

# Compatibility, Rheological, and Thermal Properties of the Melt Blends of PEN (HQ/PP) with PEN (HQ/RS)

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**ABSTRACT:** Two kinds of polyarylene ether nitriles (PEN) copolymers PEN (HQ/PP) and PEN (HQ/RS) were synthesized using 2,6-dichlorobenzonitrile (DCBN) with equal molar of phenolphthalein (PP) and hydroquinone (HQ), DCBN with equal molar of HQ and resorcin (RS), respectively. The melt-mixed blends of two PENs over the complete composition range were characterized by dynamic mechanical analyses (DMA), tensile testing, scanning electronic microscopy (SEM), and capillary rheometer test for their compatibility, thermal, mechanical, and melt flow properties study. DMA show a considerable compat-

bility between the two PENs. Morphology examinations reveal good component dispersion and strong interface adhesion. The capillary rheometer test found that the blending of PEN (HQ/RS) enhanced the fluidity of the PEN (HQ/PP)/PEN (HQ/RS) blends by reducing its viscosity, which is beneficial to the processability of PEN (HQ/PP). © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2934–2939, 2008

**Key words:** polyarylene ether nitriles; blend; compatibility; rheological properties; processability

## INTRODUCTION

In recent years, a series of high-performance engineering thermoplastic resins have been used widely for their excellent thermostability, chemical resistance, and mechanical properties. Because of these outstanding characteristics, many have been identified as preferred composites matrices, high temperature films, and cable insulation for applications in electrical, automobile, and aerospace industry.

Although the well known thermoplastic high-performance polymers such as aromatic poly(aryl etherketone),<sup>1,2</sup> aromatic polyether sulfones,<sup>3</sup> and aromatic poly(arylene ether nitrile)<sup>4,5</sup> have favorable properties in some areas and been commercially available for a long time, numerous attempts still have been devoting to resolve their insufficiency such as poor solubility,<sup>6–8</sup> high temperature processing.<sup>8,9</sup>

PEN ID 300 is the first commercialized composite product of polyarylene ether nitriles (PEN) by Idemitsu in late 1980s.<sup>10</sup> The resin of ID 300 is the homopolymer of 2,6-dichlorobenzonitrile (DCBN)

and RS, it possesses excellent thermal and mechanical properties as well as limitations mentioned above. The attempts that have been done to improve the properties of PEN to meet the different needs include: incorporation of bulky group in the backbone of polymeric chain to enhance its glass transition temperature ( $T_g$ ),<sup>11</sup> copolymerization or incorporation of pendant group to ameliorate its solubility.<sup>5–7</sup>

More recently, glass fiber-reinforced PEN (HQ/PP) composites have been prepared and its properties have been characterized in our lab,<sup>7,12,13</sup> both resin itself and composites exhibit outstanding high temperature stability as well as mechanical property. But the introduction of phenolphthalein also brings about the difficulties during the processing because of high melt viscosity, especially blending with the glass fiber. Therefore, improvement of processability by decreasing its melt viscosity is the main concern in our study. PEN (HQ/RS) has a similar structure as that of PEN (HQ/PP) but possesses properties of relatively lower melt viscosity than that of PEN (HQ/PP). Blending of high-performance polymers with low melt viscosity polymers or oligomers,<sup>14</sup> thermotropic liquid crystalline polymers (LCDs)<sup>9,15</sup> to improve the processability have been reported elsewhere. In this connection, blending the PEN (HQ/PP) with relatively low viscosity PEN (HQ/RS) and its compatibility as well as its effects on processability enhancement also attract our interest.

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TABLE I  
Relationship Between Composition and Thermal and Mechanical Properties

PEN (HQ/PP)/PEN (HQ/RS) (w/w)	100 : 0	80 : 20	60 : 40	50 : 50	40 : 60	20 : 80	0 : 100
HDT (°C)	181	175	170	165	162	159	149
Tensile strength (MPa)	86.5	89	82	77	87	95	89.5
Izod impact strength (kJ/m <sup>2</sup> )	9.72	11.5	12.6	10.9	14.2	17.5	16.5
Flexural strength (MPa)	158.5	166	172	161	189	193	210

In this article, PEN (HQ/PP) was melt-blended with PEN (HQ/RS) over the complete composition range and their compatibility, mechanical, thermal, and rheological properties were studied, and the possibility of using PEN (HQ/RS) as an aid for processability enhancement of PEN (HQ/PP) was also discussed.

