

Dynamic Mechanical Properties of Al₂O₃/Poly(ether ether ketone) Composites

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ABSTRACT: The dynamic mechanical properties of high-performance polymer matrix composites based on semicrystalline poly(ether ether ketone) (PEEK) and aluminum oxide (Al₂O₃) were evaluated in the temperature range of 30–250°C with a three-point-bending mode at a frequency of 1 Hz. The storage modulus and loss modulus changed significantly with the variation of the Al₂O₃ content in the PEEK matrix. The Al₂O₃ reinforcement was more pronounced above the glass-transition temperature (T_g). A composite containing 60 wt % (33 vol %)

Al₂O₃ exhibited about a 78% increase in the storage modulus at 50°C and about a 200% increase at 200°C. However, there was no significant change in the mechanical loss factor and T_g associated with the peak of the mechanical loss factor or loss modulus with the addition of Al₂O₃. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 568–575, 2007

Key words: composites; electron microscopy; high performance polymers; reinforcement; viscoelastic properties

INTRODUCTION

Poly(ether ether ketone) (PEEK) is a high-performance, semicrystalline, thermoplastic polymer exhibiting good resistance to moisture, chemicals, and hard radiation. It possesses excellent strength, modulus, and thermal stability, a high melting point (335°C), a high glass-transition temperature ($T_g = 143^\circ\text{C}$), and a high continuous-service temperature (up to 250°C) and hence is used in high-temperature engineering applications. It retains considerable modulus until the temperature reaches the region of 300°C, whereas other high-performance thermoplastic polymers [e.g., poly(ether sulfone)] lose modulus near T_g . In addition, PEEK possesses good fracture toughness, easy processability and reprocessability, and easier repair and bonding operations. Moreover, PEEK composites can be processed by conventional methods such as injection-molding, extrusion, compression-molding, and powder-coating techniques. Therefore, PEEK and its composites are being considered as substitutes for thermosetting polymer matrices for high-performance

applications, especially in aerospace, whereas thermosetting polymers have limitations of brittleness and water and solvent sensitivity.^{1–10}

Dynamic mechanical analysis (DMA) is used to detect weak glass transitions easily and precisely because of its higher sensitivity in comparison with differential scanning calorimetry. Furthermore, it has been increasingly used to study dynamic mechanical properties such as the storage modulus (E' ; i.e., stiffness) and mechanical loss factor ($\tan \delta$; i.e., damping) of high-performance polymer composites because of the frequent dynamic loading situation during use. By the introduction of reinforcing fillers into polymers, E' , the loss modulus (E''), and T_g can be tailored. E' and T_g increase to an extent proportional to the reinforcing effect, which in turn depends on the particle size, concentration, and shape. Moreover, the properties also depend on the particle–polymer interaction, particle–particle interaction, and polymer viscosity. Nevertheless, T_g decreases for composites exhibiting poor adhesion between the filler and polymer matrix.^{11–13}

Several studies have been conducted on the dynamic mechanical properties of polymer composites such as high-density polyethylene/glass,¹² epoxy/different fillers,¹³ epoxy/vapor-grown carbon nanofiber (VGCF),¹⁴ polystyrene/aluminum nitride (AlN),¹⁵ PEEK/VGCF,¹⁶ poly(tetrafluoroethylene)/short carbon fiber,¹⁷ and poly(vinylidene fluoride)/silica.¹⁸ Moreover, a series of cold-crystallized, melt-crystallized, and carbon-fiber-

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reinforced PEEK samples have been studied in the literature.^{19–21} Recently, we have reported that AlN plays an important role in improving the dynamic mechanical properties of PEEK.²² There are no previous reports about the dynamic mechanical properties of aluminum oxide (Al₂O₃) reinforced PEEK composites. Because of the good electrical, mechanical, and thermal properties of Al₂O₃, it is being widely used as a reinforcing filler in high-performance polymer matrix composites.

In this study, a series of PEEK composites reinforced with 0–60 wt % Al₂O₃ were prepared by a compression-molding technique to investigate the effect of Al₂O₃ on dynamic mechanical properties such as E' , $\tan \delta$, E'' , and T_g of a high-performance PEEK matrix. The resulting composites were also characterized with scanning electron microscopy (SEM) to observe the distribution of Al₂O₃ in the PEEK matrix.

