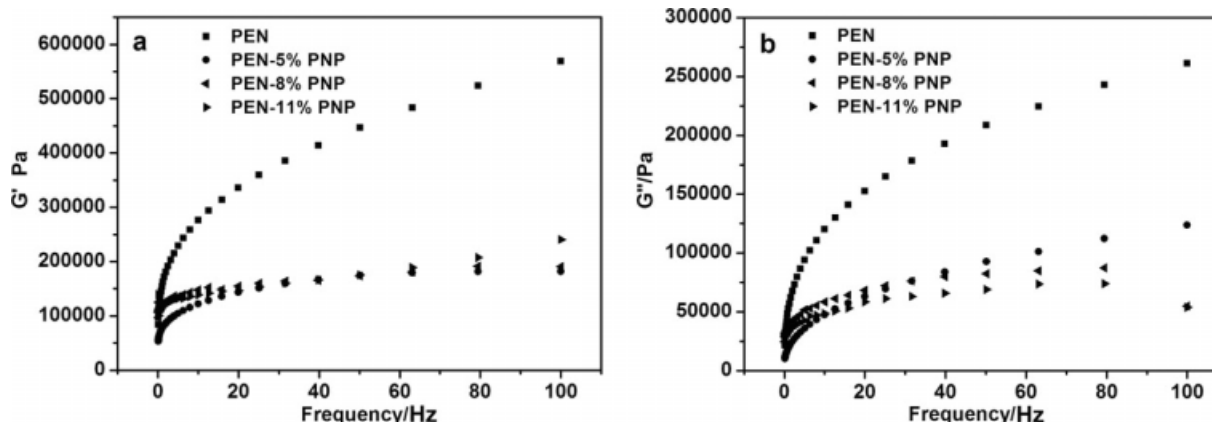


Figure 9 (a) G' and (b) G'' of pure PEN and its blends obtained from a dynamic frequency sweep at 350°C.

contents had only one T_g transition and exhibited excellent compatibility between PEN and PNP.

Rheological property studies of pure PEN and its blends have demonstrated that PNP is an effective plasticizer for reducing the melt viscosity of PEN/PNP blends, and this can be considered a feasible method for enhancing the processability of PEN.

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