Properties of a Few Aromatic Poly(thioether ketones) as Sulfur-Containing High-Performance Polymers

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ABSTRACT: Several basic physical properties of poly-(thioether ketones) (PTEKs) were studied in comparison with corresponding ether analogs, poly(ether ketones) (PEKs), and various typical engineering plastics. The water absorption of PTEK (0.13%) was lower than that of the corresponding PEK (0.16%), probably because of the hydrophobic nature of the sulfide group. The dielectric breakdown strengths of PTEK and PEK were much greater than that of commercially available polymers. PTEK had higher dielectric breakdown strength than PEK. Although the volume resistivity of PEK considerably decreased after water absorption, that of PTEK remained high even after water absorption. PTEK exhibited a remarkably high refractive index $(n_D^{23}$ 1.66). α -Transition corresponding to T_g was observed at a high temperature (PTEK-1, 235°C; PTEK-2, 269°C) in the dynamic mechanical analysis. Young's modulus and tensile strength of PTEK were comparable to those of commercial high-performance polymers. PTEK also exhibited excellent flame resistance. Although the linear thermal expansion coefficient of PTEK was greater than that of PEEK, it was still within a practically acceptable level.© 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 1869–1874, 2004

Key words: poly(thioether ketones); dielectric properties; refractive index; thermal properties; mechanical properties

INTRODUCTION

Poly(ether ether ketone) (PEEK) (Scheme 1) is one of the most useful high-performance engineering plastics. PEEK has high thermostability, strong chemical resistance, and outstanding mechanical properties, and it is used widely as superior material with important applications to numerous high-technology fields, such as the nuclear and aerospace industries. However, PEEK shows a relatively low glass transition temperature ($T_g = 143^{\circ}$ C) and low processibility due to its low solubility and high melting point (T_m) around 340°C.¹⁻⁴ Further, PEEK is a very expensive polymer because highly electrophilic but costly 4,4'difluorobenzophenone is necessary as a monomer to obtain high molecular weight PEEK.^{1,5,6} In an attempt to overcome these drawbacks, various poly(ether ketones) (PEKs) have been developed, and their properties in relation to their chemical structures have been extensively studied.2-5,7-11

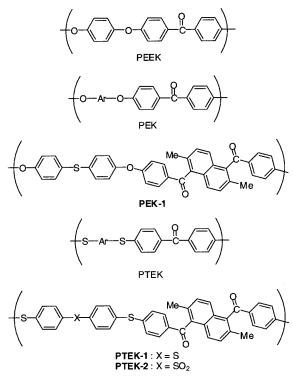
We previously prepared PEK-1 with both high T_g (228°C) and good solubility resulting from the use of a 2,6-dimethyl-1,5-bis(benzoyl)naphthalene unit in the polymer. Because of the crankshaft structure of 2,6-dimethyl-1,5-bis(benzoyl)naphthalene, the T_g was in-

creased, and because the aromatic groups of the unit were shaped into a nonplanar structure due to the steric repulsion between methyl and benzoyl groups, the solubility was increased. Further, we developed the corresponding poly(thioether ketones) (PTEKs), PTEK-1 and PTEK-2. Both PTEKs also showed high thermostability [PTEK-1: Tg 215°C, 5% weight loss temperature (T_{d5}) 436°C; PTĚK-2: T_{g} 245°C, T_{d5} 435°C] and high solubility. Although PTEKs were synthesized by polycondensation of aromatic dithiol and aromatic haloketones, high molecular weight PTEK can also be prepared by using aromatic dichloroketone, which is cheaper and less electrophilic than aromatic fluoroketone. The high nucleophilicity of thiol compensates for the lower electrophilicity of chloroketone. Because of these features, PTEK can serve as an alternate to PEEK.^{12,13}

PTEK, which has so far been viewed as a mere sulfur analog of PEKs, has not been paid much attention. Only the solubility, thermal properties, and crystallinity of PTEK^{12–17} have been studied, although a few reports have included information on tensile properties, oxygen index, and melt index.^{6,18} The effect of sulfur atoms on the properties of PTEK has been neglected because PTEK and the corresponding PEK have similar solubility, thermal properties, and crystallinity.^{6,12,13,15–17} However, the properties of the sulfur-containing functional group are far different from those of the corresponding oxygen-containing functional group. PTEK may show a lower water ab-

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Scheme 1

sorption property than the corresponding PEK because sulfide is more hydrophobic than its corresponding ether.^{19,20} Further, PTEK may exhibit a higher refractive index than corresponding PEK because the atomic refraction of sulfur is far greater than that of oxygen. Recently, much attention was paid to the development of plastic optical materials with a high refractive index.²¹ The above considerations prompted us to study the physical properties of PTEK. We found that PTEK has particularly interesting physical properties characteristic of novel class high-performance polymers.