EXPERIMENTAL

Materials

Commercial PEEK (grade 5300PF), donated by Gharda Chemicals, Ltd. (Panoli, India), under the trade name Gatone PEEK, was used as the matrix in this study. Al₂O₃, purchased from Aldrich Chemical Co., was used as a reinforcement without a surface treatment. Ethanol from Merck (Darmstadt, Germany) was used for homogenizing the Al₂O₃ and PEEK mixture. The mean particle sizes of PEEK and Al₂O₃ were 25 and 8 μm , respectively.

Sample preparation

Various compositions of PEEK reinforced with 0–60 wt % Al₂O₃ powder were prepared with a method described elsewhere.²³ A dried powder of Al₂O₃ and PEEK were well premixed in an ethanol medium with a magnetic stirrer, and the resultant slurry was dried in an oven at 120°C to remove the excess ethanol. The pure PEEK (controlled) and its composite samples were prepared with a laboratory hot press under a pressure of 15 MPa and temperature of 350°C. The resultant composite samples were coded PKAO-X, where PK, AO, and X denote PEEK, Al₂O₃, and the weight percentage of Al₂O₃, respectively.

Characterization

Thermogravimetric analysis (TGA)

The actual filler content and thermal stability of the pure PEEK and Al₂O₃/PEEK composites were determined via TGA with a Mettler–Toledo 851e (Mettler Toledo TGA/SDTA 851e, Switzerland). The samples were heated from room temperature to 1000°C at a heating rate of 10°C/min in an air atmosphere.

Microstructural analysis

For the morphological study of the composites by SEM (model XL-30, Philips, The Netherlands), small pieces of the samples were cut from the molded pellets and mounted on a block of acrylic-based polymer resin (DPI-RR cold cure). The obtained sample surfaces were manually ground and polished with successively finer grades of emery papers followed by cloth (mounted on wheel) polishing to remove scratches that developed during the emery-paper polishing. The morphology of the PEEK and Al₂O₃ powder was determined by the suspension of the powder in ethanol followed by dispersion on a metal stub. Finally, the samples were coated with a thin layer of gold with a gold sputter coater (model SC 7610, Polaron, England).

DMA

The dynamic mechanical tests were carried out in the three-point-bending mode with a PerkinElmer DMA 7e dynamic mechanical analyzer (Norwalk, CT) from 30 to 250°C at a heating rate of 5°C/min and a frequency of 1 Hz. The specimen platform had a span length of 15 mm. All the samples were polished to get a thickness of 1.82 ± 0.05 mm. The samples, annealed in a vacuum oven for 2 h at 260°C, were mounted in the DMA instrument, and the test was carried out in an argon atmosphere under a static load of 550 mN and a dynamic load of 500 mN. Before the cycle was started, the samples were held for 5 min at 30°C to stabilize the position of the knife.

RESULTS AND DISCUSSION

Various compositions of high-performance PEEK reinforced with various weight percentages of Al₂O₃ were prepared, characterized, and discussed in detail. The volume percentage of the fillers for a given weight fraction was calculated with the following well-known equation:²⁴

$$V_f = W_f / [W_f + (1 - W_f)\rho_f/\rho_m] \quad (1)$$

where V_f is the volume fraction, W_f is the weight fraction, ρ_f is the density of Al₂O₃ particles (4.0 g/cm³), and ρ_m is the density of the polymer matrix (1.29 g/cm³).

