

Copolymerization and Blending of Poly(phthalazinone ether ketone)s to Improve Their Melt Processability

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ABSTRACT: The melt processability of phthalazinone-containing poly(aryl ether)s (PAEs) was improved through copolymerization and blending. Poly(phthalazinone ether ketone) (PPEK) copolymers containing phthalazinone and bisphenol-A (BPA) moieties were synthesized through nucleophilic substitution polycondensation. The PPEK copolymers exhibited high glass transition temperatures, excellent thermooxidative properties, good mechanical properties and improved solubility, all of which can be tailored by changing the molar ratio of phthalazinone to bisphenol monomers. The rheological investigation indi-

cated that the incorporation of the flexible BPA moiety into the main chain lowered the melt viscosity of the copolymers. To improve the melt processability further, polymer blends of a PPEK copolymer/polycarbonate (PC) were prepared. The results suggested that blending is an effective approach for improving the melt processability of phthalazinone-containing PAEs. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2575–2580, 2007

Key words: poly(ether ketones); copolymerization; blending; rheology; high performance polymers

INTRODUCTION

High performance polymers have attracted increasing attention over the last several decades because of their wide range of applications in the aerospace, electrical, and automobile industries.¹ These applications generally require polymers exhibiting excellent thermal stability, good mechanical properties, and chemical and oxidative resistance. Poly(aryl ether)s (PAEs), a typical class of such high performance thermoplastics, have rigid aromatic rings in their backbones that contribute to their having these properties.

Considerable effort^{2–9} has been devoted to developing PAEs with improved thermal properties. Recently, PAEs containing phthalazinone moiety have been reported.^{10–15} Specifically, poly(phthalazinone ether ketone) (PPEK) and poly(phthalazinone ether sulfone) (PPES) with glass transition temperature (T_g) at 263 and 305°C, respectively,¹¹ were synthesized through nucleophilic substitution polycondensation. In addition, polyamides and polyimides containing phthalazinone moiety have also been investigated.^{16–18} The extremely high T_g s of these PAEs have been attributed

to the incorporation of the rigid phthalazinone moiety in the polymer backbone. All these polymers have excellent thermal properties as well as good solubility. Therefore, they are good candidates for applications as composite materials, nanofiltration, and ultrafiltration membranes, insulating coating and paint.^{19–21} Recent research also revealed their application potential as proton exchange membranes^{22,23} in fuel cells.

However, the high T_g s of these phthalazinone-containing PPEK and PPES result in extremely poor melt flow even under very high temperatures and pressure.¹¹ To expand the application of these PAEs, their melt processability needs to be improved by reducing the melt viscosity. In the research reported here, the melt processability of PAEs was investigated by employing both copolymerization and blending, two methods widely used for polymer modification because they are relatively economical to produce and generally cause a lower technical risk than developing a new polymer or polymeric composition.²⁴ Research in the area of polymeric blends, copolymers, and composites has been very active in both academic and industrial fields. Specific investigations on PAE blends with low-melt-viscosity oligomers¹¹ or liquid crystalline polymers^{13,25} have been reported. Here, we present the synthesis of PPEK copolymers containing bisphenol-A (BPA) as the flexible moiety. The chemical, thermal, mechanical, and rheological properties of these copolymers were

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investigated. In addition, a commercial polycarbonate (PC) containing the BPA moiety was employed to blend with a copolymer, and the results indicate that PC can significantly improve the melt processing properties of phthalazinone-containing PAEs.

EXPERIMENTAL

Materials

4-(4-hydroxyphenyl)-2,3-Phthalazin-1-one (DHPZ) was synthesized according to the procedure described elsewhere.¹⁰ Commercial products of bis(4-fluorophenyl) ketone (BFK) and bisphenol-A (BPA) were used without further purification. Sulfolane was refluxed over sodium hydroxide and activated carbon for 2 h and was distilled in vacuum. Anhydrous potassium carbonate and reagent-grade toluene were used without further purification. Commercial products of chloroform (CHCl₃), *N,N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylformamide (DMF), 1,2-dichloroethane (DCE), *o*-dichlorobenzene (DCB), and nitrobenzene (NB) were used as-received for the solubility test.