## EXPERIMENTAL

### Materials

2,6-dichlorobenzonitrile was provided by Tianchen fine chemical co., Yangzhou, China. Hydroquinone, resorcin, and phenolphthalein were available commercially, and purchased without any further purification. Anhydrous K<sub>2</sub>CO<sub>3</sub> was dried under vacuum at 100°C before use. *N*-methyl pyrrolidone (NMP) was vacuum distilled over calcium hydride before use.

### Polymer synthesis

PEN (HQ/PP) and PEN (HQ/RS) were synthesized in pilot production via nucleophilic substitution reaction of DCBN with PP and HQ in a molar ratio of 2 : 1 : 1 and DCBN with RS and HQ in a molar ratio of 2 : 1 : 1, using anhydrous K<sub>2</sub>CO<sub>3</sub> as catalyst in NMP medium with 30% solid content, respectively. The scheme for synthesis has been described in our earlier work.<sup>7</sup> The product was crushed and washed with hot water repeatedly, and then vacuum dried at 100°C for 10 h and 150°C for 10 h continuously. The reduced viscosity for PEN (HQ/PP) and PEN (HQ/RS) is 0.88 and 1.23 dL/g, respectively.

### Preparation of specimens

PEN (HQ/PP) and PEN (HQ/RS) were blended from a TSSJ-25/40 corotating intermeshing twin-screw extruder (Chenguang Plastics Machinery Research Institute, Chengdu, China), with a 25-mm screw diameter and *L/D* ratio is 40. The PEN (HQ/PP)/PEN (HQ/RS) compositions prepared were 80/20, 60/40, 50/50, 40/60, 20/80 (w/w). The composites was chopped into granules and dried in vacuum oven at 120°C for 24 h, followed by injection molding to prepare standard samples for tensile, flexural, Izod impact strength, and thermal testing

using a injection and molding machine CJ80M2V (Zhende Plastics Machinery Co., Guangzhou, China).

### Characterization and apparatus

The tensile and flexural strength of the composites were measured at Instron testing machine (model 4302), with a crosshead rate of 5 mm/min for tensile strength and 2 mm/min for flexural strength, respectively. Izod impact strength was measured at XJ-40A pendulum apparatus (Wuzhong material tester factory, China) using acutely notched specimens (notch depth is 2mm). The data shown in results are the average values of six replicate measurements.

The melting index (MI) of the blends was characterized by Goettfert melting index instrument at 320 and 330°C with a weight of 2.16 kg, respectively.

Heat distortion temperature of the composites was measured according to ASTM D 648-72 at ZWK computer controlled HDT vikar tester (Shenzhen new sans materials testing machine co., China).

SEM was carried out on a JEOL JSM-5900LV instrument. The specimens were fractured in liquid nitrogen and the fracture surface was coated with a thin layer of gold prior to examinations.

DMA data were obtained by a dynamic viscoelasticity equipment (model Dupont DMA983) using the bending mode at the frequency of 1 Hz.

Rheological properties of pure polymers and their blends were measured using a Rheograph capillary rheometer (model 2002, Gottfert). Capillary with diameter of 1 mm and 30 mm long (*L/D* =30) was used for measurement.

## RESULTS AND DISCUSSION

### Mechanical and thermal properties

Table I demonstrates the relationship between composition ratio and thermal and mechanical properties. The incorporation of bulky phenolphthalein makes the movement of polymeric chain difficult. Pure PEN (HQ/PP) has a higher HDT value than that of pure PEN (HQ/RS) and blending of PEN (HQ/RS) reduced the HDT of blends lineally.