TGA

TGA measurements were carried out to obtain the actual incorporated filler and thermal stability of the PEEK and its composites in an air atmosphere. The temperature at a 10 wt % loss ($T_{10,\text{air}}$) was taken as the decomposition temperature and is tabulated in Table I. Pure PEEK has a $T_{10,\text{air}}$ value of 556°C. The $T_{10,\text{air}}$ values of the composites increased with the

TABLE I
Thermal Properties of the PEEK Composites

Sample	Theoretical Al ₂ O ₃ in PEEK		Actual Al ₂ O ₃ in PEEK (wt %)	T _{10,air} (°C)
	wt %	vol %		
PKAO-0	0	0	0	556
PKAO-10	10	3.46	8.78	568
PKAO-30	30	12.14	30.88	578
PKAO-40	40	17.70	37.63	576
PKAO-50	50	24.39	49.00	582
PKAO-60	60	32.60	58.21	576

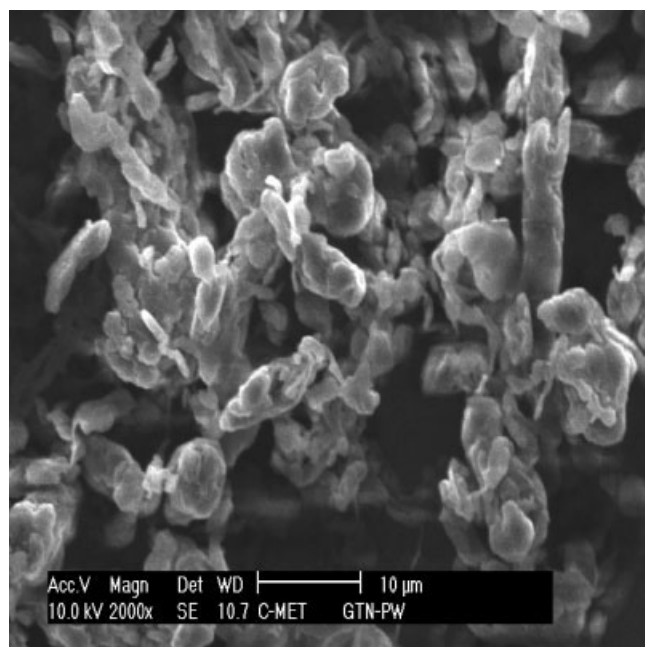
addition of Al₂O₃. T_{10,air} increased by about 26°C for PKAO-50 versus that of pure PEEK. The increase in the decomposition temperature or thermal stability could be due to an interaction between the PEEK matrix and the Al₂O₃ particles.

The actual incorporated weight percentage of Al₂O₃ in the PEEK matrix was determined by the heating of the sample to 1000°C in an air atmosphere. As reported earlier,²³ pure PEEK showed a negligible residue at 1000°C in air. Therefore, the residue of the composites remaining at 1000°C in TGA was the weight percentage of Al₂O₃ in the PEEK matrix, as summarized in Table I. There was an insignificant difference between the theoretical and actual incorporated weight percentages of Al₂O₃ in the PEEK matrix. This might be due to two reasons: first, the loss of a small quantity of Al₂O₃ or PEEK powder during the composite mixing process due to the difference in the densities of the components and second, the desorption of physisorbed water and dehydration of Al₂O₃.²⁵