This article deals with the physical properties of PTEK (i.e., water absorption, electrical properties, refractive index, mechanical properties, flame resistance, and dimensional stability) using PTEK-1 and PTEK-2 as typical PTEKs. The physical properties of the corresponding PEK were included, when appropriate, to discuss the characteristics of PTEK. We will demonstrate that PTEK may not only function as an alternate to PEEK, but that it may also serve as a superior material for various practical applications.

RESULTS AND DISCUSSION

Preparation of PTEK and PEK

PTEK-1, PTEK-2, and PEK-1 were synthesized according to the literature.^{12,13} Crude polymer was purified by repeated reprecipitation of chloroform solution into methanol. Inorganic impurities were removed by washing with boiling methanol. PTEK-1 [M_n 16,000, molecular weight distribution (MWD) 5.6], PTEK-2 (M_n 14,000, MWD 2.9), and PEK-1 (M_n 15,000, MWD 4.2) were used for the study. The films were prepared by the cast method from their chloroform solutions. (The wide MWD was attributed by the contamination of low molecular weight cyclic oligomers.^{12,13})

Water-absorption property

A polymer film of 0.7 mm thickness was dried at 50°C for 24 h and soaked in deionized water at 23°C for 24 h. The specimen was taken out of the water and was weighted within 1 min to measure the water absorption. Figure 1 shows the water absorption of PTEK-1, PEK-1, and various commercial high-performance polymers for comparison. PTEK-1 (0.13) and PEK-1 (0.16) showed the lowest water absorption among the polymers measured, except for polytetrafluoroethylene (PTFE) (0.00). The lower water absorption of PTEK-1 as compared to PEK-1 can clearly be accounted for by the fact that sulfide is more hydrophobic than the corresponding ether. Although the difference in water absorption is not great because PTEK-1 still has a hydrophilic carbonyl group, PTEKs tend to show superior water resistance than the corresponding PEKs.

Electrical properties

Figure 2 shows the dielectric breakdown strengths and volume resistivities of PTEK, PEK, and various

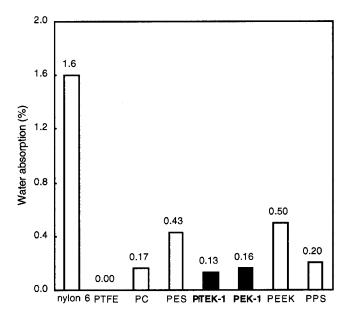


Figure 1 Water-absorption property of PTEK and PEK. Polymer structures, see Scheme 1. Data for nylon 6, PTFE, PC, and PPS were obtained from ref. 26, for PES from ref. 27, and for PEEK from ref. 28.

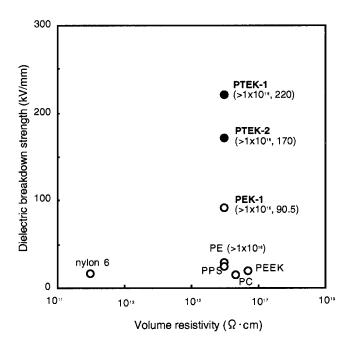


Figure 2 Volume resistivity and dielectric breakdown strength of PTEK and PEK. Polymer structures, see Scheme 1. Data for nylon 6, PC, PPS, and PE were obtained from ref. 26, and for PEEK from ref. 28.