Sample preparation

Synthesis of PPEK copolymers

The typical synthesis of the PPEK copolymers was conducted in a 500-mL three-neck round-bottom flask equipped with a Dean-Stark trap, a condenser, a thermometer, and a nitrogen inlet. The reaction vessel was charged with 300 mL sulfolane and 100 mL of toluene as the dehydrating solvent. An excessive amount (40.0 g, 0.29 mol) of anhydrous potassium carbonate (K₂CO₃) catalyst was then added to the reactor while stirring. To synthesis, a copolymer containing 20% molar content of BPA, for example, a mixture of BFK (43.6 g, 0.2 mol), DHPZ (38.08 g, 0.16 mol), and BPA (9.12 g, 0.04 mol) was added to the reactor. The reaction mixture was heated under a stream of nitrogen until the toluene began to reflux. A reflux temperature was maintained at ~160°C until the presence of water was not observed in the Dean-Stark trap. On dehydration and slow removal of the toluene from the reaction mixture, the system temperature was gradually increased to 200°C and stabilized for 8 h. At the end of the reaction, the mixture was precipitated in water and filtered, redissolved in chloroform, and filtered again. The chloroform solution was concentrated and precipitated in ethanol. This purification procedure was repeated twice. Finally, the white fluffy PPEK copolymers were filtered and dried in a vacuum oven at 80°C for 48 h.

Preparation of PPEK copolymer/PC blends

A PPEK copolymer containing 40% molar ratio BPA was selected as the matrix to blend with a commer-

cial PC. The blends of various compositions were dissolved in chloroform (5 wt %) and stirred for 30 min. This solution was slowly poured into ethanol (5 times in volume). The resulting dispersion was filtered and the desired blends were obtained. Before processing and characterization, the blends were dried under vacuum at 140°C for 48 h.

Characterization

The inherent viscosities (IVs) of the PPEK copolymers were determined using an Ubbelohde viscometer at a concentration of 0.4 g/dL in chloroform at 25°C. The Fourier transform infrared (FTIR) spectra obtained in this work were recorded in air on a Nicolet-5DX spectrophotometer using a KBr disk. The samples were scanned from 4000 to 500 cm⁻¹ at a resolution of 4 cm⁻¹, with 120 scans being averaged for each spectrum. The glass transition temperatures were examined using a Dupont 2000 differential scanning calorimeter (DSC) at a heating rate of 10°C/min under a nitrogen flow. The thermooxidative stability was measured by thermogravimetric analysis (TGA) in an atmosphere of nitrogen at a heating rate of 10°C/min. The mechanical properties were measured at 23°C using a Shimadzu AG-2000A tester at a crosshead speed of 50 mm/min. The samples having dimensions of 4.0 × 6.0 × 55 mm³ were cut from the 55-mm² molding. At least five samples for each composition were tested, and the average value was reported.

A Shimadzu AG-2000A capillary rheometer was used to perform the rheological characterization using a 10-mm-long, 1-mm-diameter capillary (L/D = 10). The shear rate range studied was between 8.33 and 83.33 s⁻¹. The Rabinowitch correction and the entrance effect were taken into consideration because of the short capillary employed. The samples were placed into the capillary as fast as possible and kept in the molten state for 5 min prior to testing.

RESULTS AND DISCUSSION

PPEK copolymers

The PPEK copolymers containing phthalazinone and BPA moieties were prepared via nucleophilic polycondensation, according to the procedure depicted in Figure 1. The copolymers are denoted by BPA-COPPEK-*x*, where *x* refers to the BPA content by molar ratio.

