

# Synthesis of Novel Poly(phthalazinone ether sulfone ketone)s and Improvement of Their Melt Flow Properties

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**ABSTRACT:** A series of novel poly(phthalazinone ether sulfone ketone)s was synthesized from bis(4-fluorophenyl) ketone, bis(4-chlorophenyl) sulfone, and 4-(4-hydroxybenzyl)-2,3-phthalazin-1-one through nucleophilic substitution polycondensation. The synthesized polymers exhibited surprisingly high glass transition temperatures and had excellent thermooxidative properties. The melt viscosities of these synthesized polymers are generally too high to be processed by common processing methods because of their very high glass transition temperatures and amorphous microstructure. An attempt was made to reduce their melt viscosities by solution blending the synthesized polymer with two kinds of oligomers: low molecular weight poly(phthalazinone ether sulfone ketone) and commercial poly(ether sulfone). The results proved that the addition of the oligomers to the polymers led to a marked decrease in melt viscosities. Furthermore, no obvious changes were observed in the thermal and mechanical properties of these blends after oligomer additions. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1425–1432, 1997

**Key words:** poly(phthalazinone ether sulfone ketone); phthalazinone; bis(4-fluorophenyl) ketone; bis(4-chlorophenyl) sulfone; rheological properties

## INTRODUCTION

In recent years there has been growing interest in the development of high performance polymers for the aerospace, electrical, nuclear, and automobile industries. This is because these types of polymers are technologically important, with applications such as composites matrices, high temperature films and adhesives, and cable insulation. The high performance plastics generally exhibit

outstanding high temperature stability, excellent mechanical properties, and radiation and hydrolytic stability.

The best known example is the poly(arylene ether)s or PAEs. Polymers in this category include poly(arylene ether sulfone) (PAES) and poly(arylene ether ketone) (PAEK). The typical commercially available PAEs include poly(ether ether ketone) (PEEK)<sup>1</sup> and poly(ether sulfone) (PES).<sup>2,3</sup> The molecular chains in these polymers contain rigid aromatic rings that give them a very high glass transition temperature ( $T_g$ ) and superior dimensional stability. The  $T_g$ s of PEEK and PES are 144 and 225°C, respectively. The value

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of  $T_g$  depends on the size and flexibility of linkages in the molecular chain. Some modified PAEs have been synthesized, which may be used at a temperature up to 260°C.<sup>4–7</sup> A great deal of effort has been expended in developing new high performance PAEs with high heat resistance. The result of this effort is the commercialization of PEEK and PES by ICI in the late 1980s and of poly(ether ketone ether ketone ketone) (PEKEKK) (Ultrapek) and poly(ether ketone ketone) (PEKK) (Hostatek) by BASF and Hoechst, respectively.

More recently we synthesized two amorphous thermoplastic resins with very high  $T_g$  values: poly(phthalazinone ether sulfone) (PPES) and poly(phthalazinone ether ketone) (PPEK).<sup>8,9</sup> The  $T_g$ s of PPES and PPEK are 305 and 263°C, respectively. It is generally known that some difficulties are encountered during the melt processing of thermoplastics that have high  $T_g$ s.<sup>10</sup> Therefore, improvement in the processing by decreasing melt viscosity has attracted considerable attention for these high-performance polymers. In this connection, blending the high performance polymers with low melt viscosity polymers such as liquid crystalline polymers<sup>11</sup> and synthesis of extremely low melt viscosity macrocyclic oligomers are reported to be useful to improve the melt processing of such plastics.<sup>12–14</sup>

As part of an ongoing project dealing with the synthesis and characterization of the PAEs containing phthalazinone moiety, this article reports on the synthesis and characterization of the PAEs, poly(phthalazinone ether sulfone ketone) (PPESK), based on 4-(4-hydroxyphenyl)-2,3-phthalazin-1-one. The blends of the PPESK with two kinds of PAE oligomers [low molecular weight poly(phthalazinone ether sulfone ketone) and commercial poly(ether sulfone)] were prepared by solution mixing. The rheological properties of these blends were tested and the results proved that the addition of oligomers can markedly improve their processing properties.