commercially available polymers. These measurements were taken following the conditioning of a polymer film with 0.03 mm thickness under standard atmospheric conditions [22 \pm 2°C, 65 \pm 5% relative humidity (RH), 90 h]. The volume resistivities of PTEK-1, PTEK-2, and PEK-1 were greater than 1 $imes 10^{16} \ \Omega$ cm, which is the upper limit of the ohmmeter. On the other hand, the dielectric breakdown strengths of PTEK-1, PTEK-2, and PEK-1 were much higher than those of the other electrical insulator polymers. These results indicated that PTEK-1, PTEK-2, and PEK-1 are better electrical insulators than PEEK and polyethylene (PE), a representative electrical insulation material. Although it is still unclear why PTEK-1, PTEK-2, and PEK-1 have superior dielectric breakdown strengths, one of the possible explanations could be that PTEK and PEK contain no ionic impurities that hasten electron avalanches.^{22,23} Although PTEK and PEK can be readily purified by reprecipitation because of their high solubility, the complete removal of inorganic impurities from insoluble highperformance polymers such as PEEK remains very difficult.^{18,24} Interestingly, the dielectric breakdown strength of PTEK-1 was higher than that of PEK-1. This may be explained by the fact that PTEK-1 absorbed less water than PEK-1 under standard atmospheric conditions.

To reveal the effect of water on the electrical properties of PTEK-1, the volume and surface resistivity of PTEK-1 and PEK-1 were measured after the specimens were soaked in deionized water at 23°C for 24 h. The

TABLE I Volume and Surface Resistivities of PTEK and PEK^a

Polymer	PTEK-1	PEK-1				
Before water absorption ^b						
Volume resistivity (Ω cm) Surface resistivity (Ω)	$>1 \times 10^{16}$ $>1 \times 10^{16}$	$>1 \times 10^{16}$ $>1 \times 10^{16}$				
After water absorption ^c						
Volume resistivity (Ω cm) Surface resistivity (Ω)	$>1 \times 10^{16}$ $>1 \times 10^{16}$	$7.5 imes 10^{14} \ > 1 imes 10^{16}$				

^a Volume and surface resistivities were measured after applying direct current 500 V for 1 min

After conditioned at 22 \pm 2°C under 65 \pm 5% RH for 90 h.

^c After soaking in deionized water at room temperature for 24 h.

results are summarized in Table I. Although the electrical insulation ability of PEK-1 considerably decreased after water treatment, PTEK-1 kept a high volume resistivity even following water treatment. These findings highlight the importance of the waterabsorption property in relation to the electrical insulation property. A less hydrophilic PTEK-1 can be used as superior insulator under moist conditions.

Refractive index of PTEK

Because the sulfide group and the aromatic ring have a high atomic refraction, the refractive index of PTEKs caught our interest. Table II shows the refractive index of PTEKs and various other typical polymers for comparison. As expected, both PTEKs exhibited a high refractive index (1.66). These values are higher than those of any commercial high-performance polymers and are close to that (1.68) of poly(vinyl carbazole) (PVK), which is a representative optical material with a high refractive index.²⁵ These observations indicate that PTEK can be used as a thermally stable plastic optical material.

Mechanical properties

The mechanical properties of PTEKs were investigated to study their application to engineering plastics. Fig-

TABLE II Refractive Indexes						
Polymer ^a	PTEK-1	PTEK-2	PC	PTFE	PES	PVK
Refractive index ^b	1.66	1.66	1.59 ^c	1.35 ^c	1.65 ^d	1.68 ^e

^a Polymer structures; see Scheme 1.

^b Measured using Abbe's refractometer with a Na-D line laser.

^c Ref. 26.

^d Ref. 27.

^e Ref. 25.

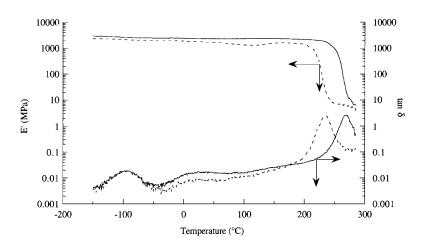


Figure 3 Temperature dependent storage modulus and loss tangent of PTEK-1 (dotted lines) and PTEK-2 (solid lines).