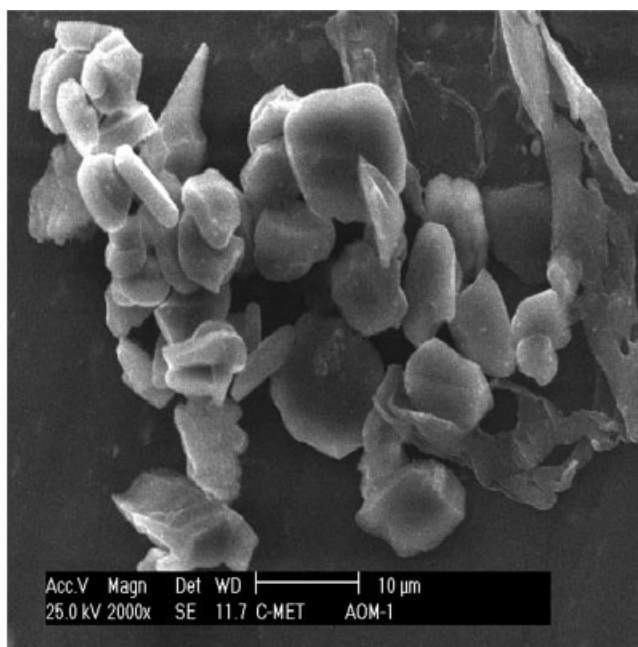
SEM

The morphology and filler distribution in the PEEK matrix were studied with SEM. Figure 1(a,b) shows the morphology of the pure PEEK and Al₂O₃ powder, respectively. As shown in Figure 1(a), PEEK had irregular particles of a rodlike shape with a length ranging from 10 to 50 μm. Figure 1(b) shows flat, platelet-shaped Al₂O₃ particles. The size of the Al₂O₃ particles ranged from 3 to 15 μm. The polished samples of PKAO-10, PKAO-30, PKAO-50, and PKAO-60 were also examined at a magnification of 500× and are shown in Figure 2(a–d), respectively. All these samples showed a uniform distribution of Al₂O₃ particles in the PEEK matrix. There were no large aggregates of Al₂O₃ in the PEEK matrix, as expected because of the good processing conditions.

The interfacial adhesion between Al₂O₃ and the PEEK matrix was studied for the etched samples. The polished sample was etched for 5 min in a 2% (w/v) solution of potassium permanganate in a mixture of 4 vol of orthophosphoric acid and 1 vol of water. Figure 3(a,b) shows the morphology of an etched PEEK sample reinforced with 40 wt % Al₂O₃ (PKAO-40) at magnifications of 500 and 2000×, respectively. The etching method leached out the amorphous PEEK and loosely bound PEEK from the surface and vicinity of Al₂O₃ particles. As shown in Figure 3, this resulted in a distinct boundary between the Al₂O₃ and PEEK matrix because of the poor adhesion between the Al₂O₃ particles and the PEEK matrix. This is in contrast to our earlier study on AlN/PEEK composites, in which we did not find any distinct boundary between AlN



(a)



(b)

Figure 1 SEM micrographs of (a) PEEK powder (2000×) and (b) Al₂O₃ powder (2000×).