The structure of the BPA-COPPEK copolymers was characterized by FTIR, as presented in Figure 2. The two strong absorption peaks at 1669 cm⁻¹ in the FTIR spectra of the copolymers were attributed to the carbonyl groups, with the peaks at 1592 and 1499 cm⁻¹ indicating phenyl groups. The C—H vibration appearing at 843 cm⁻¹ indicated the presence of BPA content in the copolymers. The fact that the

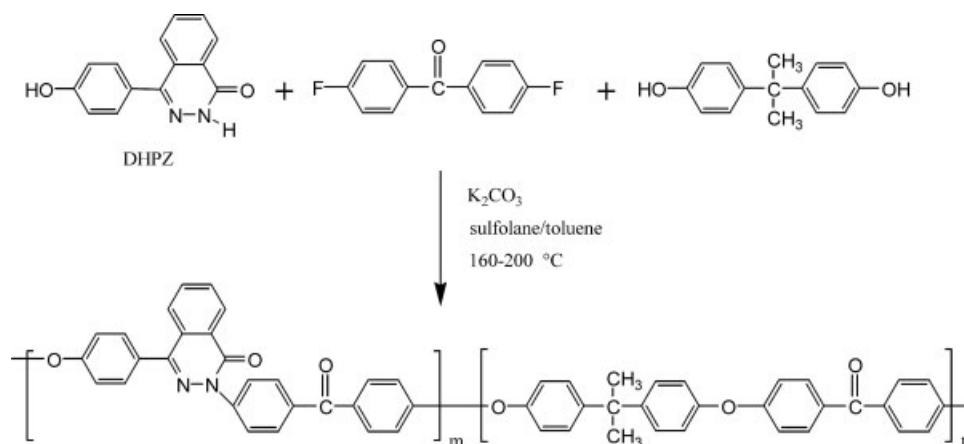


Figure 1 Synthesis scheme of PPEK copolymers.

hydroxyl group absorption peak at 3200 cm^{-1} was not observed, combined with the strong peak at 1237 cm^{-1} assigned to C—O—C absorption, implies that polycondensation occurred as expected.

The high molecular weight characteristics of the copolymers were indicated by the inherent viscosity (IV), which is between 0.58 and 0.74 dL/g for BPA-COPPEKs (cf. Table I) compared with the IV of 0.45 dL/g for the PPEK homopolymer obtained under the same reaction condition. From a statistical point of view, however, it may be difficult to form a long block chain of either BPA or DHPZ in the copolymers. Hence, random copolymers were expected, although further research needs to be conducted to clarify the structure.

The thermal properties of the BPA-COPPEK copolymers are shown in Table I. As this table shows, all of the copolymers exhibited T_g s higher than 170°C and their values were lower than that of the PPEK homopolymer. The rigid phthalazinone moiety contributed to the high T_g of the PPEK homopolymer at 263°C . The incorporation of the flexible aliphatic BPA moiety resulted in a decrease in the molecular rigidity and subsequently the

T_g , of the copolymers. It was also observed that the T_g depended on the BPA molar content linearly, indicating that the T_g s of the copolymer can be tailored by varying the molar content of the components. The thermogravimetric analysis (TGA) (cf. Table I) revealed that all of these copolymers were thermooxidatively stable, with the 5% weight loss temperature being higher than 485°C . The thermal stability decreased slightly with the incorporation of BPA. This result was attributed to the methyl groups in the BPA, which is less stable than the wholly aromatic structure in DHPZ.

The mechanical tensile strengths are presented in Table I. From these data, it can be seen that PPEK exhibited highest tensile strength of 87.4 MPa. The incorporation of 20 and 40% molar content of BPA resulted in gradual decreases in the tensile strength. With more BPA content in the copolymers, the tensile strength decreased significantly. The copolymer containing 80% molar content of BPA exhibited a tensile strength of 54.1 MPa. This strength decrease was also attributed to the flexibility associated with the aliphatic structure of BPA.