The Melting Index (MI) of the pure PEN (HQ/PP), PEN (HQ/RS), and their polymeric blends were characterized and listed in Table II. The melt fluidity

TABLE II  
Melting Index (MI) of PEN (HQ/PP)/PEN (HQ/RS)

MI (g)	Weight (Kg)	Ratio						
		100 : 0	80 : 20	60 : 40	50 : 50	40 : 60	20 : 80	0 : 100
320°C	2.16	0.24	0.298	0.404	0.418	0.580	0.78	1.212
330°C	2.16	0.358	0.387	0.584	0.652	0.908	1.285	1.588

of PEN (HQ/RS) is much better than that of PEN (HQ/PP) and is more sensitive to the variation of temperature. The fluidity of polymeric blends increased with PEN (HQ/RS) composition increasing. For blends with high content of PEN (HQ/RS), the extent of fluidity change is larger than that with low content.

For tensile strength results, blends with various compositions have no obvious difference, but both tensile strength and flexural strength of the blends are better than that of pure PEN (HQ/PP), and Izod impact strength and flexural strength increased monotonically with increasing PEN (HQ/RS). These results indicate a strong interfacial layer has been formed between two PENs; otherwise, the mechanical properties would be greatly decreased compared to that of pure PENs if two components are immiscible or semimiscible.

### SEM observation

SEM provided additional information on morphology and phase adhesion. Figure 1(a–c) characterizes a high degree of phase adhesion in heterogeneous blend with various compositions; no phase separation was observed. Whether at high or low PEN (HQ/RS) composition level, cryofractured specimens show a homogeneous solid surface.

It can be seen from Figure 1(c) the surface of the polymeric blend with 80 wt % PEN (HQ/RS) is more rough than that of 50 and 20 wt % ones. [displayed in Fig. 1(a,b)], suggesting that blends with high PEN (HQ/RS) composition are apt to toughness fracture, which is in accordance with the results got in Izod impact strength tests that toughness of 80 wt % PEN (HQ/RS) one is better than that of other blends.

### Dynamic mechanical analysis

Figure 2(a,b) exhibits the storage moduli  $E'$  and loss modulus  $E''$  of pure PEN and their blends, respectively. As seen in Figure 2(a), pure PEN (HQ/PP) has a highest  $E'$  values due to the rigid and bulky phenolphthalein group in the molecular chain, and the  $E'$  value of pure PEN (HQ/PP) has 60% maintenance at 200°C, while pure PEN (HQ/RS) got its lowest  $E'$  value at 180°C. The moduli of blends at