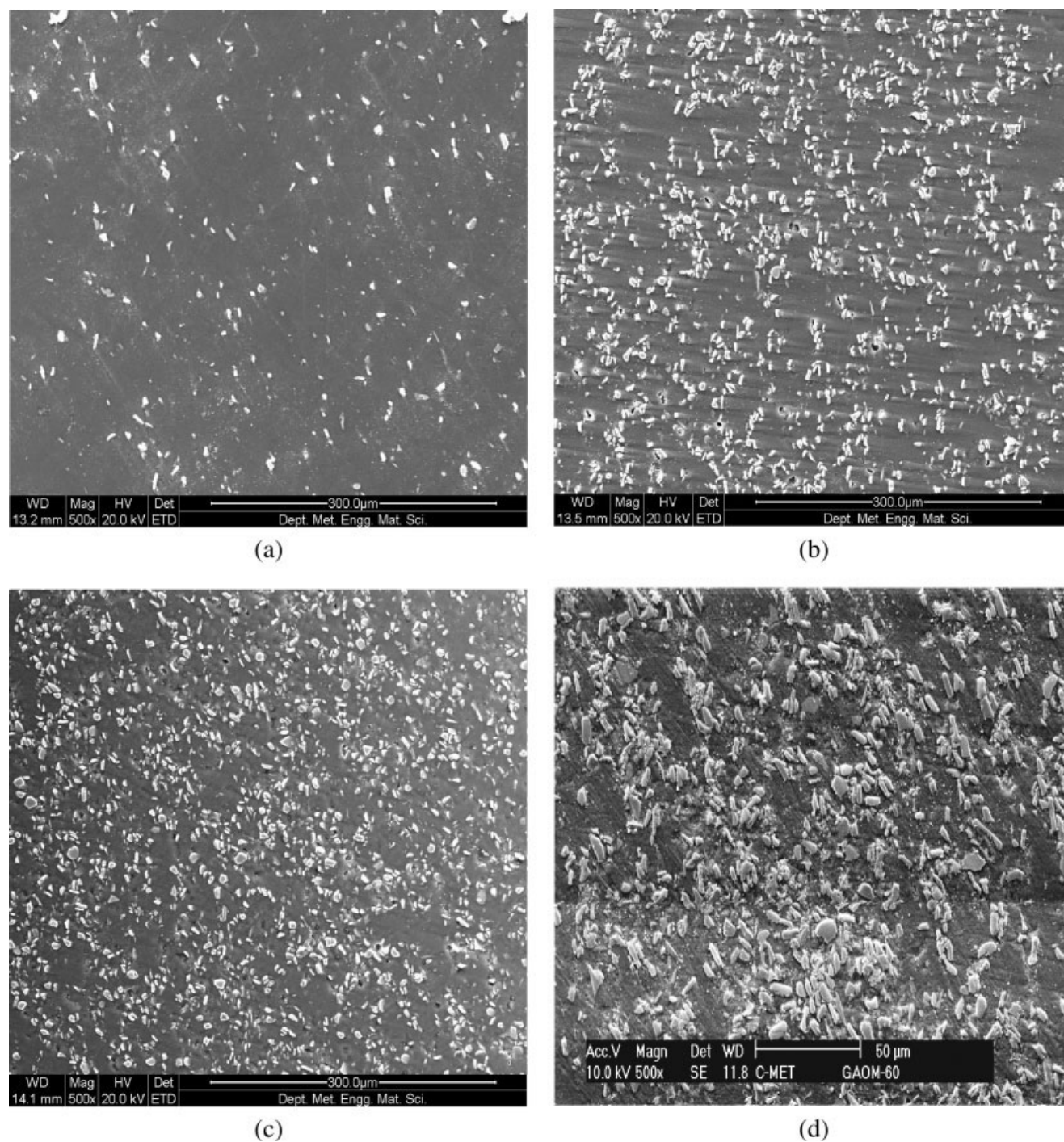


Figure 2 SEM micrographs of polished (a) PKAO-10, (b) PKAO-30, (c) PKAO-50, and (d) PKAO-60.

and PEEK because of the good interfacial adhesion between AlN and PEEK.²²

DMA

The dynamic mechanical properties, such as E' , $\tan \delta$, and E'' , of PEEK and its composites, studied as a function of temperature, are shown in Figures 4–7. Figure 4 shows E' versus the temperature for PEEK reinforced with 0–60 wt % Al₂O₃. As the temperature

increased, E' of the samples gradually decreased, dramatically decreased in the glass-transition region, and finally fell down 1 order of magnitude lower than the value at room temperature because of the softening of PEEK. As expected, E' increased with an increase in Al₂O₃ in the PEEK matrix. The reinforcing effect of Al₂O₃ was more intense above T_g . This was similar to a previous study of AlN/PEEK²² and reported VGCF/PEEK composites, for which the modulus increased with the filler content.¹⁷ However, this was in