The solubility of the BPA-COPPEK copolymers at ambient condition was compared with that of PPEK homopolymer and commercial PEEK, as shown in Table II. PPEK and its copolymers exhibited better solubility than the commercial PEEK because of the incorporation of the phthalazinone moiety into the main chain. The crank and twisted noncoplanar phthalazinone moiety interrupted the regularity of the molecular chain that interferes with the packing of the chains, consequently facilitating the interaction between the polymer chains and the solvent molecules. Increasing the BPA content in the copolymers resulted in a significant improvement in their solubility. With the BPA molar content at 80%, the copolymer was soluble in all of the solvents investigated here. This improved solubility, combined with their excellent thermal stability, may allow these copolymers to be used in applications where solubility is required.

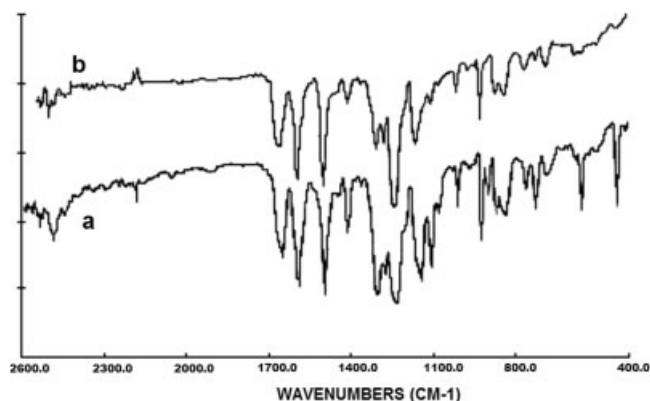


Figure 2 FTIR spectra of BPA-COPPEK copolymers (a) BPA-COPPEK-20; (b) BPA-COPPEK-40.

TABLE I
Thermal and Mechanical Properties of PPEK
and BPA-COPPEK Copolymers

Sample	IVs (dL/g)	T_g (°C)	TGA 5% loss (°C)	Tensile strength at break (MPa)
PPEK	0.45	263	500	87.4
BPA-COPPEK-20	0.58	242	495	82
BPA-COPPEK-40	0.62	218	487	81.8
BPA-COPPEK-60	0.74	183	490	68
BPA-COPPEK-80	0.66	170	485	54.1

The rheological properties of the BPA-COPPEK copolymers of various compositions are presented in Figure 3. Because the rigidity of BPA is lower than that of DHPZ, it was expected that the incorporation of the flexible BPA moiety into the main chain would improve the processability of PPEK. Experimentally, the copolymers can be processed at a much lower temperature than that of the PPEK homopolymer, which has a very high melt viscosity (10^5 – 10^6 Pa S) at processing temperatures close to 300°C.¹² From Figure 3, it is observed that with the introduction of BPA into the copolymers, the melt viscosity decreased gradually with increasing BPA contents. In addition, the pseudoplastic characteristics were evident, i.e., the melt viscosity decreased with the increase in the shear rate. However, the BPA-COPPEK copolymers still exhibited relatively high melt viscosities ($>10^4$ Pa S), which may cause difficulties during processing.

BPA-COPPEK/PC blends

Commercial polycarbonate (PC) has a better melt processability than phthalazinone-containing PPEK. To improve the melt processability further, polymer blends of BPA-COPPEK/PC were investigated. The BPA moiety, existing in both BPA-COPPEK and PC molecular main chains, was expected to increase the compatibility between the two polymers.