## EXPERIMENTAL

### Materials

4-(4-Hydroxyphenyl)-2,3-phthalazin-1-one (DHPZ) was synthesized according to the procedure reported by Berard and Hay.<sup>15</sup> Bis(4-fluorophenyl)ketone (BFK) and bis(4-chlorophenyl) sulfone (BCS) were obtained from Jilin University (China). These two monomers were purified by

recrystallizing them from ethanol. Anhydrous potassium carbonate and the reagent-grade solvents *N,N'*-dimethylacetamide (DMAc), sulfolane (TMSO<sub>2</sub>), and chlorobenzene (MCB) were used without further purification. Commercial PES oligomer was also supplied by Jilin University (China).

### Sample Preparation

#### General Procedure for Synthesis of PPESKs

The synthesis of a PPESK copolymer with an equivalent molar ratio of sulfone to ketone is used as an example. The synthesis of PPESKs 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 solvent DMAc (350 mL) (sulfolane was used as solvent when PPEK was synthesized), chlorobenzene (100 mL) as the dehydration solvent, and anhydrous potassium carbonate as the catalyst (40.606 g, 0.2938 mol). Then a mixture of 4-(4-hydroxyphenyl)-2,3-phthalazin-1-one (49.954 g, 0.20989 mol), bis(4-fluorophenyl) ketone (22.879 g, 0.10495 mol), and bis(4-chlorophenyl) sulfone (30.121 g, 0.10495 mol) was added to the reactor. The mixture was mechanically stirred and heated to reflux under a nitrogen atmosphere for 20 min. The condenser was removed and the chlorobenzene was distilled out over a 1.5–2.0 h period. At this stage, the temperature in the reactor rose stepwise from 145 to 164°C as chlorobenzene was distilled out. Subsequently, the resulting solution was kept at 164–165°C for a further 12–24 h. The PPESK oligomer was synthesized within a relative short period of polycondensation. At the end of polycondensation, a small amount of phenol was added to the reactor to endcap the PPESK formed. The reaction mixture was filtered and slowly poured into a mixture of ethanol and water (3 : 1 volume ratio) while being vigorously stirred. The PPESK produced was precipitated, and the resulting dispersion solution was filtered again. The obtained PPESK was dissolved in chloroform (10 wt %), filtered, and precipitated in methanol. The above purification procedure was repeated twice. Finally, the purified PPESK was dried at 50°C under vacuum, and a fluffy fluorescent white powder was obtained. The yield was generally higher than 85%.

#### Preparation of PPESK Blends Containing PAE Oligomers

The PPESK synthesized with an equivalent molar ratio of sulfone to ketone was selected as the ma-

trix (IVs = 0.6) in this work. The blends were composed of 5, 15, 20, 30, 40, and 50 wt % PPESK oligomer (IVs = 0.18), and 5, 10, 15, 20, 25, and 30 wt % PES oligomer [inherent viscosities (IVs) = 0.20], respectively. The mixtures of PPESK matrix with PPESK oligomer or PES oligomer were then dissolved in chloroform (20 wt %) and stirred for 30 min. The solution was slowly poured into methanol (5 times more than the chloroform solution in volume). The resulting dispersion solution was filtered and the desired blends thus obtained. Finally, the blends were dried under a vacuum at 140°C for 48 h.

### Instrumentation

The IVs of PPES and PPESK were determined using an Ubbelohde viscometer at a concentration of 0.5 g/dL in chloroform at 25°C. A concentration of 0.4 g/dL in phenol/chloroform (1 : 3 weight ratio) at 30°C was used for the viscosity measurement of PPEK. The glass transition temperatures were determined using a Perkin–Elmer differential scanning calorimeter (model DSC-7) at a heating rate of 10°C/min under a nitrogen flow, and the reported  $T_g$  values were recorded from the second scan after the first heating and quenching. The thermogravimetric analysis was performed with a Perkin–Elmer TGA-7 at a heating