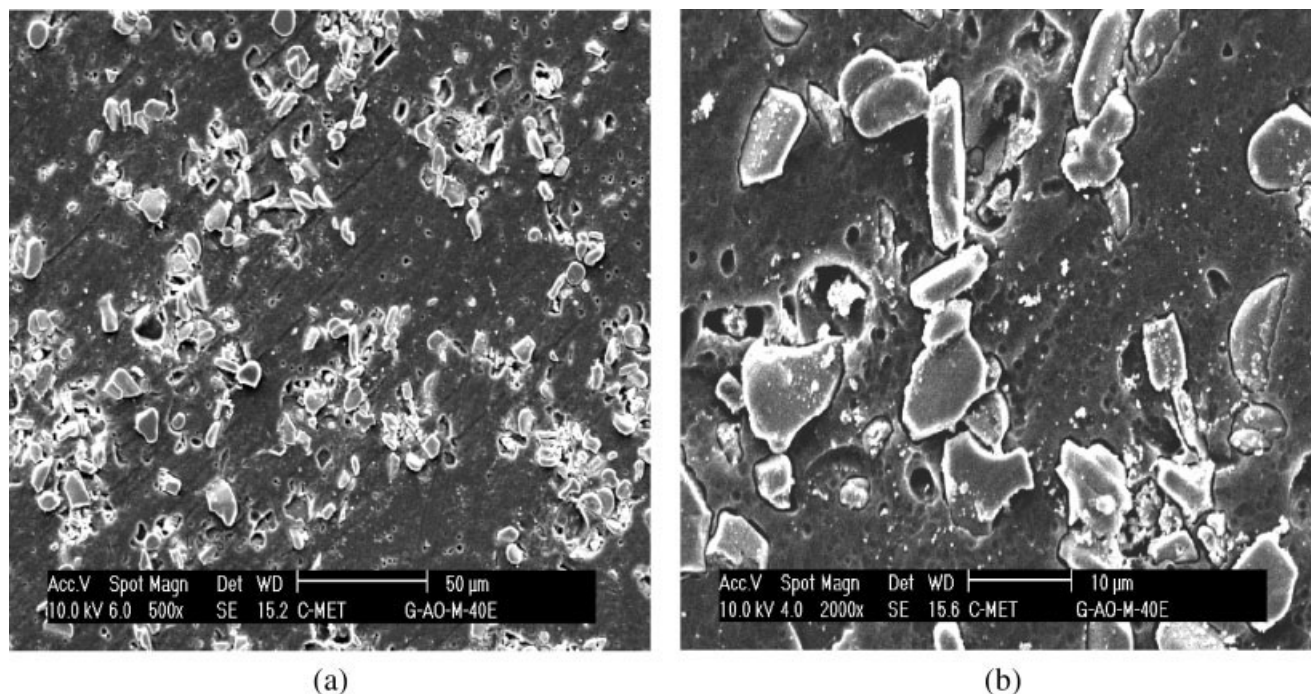


Figure 3 SEM micrographs of an etched PKAO-40 sample: (a) 500 and (b) 2000 \times .

contrast to a short-carbon-fiber-reinforced/poly(ether ether ketone) (SCFR-PEEK) composite, for which an intense increase in the modulus was observed below T_g , and afterwards, it decreased rapidly as in pure PEEK.⁹

Figure 5 shows E' as a function of the Al_2O_3 content at 50, 100, 150, 200, and 250 $^\circ\text{C}$. E' increased nonlinearly with an increase in the Al_2O_3 content at all

temperatures. Nevertheless, E' at 50 $^\circ\text{C}$ was higher than that at higher temperatures. This was due to the fact that molecular relaxation increased with increasing temperature. E' of the PKAO-60 composite increased by 78% to 5.04 GPa versus 2.84 GPa for pure PEEK at 50 $^\circ\text{C}$ and by 195% to 1.09 GPa versus 0.37 GPa for pure PEEK at 200 $^\circ\text{C}$. The modulus increased because of the high modulus of Al_2O_3 (385 GPa) and the interface that formed because of the interaction between Al_2O_3 and

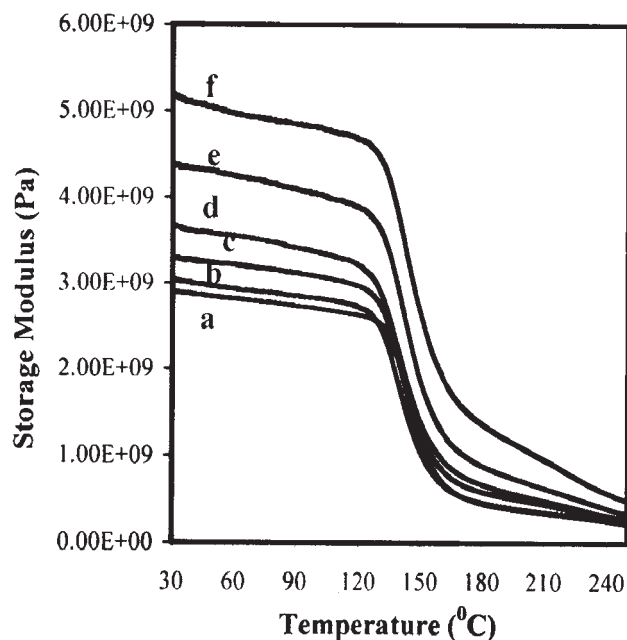


Figure 4 E' versus the temperature for the PEEK composites: (a) PKAO-0, (b) PKAO-10, (c) PKAO-30, (d) PKAO-40, (e) PKAO-50, and (f) PKAO-60.