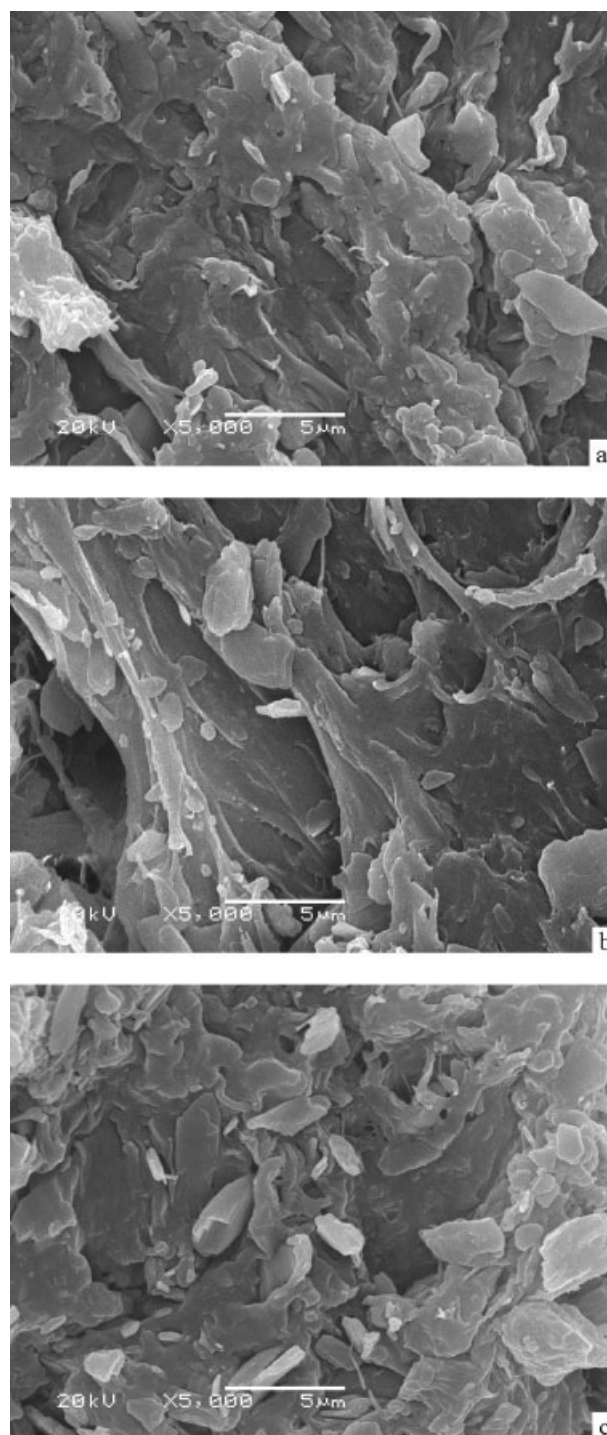
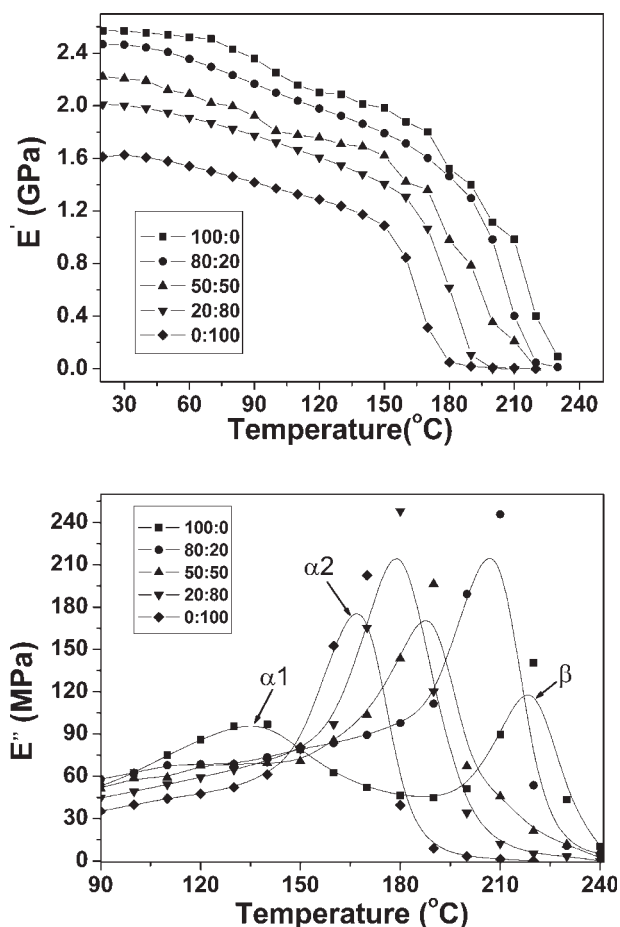


Figure 1 SEM images of cryo-fractured of blends with various PEN (HQ/RS) composition. (From a–c, the PEN (HQ/RS) content is 20, 50, and 80 wt %, respectively).





**Figure 2** (a) Temperature dependence of storage modulus of PEN (HQ/PP)/PEN (HQ/RS). (b) Temperature dependence of loss modulus of PEN (HQ/PP)/PEN (HQ/RS).

room temperature decrease with increasing amount of PEN (HQ/RS) in the blend, which also revealing that PEN (HQ/RS) is more of flexibility or less stiffness compared with PEN (HQ/PP).