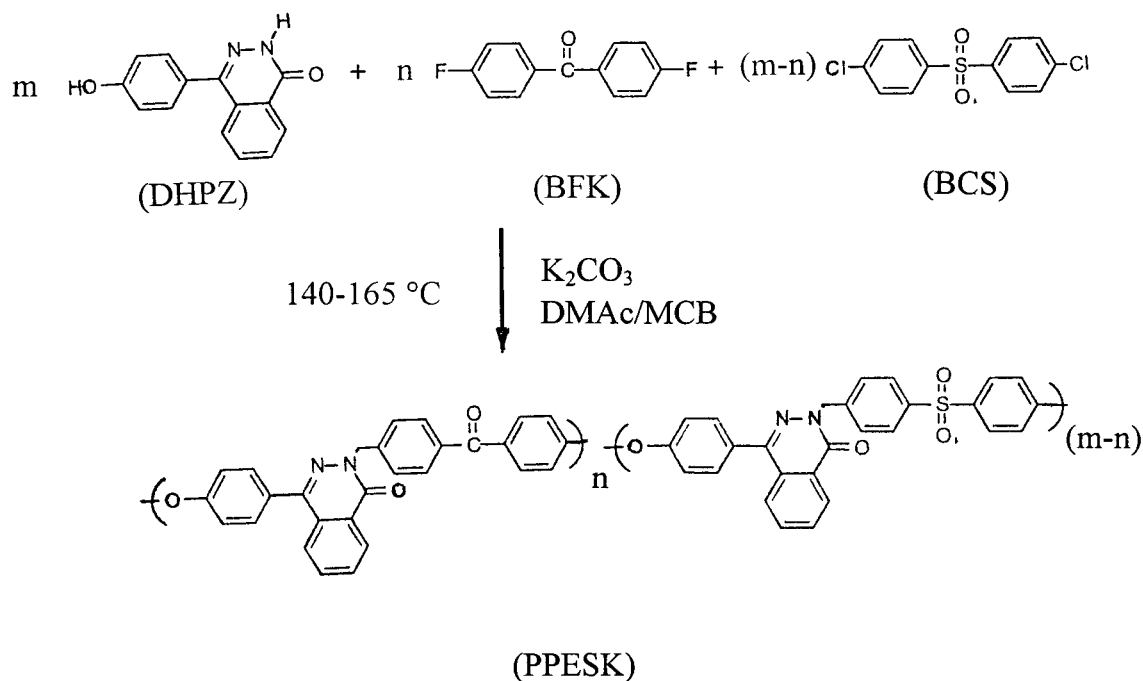
rate of 10°C/min in air and nitrogen. The structures of the as-cast and annealed samples were examined by means of wide angle X-ray diffraction (WAXD). The mechanical properties of PPESKs were determined at 23°C using a Shimadzu AG-2000A tester at a crosshead speed of 50 mm/min. The  $0.2 \times 6.0 \times 50 \text{ mm}^3$  samples were prepared by the solution casting method. At least five samples for each composition were tested and the average value was reported.

For the rheological tests, PPESKs and their blends in fluffy powder form were dried in a vacuum oven at 140°C for 48 h prior to testing. A Shimadzu AG-2000A capillary rheometer was used to perform the rheological characterization using a 5-mm long and 1-mm diameter capillary ( $L/D = 5$ ) at a temperature of 360°C. The shear rate range studied was within 10–200  $\text{S}^{-1}$ . The Rabinowitch correction and entrance effect were taken into consideration because of the short capillary employed. The samples were added into the capillary as fast as possible and kept in the melt for 5 min before testing.

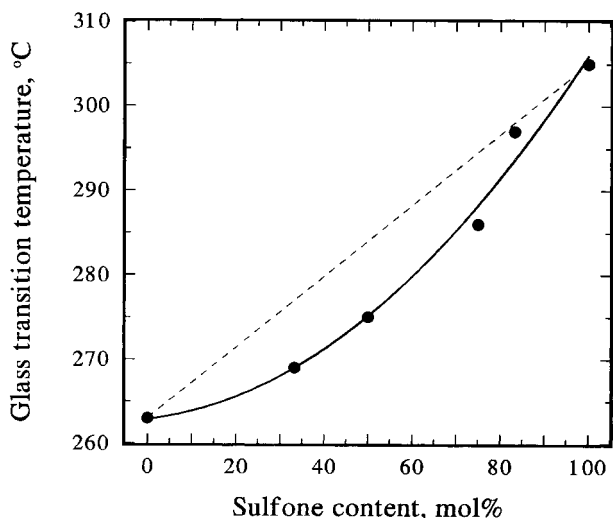
## RESULTS AND DISCUSSION

### Synthesis and Characterization of PPESKs

A series of PPESKs were prepared via nucleophilic polycondensation in the presence of anhydrous po-