ure 3 shows the temperature-dependent storage modulus (E') and the loss tangent (tan δ) of PTEK-1 and PTEK-2. Broad β -transition and γ -transition were observed around room temperature and at -95°C, respectively, for both PTEK-1 and PTEK-2. α-Transitions, 235°C for PTEK-1 and 269°C for PTEK-2, corresponded to their T_{q} 's obtained by differential scanning calorimetry measurement. Because the sulfonyl group in PTEK-2 is more polar and bulky than the sulfide group in PTEK-1, PTEK-2 has a higher T_g . The dynamic storage modulus (Young's modulus), tensile strength, and elongation at break of PTEKs and various typical engineering plastics are summarized in Table III. Young's modulus of PTEKs at room temperature (PTEK-1 1770 MPa, PTEK-2 2330 MPa) is comparable to that of other typical high-performance polymers. The dynamic storage modulus of PTEKs decreased slightly until around 190°C for PTEK-1 and 235°C for PTEK-2 because of their high T_g 's, whereas that of PEEK decreased remarkably above the T_{q} (143°C). Thus, PTEKs can be used at higher temperatures without any decrease in their strength. However, noncrystalline PTEKs lost their strength drastically above their $T_{g'}$ and semicrystalline PEEK slowly lost its strength until 300°C because of the maintenance effect of the modulus by the crystal phase. Therefore, PTEKs have a higher modulus than PEEK above around 140°C below the T_g 's of PTEKs, although PEEK has a higher modulus above the T_g 's of PTEKs. PTEK-1 and PTEK-2 have as high tensile strengths as PEEK, polyimide (PI), and poly(ether sulfone) (PES). Tensile yield behavior was observed during measurement at room temperature for both PTEKs. The above results indicate that PTEKs are as strong as conventional high-performance polymers.

Flame-resistant property

Because wholly aromatic polymers such as PEEK and poly(phenylene sulfide) (PPS) have good flame-resistant properties, the flame resistance of PTEK-1 was investigated (UL 94 VTM). PTEK-1 showed VTM-0 without the addition of any flame retardant. The excellent flame resistance of PTEK-1 may be attributed to its high-aromatic ring content, although PTEK-1 has methyl groups, which generally decrease flame resistance.

TABLE	E III
Mechanical I	Properties

		1			
Polymer ^a	PTEK-1	PTEK-2	PEEK	PI	PES
Tensile strength ^b (N/mm ²) Elongation at break ^b (%) Young's modulus ^e (MPa)	91.2 10 1770	106 11 2330	97.1 ^c 80 ^c 2840 ^c	118 ^d 10 ^d 2070 ^d	84.3 ^d 40–80 ^d 2450 ^d

^a Polymer structures; see Scheme 1.

^b Measured at a cross-head speed of 5 mm/min. Specimen: JIS K 6251, dumbbell shape No. 6.

^d Ref. 27.

^e Dynamic storage modulus at room temperature which was measured by DMA using film-tension geometry at a heating rate of 2°C/min, a frequency of 10 Hz, and a dynamic strain of 0.1%.

^c Ref. 28

Dimensional Stability ^a						
Polymer ^b	PTEK-1	PTEK-2	PEEK	PES	PPS	PC
Linear thermal expansion coefficient $(\times 10^{-5} \circ C^{-1})$	5.1	5.4	4.6 ^c	5.5 ^d	5.5°	6.6 ^e
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TABLE IN

^a Measured by TMA using tension geometry with a load of 2 g at a heating rate of 5° C/min in N₂ atmosphere.

^b Polymer structures; see Scheme 1.

^c Ref. 28.

^d Ref. 27.

^e Ref. 26.

Dimensional stability

Although PEEK is a semicrystalline polymer, PTEK is an amorphous polymer. Therefore, better dimensional stability is expected for PTEK. The linear thermal expansion coefficient of PTEKs was measured, and the results are summarized in Table IV. However, the linear thermal expansion coefficients of PTEK-1 and PTEK-2 are greater than that of PEEK, although they are within the practically acceptable level.

CONCLUSION

In this study, the fundamental physical properties of PTEK were measured and compared with those of the corresponding PEK and various typical engineering plastics. It was demonstrated that PTEK has significant advantages in terms of polymer properties to serve as novel high-performance polymers, underlining the fact that PTEK is more than a simple sulfur analog of PEK. PTEK has high water resistance because of the hydrophobic nature of their sulfide group. Further, PTEK shows high-dielectric breakdown strength and high-volume resistivity even after water absorption. By use of PTEK, smaller electrical devices that are moisture-safe may be developed, because thinner electrical insulation films can be prepared with PTEK. The high refractive index of PTEK is adequate for thermally stable optical materials. Thus, PTEK has well-balanced properties, namely good processibility, high electrical insulation, good mechanical properties, high thermostability, and excellent flame resistance. It was shown that PTEK constitutes useful novel high-performance polymers and potential substitute for PEEK. Further, it was demonstrated that the introduction of a sulfur-containing functional group was a useful approach to the creation of a novel polymer with unconventional properties.