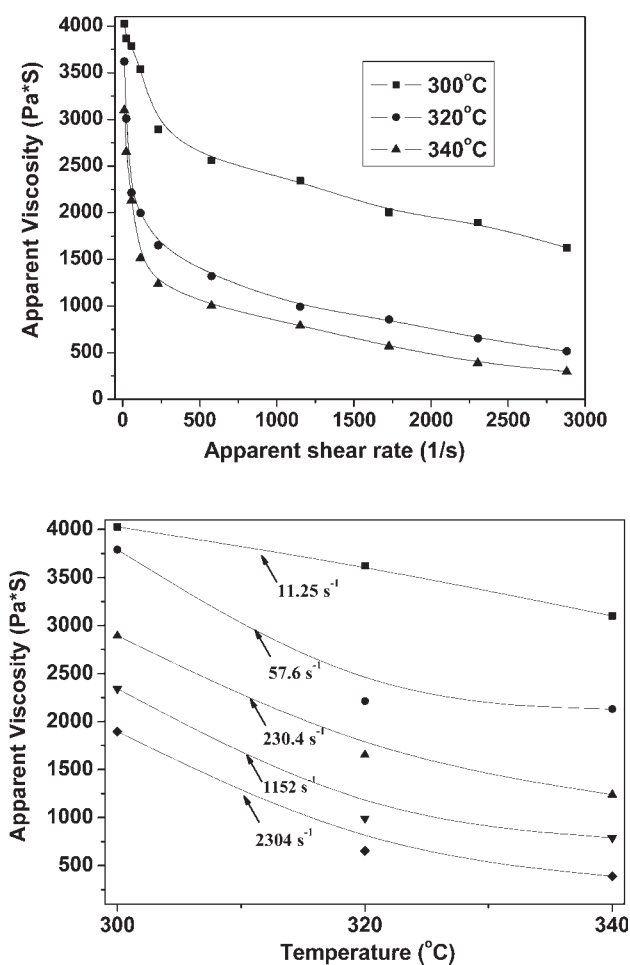
From Figure 2(b), it can be seen that pure PEN (HQ/PP) has two peaks at 136 and 220°C, designated as  $\alpha_1$  and  $\beta$ , corresponding to the  $T_g$  relaxation of soft segment of HQ homopolymer and rigid segment of PP homopolymer in polymeric chain, respectively. Pure PEN (HQ/RS) has only one peak at 168°C, designated as  $\alpha_2$ . The compatibilization between two components is evident from the fact that both original  $T_g$  relaxations disappeared and merged into a single  $T_g$  relaxation for the blends with different composition of PEN (HQ/RS), and the new  $T_g$  is in the middle of the original  $T_g$  peaks.

### Rheological measurements

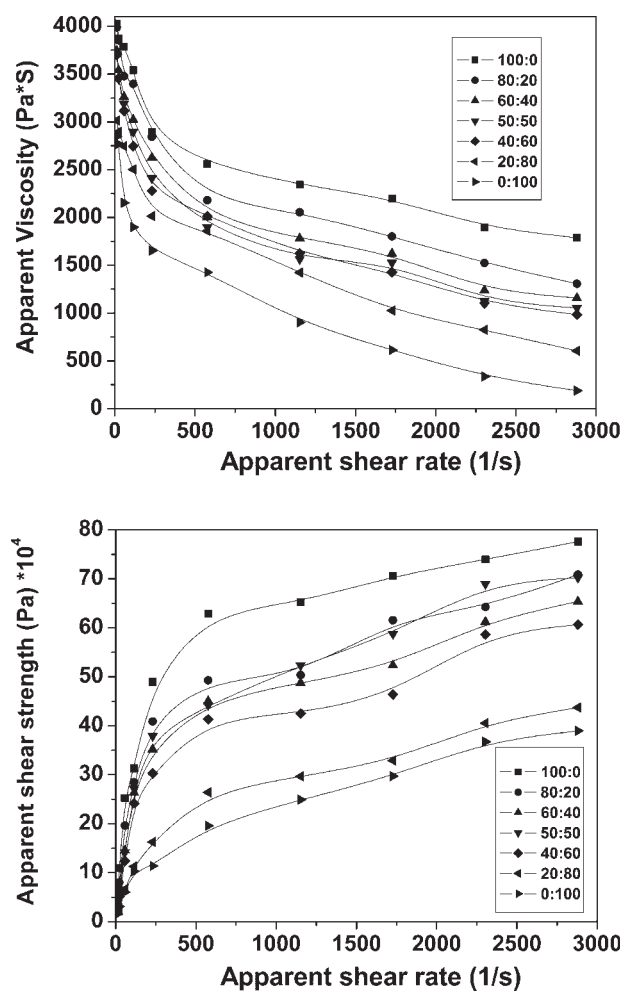
The rheological properties of pure PEN and their melt blend also studied in our article. Figure 3(a)

demonstrates the relationship between apparent viscosity and shear rate for pure PEN (HQ/PP) at different temperature. It can be seen that viscosity at 300°C is quite high, but decreases sharply at 320 and 340°C. The variation of viscosity between 320 and 340°C is small, revealing that the more temperature raising has little effect on its viscosity decreasing.