BPA-COPPEK-40 (40% BPA by molar ratio) was selected to form blends with PC at various weight compositions. Their T_g s and tensile strengths can be seen in Table III. The T_g is an indication of the extent

TABLE II
The Solubility of PEEK, PPEK, and BPA-COPPEK

	CHCl ₃	DMF	DMAc	DCE	DCB	NB	NMP
PEEK	–	–	–	–	–	–	–
PPEK	±	±	±	–	–	–	±
BPA-COPPEK-20	+	±	+	±	–	+	+
BPA-COPPEK-40	+	±	+	+	+	+	+
BPA-COPPEK-60	+	±	+	+	+	+	+
BPA-COPPEK-80	+	+	+	+	+	+	+

Key: +, fully soluble; ±, partially soluble; –, insoluble.

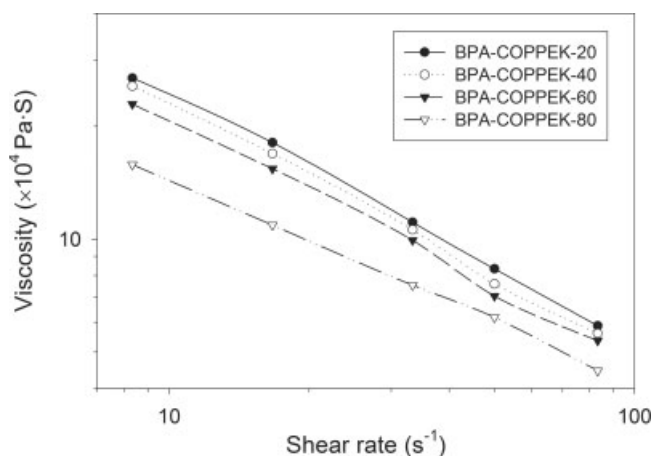


Figure 3 Melt viscosity versus shear rate for BPA-COPPEK copolymers at testing temperatures 20°C higher than their T_g s. (Data points are shown, the lines serving as guides.)

of miscibility in polymer blends. For establishing miscibility in a blend system, one would expect a single glass-rubber relaxation peak.^{26,27} It is observed that there were two T_g s in the blends having comparable contents of each component. The value of T_g shifted toward the median of the T_g s of the parent polymers. This phenomenon indicated that the polymer blends were partially miscible, although the blends with one dominating component exhibited single T_g s. The weak interaction between the two polymers was corroborated by FTIR, with the resulting spectrum a superposition of the individual BPA-COPPEK and PC spectra. This poor miscibility could be attributed to the random copolymer characteristics of the BPA-COPPEK, which may be less effective than a block copolymer in interacting with the BPA moiety in PC molecular chains. In addition, the introduction of PC resulted in a gradual decrease in the T_g of the blends because PC has a lower T_g than that of the PPEK.

All the blends exhibited relatively high tensile strengths because of the good mechanical properties of PC. Table III shows that the incorporation of PC

TABLE III
The T_g s and Tensile Strengths of
BPA-COPPEK-40/PC Blends

BPA-COPPEK- 40/PC	T_g 1 (°C)	T_g 2 (°C)	ΔT_g (°C)	Tensile strength at break (MPa)
100/0	218	–	–	81.8
80/20	204	–	–	69.1
60/40	182	215	33	65.5
40/60	179	215	36	59.3
20/80	178	–	–	49.3
0/100	150	–	–	58.8

caused a continuous decrease in the tensile strengths of the blends. For the blend with 80 wt % PC, the tensile strength was lower than that of neat PC. This irregular result may be caused by the partially miscible nature of the blends.

Figure 4 demonstrates the rheological properties of the BPA-COPPEK-40/PC blends with various compositions at 240°C. With the introduction of PC, the melt viscosity decreased significantly. Compared with that of BPA-COPPEK-40, the blends exhibited a much lower melt viscosity. This melt flow improvement can be clearly seen with the addition of PC as low as 10 wt %, the melt viscosity under this condition decreasing more than 10 times. Increasing the concentration of PC resulted in a further decrease in the melt viscosity. The blend containing 50 wt % PC exhibited viscosities two orders of magnitude smaller than that of the BPA-COPPEK-40 copolymer. In addition, the extrudate surface of the blends was smoother than that of the copolymer, indicating an improvement in the melt flow properties.