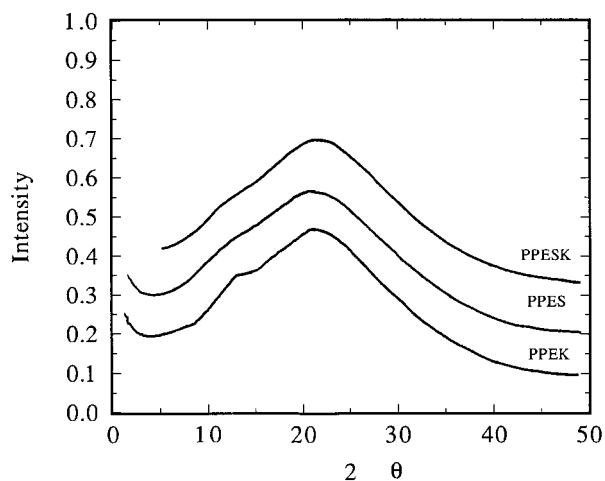
**Figure 1** Synthesis scheme of PPESKs.



**Figure 2** Variation of PPESKs  $T_g$ s with sulfone molar content in PPESKs.

tassium carbonate catalyst. The synthetic scheme is shown in Figure 1, and the detailed procedure was outlined in the Experimental section. The PPESKs obtained generally have very high molecular weights. The PPESK oligomer can be obtained in a relative short polycondensation time because the molecular weight increases with increasing reaction time for polycondensation systems. The PPESKs obtained were endcapped with phenol to increase the thermooxidative stability.

Figure 2 shows the variation of glass transition temperature of the PPESKs with the molar sulfone content based on the sulfone and ketone moles within the PPESKs. When the molar sulfone content of PPESKs equals 0 mol %, the copolymer corresponds to the homopolymer PPEK. Similarly, the 100 mol % molar sulfone content of PPESKs corresponds to the homopolymer PPES. From Figure 2 it can be seen that the PPESKs, PPEK, and PPES all have very high glass transition temperatures and the change of  $T_g$  values with molar sulfone content fits the rule



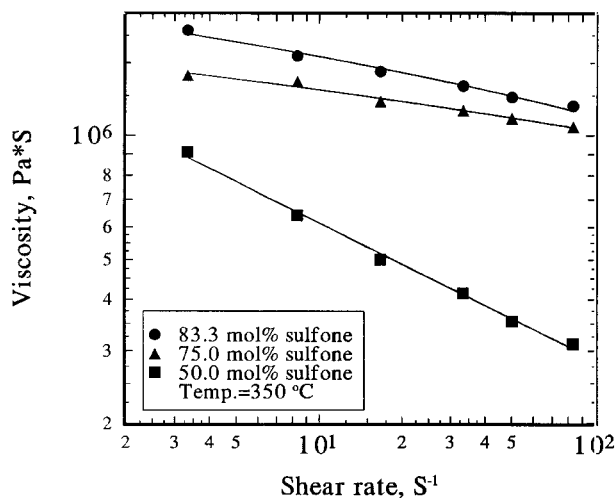
**Figure 3** WAXD traces of (a) PPEK, (b) PPES, and (c) PPESK (equivalent molar ratio of sulfone to ketone).

of random copolymers. The  $T_g$ s of PPESKs tend to increase with increasing molar sulfone content in PPESKs because the polysulfone generally has a higher glass transition temperature than the polyketone. Therefore, the  $T_g$ s of PPESKs can be tailored by changing the molar sulfone or ketone content in the PPESKs. Furthermore, the thermogravimetric data, as shown in Table I, reveal that the PPESKs are thermooxidatively stable.