Figure 3(b) demonstrates the relationship between apparent viscosity and temperature for PEN (HQ/PP) at various shear rates. Viscosity also decrease with increasing shear rate, but the variation of viscosity resulted from shear rate variation is less obvious than that resulted from temperature change. Generally, polymers with rigid molecular chain have higher flowing activation energy and are sensitive to temperature variation.<sup>9</sup> The results got in viscosity versus shear rate and viscosity versus temperature revealed that PEN (HQ/PP) is such kind of polymer,



**Figure 3** (a) Plots for viscosity versus shear rate for PEN (HQ/PP) at various temperatures. (b) Plots for viscosity versus temperature for PEN (HQ/PP) at various shear rates.



**Figure 4** (a) Plots for viscosity versus shear rate for PEN blends at 300°C. (b) Plots for the shear strength versus shear rate for PEN blends at 300°C.

and raising the temperature is an effective alternative to reduce the melt viscosity of PEN (HQ/PP).

Raising the processing temperature also presents such problems as thermal oxidation and degradation reactions. For PEN, because of pendant cyano group on the molecular chain, crosslinking reaction may happen at high temperature,<sup>16,17</sup> which will influence the course of process as well as the quality of products made from blending.

The viscosity curves for the PEN (HQ/PP)/PEN (HQ/RS) blends at 300°C were shown in Figure 4(a). Because of the similar molecular structure, both curves of pure PENs are alike. But the viscosity of pure PEN (HQ/RS) decreases sharply with increasing shear rate because its molecular chain is more apt to align along the flow direction. Over the entire range of shear rate studied, the viscosity of the blends decrease monotonically with increasing PEN (HQ/RS) concentration. That is to say, PEN (HQ/RS) acts as a low molecular PEN (HQ/PP) or a compatible plasticizer in blends.

Raising temperature or increasing shear rate are two methods often taken during the process of high-performance thermoplastic resins, especially these with rigid molecular chain or bulky side chain. Raising temperature can bring the problems mentioned earlier, while increasing shear rate renders the shear strength elevated, which is also unfavorable to the processability.

Although the viscosity of all blends as well as PEN (HQ/PP) decreased monotonically with increasing shear rate, as seen in Figure 4(a), the another problem present simultaneously is high shear strength at high shear rate, as seen in Figure 4(b).

In Figure 4(b), it can be seen that the shear strength values of both pure PENs and blends increase with increasing shear rate, PEN (HQ/PP) has the highest shear strength, followed by blends, and PEN (HQ/RS) possesses the lowest shear strength over the entire range of shear rates studied. Although the shear strength increasing, the extent of increase is obviously differ, the shear strength values of pure PEN (HQ/RS) is no more than half of that of pure PEN (HQ/PP) in the range of shear rates between 500 and 3000 s<sup>-1</sup>. The shear strength of the blends decreased monotonically with increasing PEN (HQ/RS) composition at all shear rates. All these results revealed that the shear strength of PEN (HQ/PP) have been greatly decreased during melt flow by blending with PEN (HQ/RS).

## CONCLUSION

The new PEN blends have been prepared through melt mixed. The blends possess both excellent thermal stability properties of PEN (HQ/PP) and processability of PEN (HQ/RS) as well as excellent mechanical properties. DMA analyses show that all blends with various composition have only one  $T_g$  and exhibit excellent compatibility between the two PENs.

Rheological property studies of pure PEN and their blends demonstrates that temperature has a more obvious influence rather than shear rate on the viscosity variation of PEN (HQ/PP), and raising temperature can reduce its viscosity effectively. Blending of PEN (HQ/RS) with PEN (HQ/PP) can reduce the viscosity of the latter at all shear rate, which can be taken as a feasible method to enhance the processability of the PEN (HQ/PP).

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