The effect of temperature on the viscosity of the blends was investigated with BPA-COPPEK-40/PC (75:25), as shown in Figure 5. The results indicated that increasing the test temperature generally led to a reduction in the melt viscosity. However, the reduction in viscosity caused by increasing the temperature was less significant than changing the composition of the blends. It has been reported that increasing temperature may cause crosslinking reactions due to traces of unendcapped end groups in the PAEs.¹¹ In addition, the degradation of PC at temperatures higher than 300°C may also limit the processing temperature. Therefore, increasing the processing temperature may not be an effective method for reducing the melt viscosity of the blends.

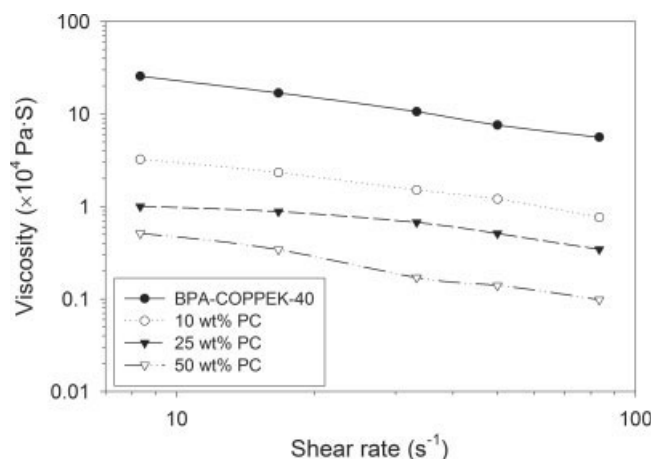


Figure 4 Melt viscosity versus shear rate for BPA-COPPEK-40/PC blends with various compositions at 240°C. (Data points are shown, the lines serving as guides.)

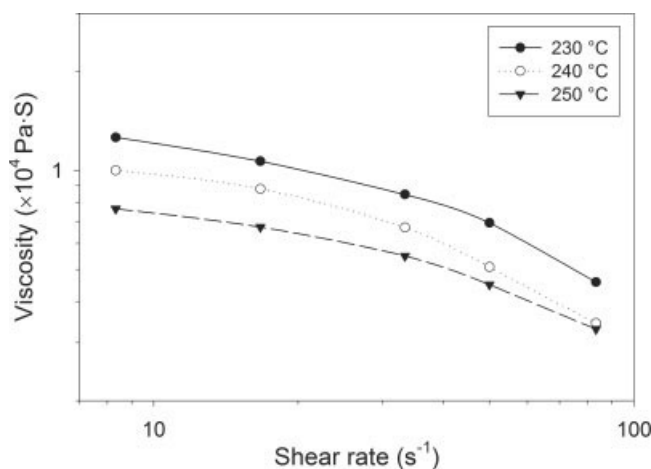


Figure 5 Melt viscosity versus shear rate for BPA-COPPEK-40/PC (75:25) blends at different temperatures. (Data points are shown, the lines serving as guides.)

CONCLUSIONS

Copolymerization and blending approaches were applied to improve the melt processability of phthalazinone-containing PAEs. PPEK copolymers containing phthalazinone and BPA moieties exhibited high glass transition temperatures, excellent thermooxidative properties, good mechanical properties, and improved solubility, all of which can be tailored by changing the molar ratios of bisphenol to phthalazinone monomer. The rheological investigation indicated that the incorporation of the flexible BPA moiety into the main chain lowered the melt viscosity of the copolymers. Polymer blends of BPA-COPPEK-40/PC of various weight compositions were prepared and their mechanical, glass transition, and rheological properties investigated. These blends exhibited significantly improved melt flow properties with a small sacrifice of the thermal and mechanical properties. These results suggested that blending is an effective approach for improving the melt processability of phthalazinone-containing PAEs.

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