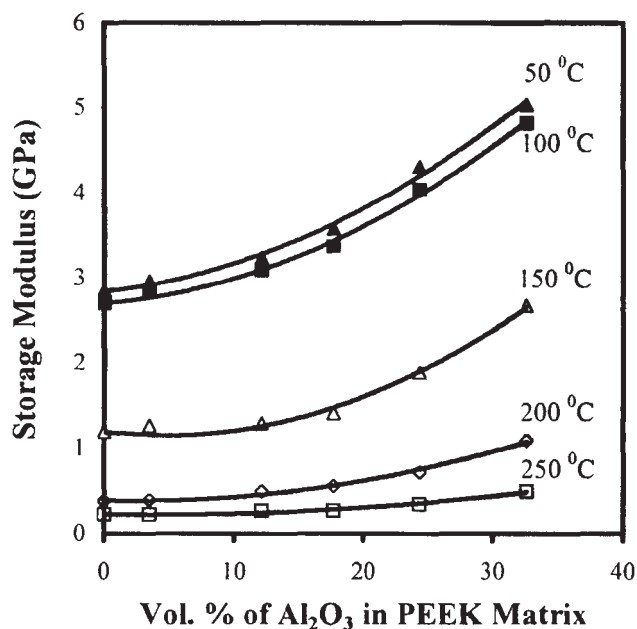


Figure 5 E' versus the volume percentage of Al_2O_3 in PEEK.

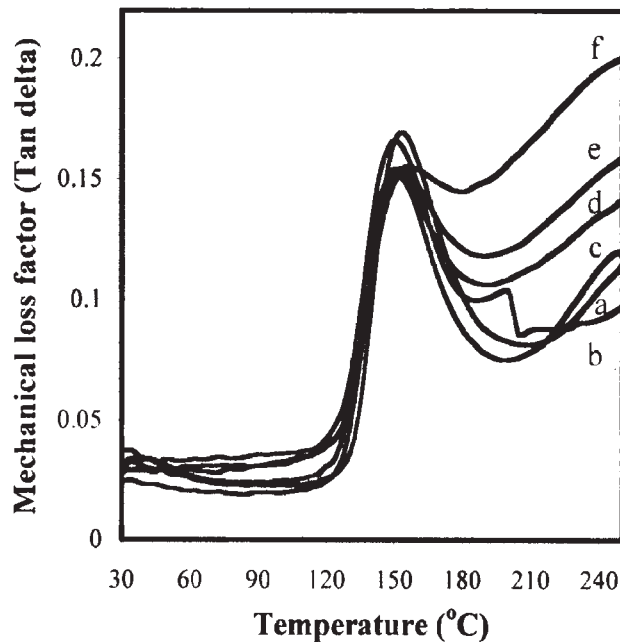


Figure 6 Tan δ versus the temperature for the PEEK composites: (a) PKAO-0, (b) PKAO-10, (c) PKAO-30, (d) PKAO-40, (e) PKAO-50, and (f) PKAO-60.

the matrix. It has been reported that a strong interface can transfer an efficient load to fillers from the matrix. In this study, the significant improvement in E' might be attributed to the uniformly dispersed Al₂O₃ particles in the matrix, which increased the interfacial area between Al₂O₃ and the PEEK matrix.

Figure 6 shows tan δ or damping as a function of the temperature for the composites. Tan δ shifted