Figure 3 shows the WAXD traces of PPEK, PPES, and PPESK with equivalent molar ratios of sulfone to ketone. As is evident, only very broad diffraction traces were observed and no sharp peaks were observed in these traces. This demonstrates that the synthesized polymers are amorphous in structure. Generally, PAEs containing sulfone groups are amorphous, whereas those containing ketone groups are semicrystalline. However, PPEK appears to exhibit an amorphous structure because of the incorporation of phthalazinone moiety into the main chain. In this case, the regularity of the molecular chain is inter-

**Table I** Thermogravimetric Data for PPESKs, PPEK, and PPES

	Sulfone Molar Content (%)					
	0	33.3	50.0	75.0	83.3	100
Inherent viscosities (dL/g)	0.35	0.28	0.56	0.49	0.31	0.52
5% temperature loss (°C)						
Air	508	501	505	504	503	510
N <sub>2</sub>	515	506	511	512	509	520

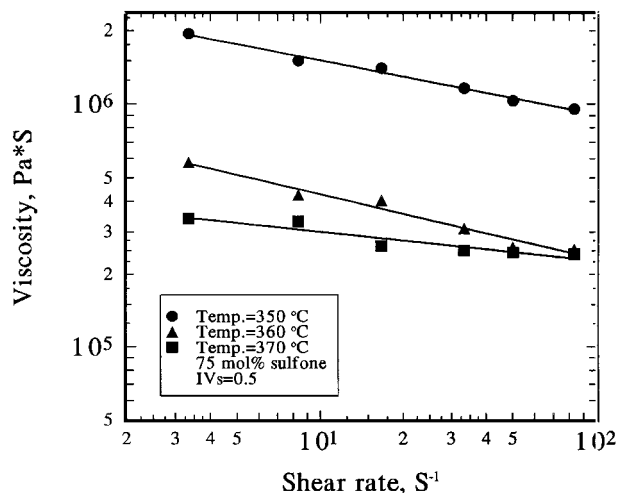


**Figure 4** Melt viscosity versus shear rate for PPESKs with various molar ratios of sulfone to ketone.

rupted by the unsymmetrical phthalazinone moiety compared with commercial PEEK. However, the amorphous structure of PPESK results in better solubility but higher melt viscosity.

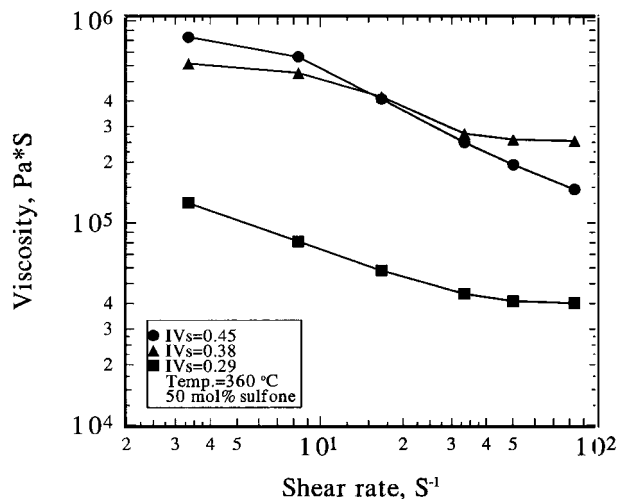
Figure 4 shows the relationship between melt viscosity and shear rate for the PPESKs with different sulfone molar contents. It can be seen that the viscosities tend to decrease with increasing ketone molar content in PPESKs due to the higher chain segment mobility of the bisphenylketone moiety compared to the bisphenylsulfone moiety. The PPESK containing 50 mol % sulfone demonstrates a clearer pseudoplastic behavior than do those containing 83.3 and 75.0 mol % sulfone because the PPESK has a lower sulfone molar content and lower melt flow temperature ( $T_f$ ). The increased flexibility of the molecular chain makes it possible for the molecular conformation to vary with the shear rate, with the result that the viscosity decreases as the shear rate is increased, a pseudoplastic phenomenon. However, all the PPESKs have very high melt viscosities (high than  $10^4$  PaS) and are difficult to process.