EXPERIMENTAL

Materials

PTEK-1 (M_n 16,000, MWD 5.6), PTEK-2 (M_n 14,000, MWD 2.9), and PEK-1 (M_n 15,000, MWD 4.2) were synthesized according to the literature.^{12,13} Molecular weight and molecular weight distribution were measured by gel permeation chromatography (GPC) on a JASCO HSS-1500 system (Tokyo, Japan) equipped with three consecutive polystyrene gel columns (TOSOH TSKgel G5000HXL, G4000HXL, and G2500HXL; Yamaguchi, Japan) eluted with THF at a flow rate of 1.0 mL/min calibrated by polystyrene standards.

Preparation of cast films

A polymer was dissolved in CHCl₃ to obtain $\sim 3\%$ solution. The solution was filtered through membrane filter (pore size, 0.45 μ m) to be placed in a Petri dish. After most CHCl₃ was evaporated at room temperature over a period of 3 days, the film was dried in vacuo for an additional 2 days at 40°C. The film (~ 0.030 mm thick) was peeled from the dish. For the measurement of water absorption, rather thick film (~ 0.7 mm thick) was prepared as well from the concentrated CHCl₃ solution with extremely slow evaporation.

Water absorption

Water absorption was measured according to Japanese Industrial Standard (JIS) K 6911: A specimen of 70 mm diameter \times 0.7 mm thickness was dried in an oven at 50°C for 24 h and was cooled to room temperature in a desiccator over silica gel. After the dry specimen was weighted by using a Shimadzu Analytical Balance AX200 (Kyoto, Japan), it was soaked in deionized water at $23 \pm 1^{\circ}$ C for 24 h. After the specimen was taken out from the water, the external water was removed, and the specimen was weighted in 1 min. Three specimens were used for each polymer, and the water absorption was reported as the average.

Dielectric breakdown strength

After a specimen of 90 mm diameter \times 0.03 mm thickness was conditioned at 22 ± 2°C under 65 \pm 5%RH for 90 h, dielectric breakdown strength was

measured with alternating current according to shorttime breakdown method according to JIS C 2110, on a Kojimadenki type SO Dielectric Strength apparatus (Osaka, Japan). Three specimens were used, and the dielectric breakdown strength was reported as the average.

Resistivity

After a specimen of 90 mm diameter \times 0.03 mm thickness was conditioned at 22 ± 2°C under 65 ± 5% RH for 90 h, volume and surface resistivities were measured by using a Kawaguchidenki Teraohmmeter R-503 instrument (Tokyo, Japan) according to JIS K 6911. Two specimens were used for each polymer, and the resistivity was reported as the average. After a specimen was soaked in deionized water at 23 ± 1°C for 24 h, it was taken out, and the external water was removed. Resistivity was measured as well in 1 min.

Refractive index

Refractive index was measured at $23 \pm 1^{\circ}$ C by using an Atago Abbe's Refractometer Type 4T instrument with a Na-D line (589.3 nm) laser (Tokyo, Japan) according to method A of JIS K 7142.

Dynamic mechanical analysis

A cast film with dimensions of $0.02 \times 5 \times 40$ mm was used for the analysis. Dynamic mechanical analysis (DMA) was performed on a Rheometric Scientific F. E. Viscoelasticity Analyzer RSA-II instrument (New Jersey) by using film-tension geometry from -150 to 290°C at a frequency of 10 Hz, a heating rate of 2°C/ min, and a dynamic strain of 0.1% according to method A of JIS K 7198.

Tensile properties

A specimen (JIS K 6251, dumbbell-shape No. 6) was used to measure tensile properties on a Shimadzu Auto Graph AGS-10kNG instrument at a cross-head speed of 5 mm/min according to JIS K 7127. Five specimens were used for each polymer, and the tensile strength and elongation at break were reported as the average.

Flame-resistant property

A specimen with dimensions of $0.02 \times 50 \times 200$ mm was used to measure flame-resistant property on a Sugashikenki Combustive Apparatus UL-94V type (Tokyo, Japan) with a flame of 20 mm high for ignition time of 3 s according to the UL 94VTM method.

Static thermomechanical analysis

A cast film with dimensions of $0.04 \times 4 \times 30$ mm was used for the analysis. Static thermomechanical analysis (TMA) was performed on a Seiko Instruments (Chiba, Japan) Thermomechanical Analyzer TMA120 in the tension mode with a load of 2 g at a heating rate of 5°C/min in N₂ atmosphere (flow rate of 200 mL/ min).

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