To investigate the effect of temperature on the viscosity of the PPESKs, the PPESK with an equivalent molar ratio of sulfone to ketone was selected and tested. The results are shown in Figure 5. It is apparent that increasing the test temperature from 350 to 360 °C generally leads to a reduction in the melt viscosity of PPESK. However, this decreasing tendency in melt viscosities becomes smaller when the temperature reaches 370 °C. It is believed that this behavior is caused by the crosslinking reactions of PPESK at a tem-

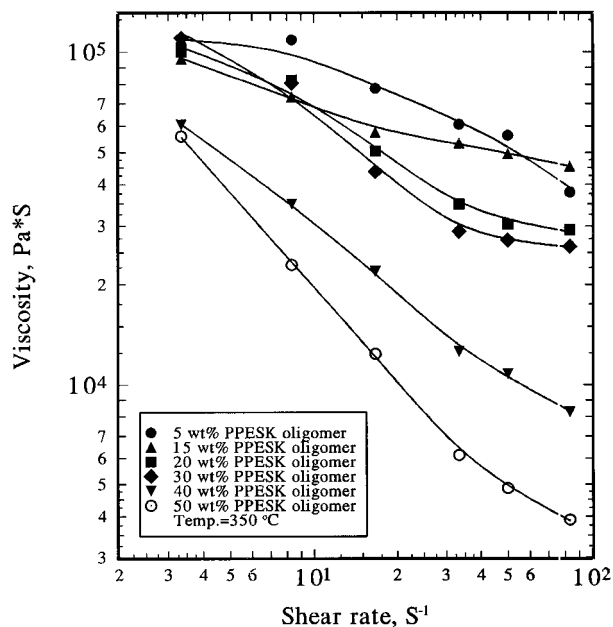


**Figure 5** Melt viscosity versus shear rate for PPESK at different temperatures.

perature<sup>16</sup> higher than 360 °C due to traces of un-encapped end groups. Therefore, raising the processing temperature may not be an effective method to reduce the PPESK's melt viscosity. Figure 6 shows the variation of melt viscosity with shear rate for PPESKs with different inherent viscosities. It is well known that low molecular weight polymer acts as an effective plasticizer for high molecular weight polymers, and this leads a decrease in melt viscosity. The relationship between weight-average molecular weight and zero-shear viscosity can be depicted by the following equation:



**Figure 6** Melt viscosity versus shear rate for equivalent molar ratio PPESK with various inherent viscosities.



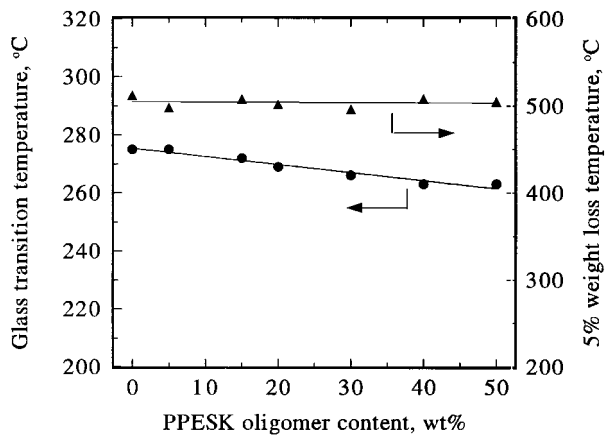
**Figure 7** Melt viscosity versus shear rate for blends with various PPEsk oligomer contents.

$$\eta_o = KM_w^n \quad (1)$$

when  $\bar{M}_w > \bar{M}_c$ ,  $n = 3.4$ ; when  $\bar{M}_w < \bar{M}_c$ ,  $n = 1.0-1.6$ ; and  $K$  and  $\bar{M}_c$  are constant and ceiling weight-average molecular weight, respectively. Equation (1) shows that the melt viscosity increases with increasing molecular weight or inherent viscosity in a power series. Evidently the PPEsk with lower inherent viscosity has a relative low melt viscosity, especially for the specimens with inherent viscosity lower than 0.3 dL/g as shown in Figure 6.

### Blends of PPEsk and PPEsk Oligomer

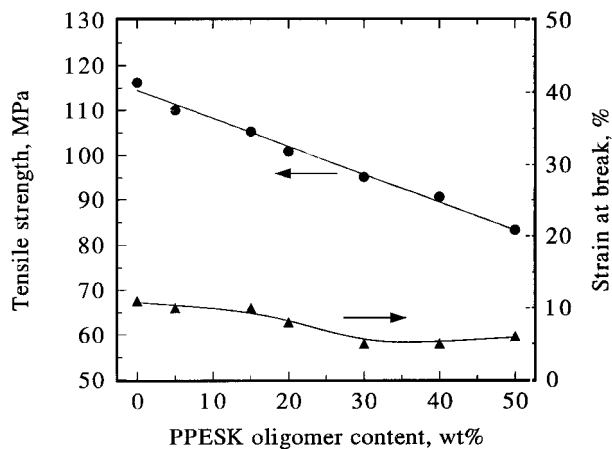
As stated above, low molecular weight PPEsk exhibits a relatively low melt viscosity. Therefore, blending PPEsk with PPEsk oligomer (IVs = 0.20) is beneficial in reducing the melt viscosity of PPEsk. Figure 7 demonstrates that the addition of PPEsk oligomer to PPEsk reduces the melt viscosity of PPEsk, especially when the PPEsk oligomer content reaches 50 wt %. The addition of PPEsk oligomer not only obviously reduces the PPEsk's melt viscosity, but also makes the pseudoplastic phenomena become more apparent: the melt viscosity decreases sharply with increasing shear rate. This is because the PPEsk oligomer acts as a plasticizer for PPEsk and results in the broadening of the



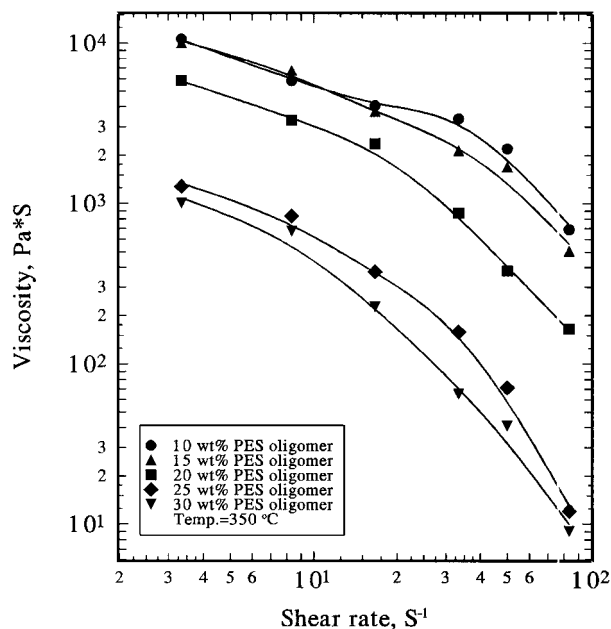
**Figure 8** The  $T_g$ s and 5% weight loss temperatures of the blends containing PPEsk oligomer.

molecular weight distribution of the blends. The blend containing 50 wt % PPEsk oligomer has the lowest melt viscosity, and the extrudate surface is smoother.

Figure 8 shows the  $T_g$ s and 5 wt % weight loss temperatures of the blends versus different PPEsk oligomer contents. The addition of PPEsk oligomer to PPEsk does not lead to an obvious change in the thermal properties. The  $T_g$  value of the blends decreases from 275 to 263°C with increasing PPEsk oligomer content from 0 to 50 wt %. Furthermore, the one  $T_g$  observed for these blends indicates that the PPEsk and its oligomer are miscible. The mechanical properties of the blends were also carefully investigated. Figure 9 shows the relationship between the tensile strength and the strain at break with the PPEsk oligomer content. The addition of PPEsk oligo-



**Figure 9** The mechanical properties of blends containing PPEsk oligomer.



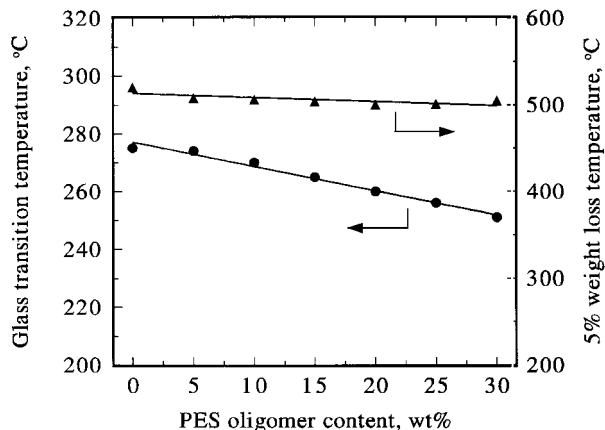
**Figure 10** Melt viscosity versus shear rate for the blends with various PES oligomer contents.

mer to PPESK results in a decrease of the tensile strength due to the relatively poor mechanical properties of the PPESK oligomer. The tensile strength decreases from 112 to 87 MPa with increasing PPESK oligomer content. However, no obvious change is observed in the strain at break for the blends. Despite this decrease in tensile strength, the blends have good mechanical properties and potentially could still be used as high-performance engineering plastics.

#### Blends of PPESK and PES Oligomer

Commercial PES oligomer, which has even more flexibility of the molecular chain, was also selected as a melt viscosity improvement agent. Figure 10 shows the relationship between the viscosity and shear rate for the blends containing various PES oligomer content. Compared with Figure 7, it is apparent that the PES oligomer is more efficient than the PPESK oligomer in reducing the melt viscosity because of the greater flexibility of the PES molecular chain compared with PPESK. The viscosity is sharply decreased by more than 20 with increasing PES oligomer content. In this case, the blends containing 20 wt % PES oligomer and above can be processed by injection molding.

Figures 11 and 12 show the thermal and mechanical properties of the blends containing various PES oligomer contents. Similar to the blends

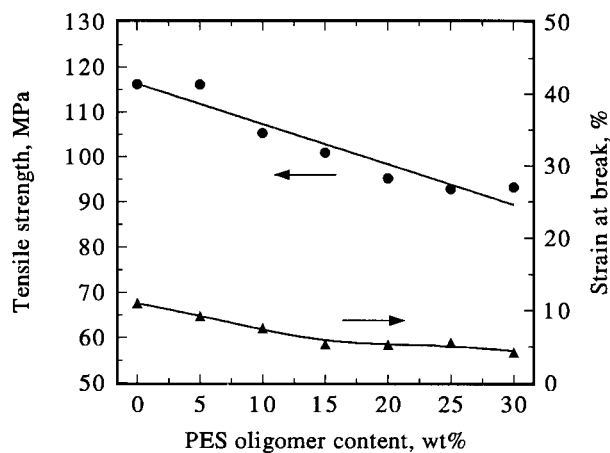


**Figure 11** The  $T_g$ s and 5% weight loss temperatures of the blends containing PES oligomer.

containing PPESK oligomer, only one  $T_g$  is observed for these blends. The addition of PES oligomer also causes decreases in the  $T_g$ s (from 275 to 251°C) and tensile strength (from 112 to 91 MPa) of the blends. An improvement in the melt viscosity of the blends containing PES oligomer is achieved at the expense of the heat resistance. However, the blends still exhibit remarkably high  $T_g$ s of higher than 250°C, which is 25°C higher than that of commercial PES.

#### CONCLUSIONS

PPESKs all have surprisingly high glass transition temperatures together with excellent thermo-oxidative properties. The  $T_g$ s of the novel PPESKs can be tailored by modifying the sulfone



**Figure 12** The mechanical properties of blends containing PES oligomer.

or ketone molar content in the PPESKs. The PPESKs have high melt viscosity due to their extremely high  $T_g$ s and their amorphous microstructure.

The melt viscosity of the novel PPESK is markedly improved by blending with PPESK oligomer or PES oligomer. However, PES oligomer addition is more efficient than the PPESK oligomer in reducing the melt viscosity. In spite of the slight decrease in glass transition temperature and mechanical strength, the blends of PPESK with PES oligomer or PPESK oligomer appear to have good heat-resistant and mechanical properties.

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