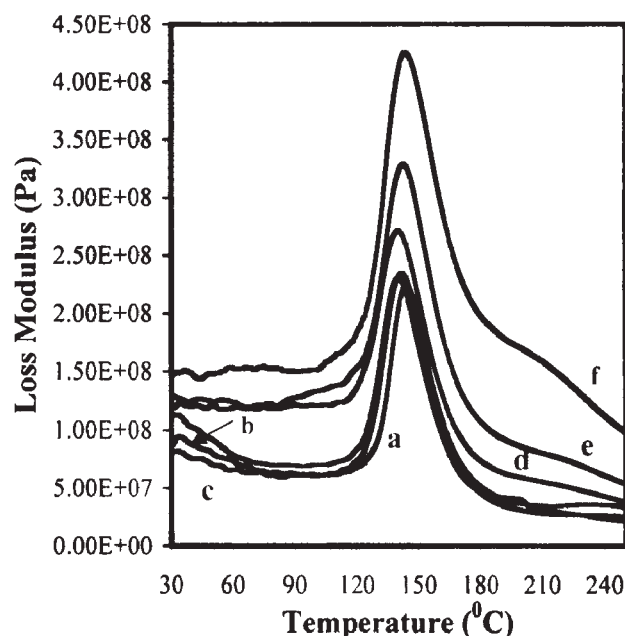


Figure 7 E'' versus the temperature for the PEEK composites: (a) PKAO-0, (b) PKAO-10, (c) PKAO-30, (d) PKAO-40, (e) PKAO-50, and (f) PKAO-60.

slightly with respect to the filler content below T_g . However, the shifting was not as significant as that observed for the AlN/PEEK composites.²² However, at temperatures higher than T_g , tan δ increased significantly. This was due to the fact that at lower temperatures, the contraction of PEEK around the filler particles produced tan δ values close to that of the pure PEEK, but contraction was released as the temperature increased. Hence, tan δ for the composites significantly increased because of the particle–polymer fraction at the interface. Nevertheless, a decrease in tan δ could be observed if good adhesion existed between the filler and polymer matrix, as reported in previous studies.^{12,22} The composites exhibited a peak value of tan δ in the transition region in which the free volume reached a critical level. Table II shows the peak height of tan δ (tan δ_{\max}) for PEEK composites as a function of the Al₂O₃ content. As expected, tan δ of the composites at the glass transition was lower than that of the pure PEEK matrix. Tan δ_{\max} of the composites decreased slightly with the Al₂O₃ content. The tan δ_{\max} value of pure PEEK (0.17) was reduced to 0.15 for PKAO-30. This may be attributed to the increased crystallinity²³ and reduced fraction of PEEK in the composite.¹² However, it increased to 0.16 for PKAO-60 but was still lower than that of pure PEEK. A significant drop in tan δ_{\max} was not observed at a higher volume fraction. This was in contrast to a previous study of the AlN/PEEK composite system.²² We believe that because of poor interfacial adhesion between Al₂O₃ and PEEK, as confirmed by the Kubat parameter and SEM micrographs, the particle–particle interaction played a dominant role, which resulted in increased heat dissipation with increased Al₂O₃ content. In the SCFR–PEEK composite system, the peak height of the composite was double than that of the pure PEEK matrix. It has been reported that a poor interface between a carbon fiber and a matrix leads to an increase in tan δ .⁹ We also noted a broadening of the tan δ peak at a higher volume fraction of the Al₂O₃ filler. This may be due to the combined effect of (1) unconstrained segments of the PEEK molecules, which

TABLE II
Values of T_g and Tan δ_{\max} for the PEEK Composites

Sample	$T_{g,\delta}$ (°C) ^a	$T_{g,E''}$ (°C) ^b	Tan δ_{\max}
PKAO-0	154	145	0.17
PKAO-10	151	142	0.166
PKAO-30	153	143	0.152
PKAO-40	152	142	0.155
PKAO-50	155	144	0.155
PKAO-60	157	146	0.156

^a Glass-transition temperature reported as the temperature at the tan δ peak.

^b Glass-transition temperature reported as the temperature at the E'' peak.

TABLE III
Kubat Parameter for the PEEK Composites

Composition	PKAO-0	PKAO-10	PKAO-30	PKAO-40	PKAO-50	PKAO-60
Kubat parameter	0	0.011	0.018	0.108	0.206	0.361

retained the bulk polymer T_g , and (2) constrained segments of PEEK, that is, molecules close to the filler surface, which had less mobility and hence resulted in an increase in the bulk T_g .

Table II shows T_g characterized as the temperature at the peak value of $\tan \delta$. T_g was influenced by only $\pm 3^\circ\text{C}$ from 154°C for pure PEEK. T_g initially decreased from 154°C for the pure PEEK to 151°C for PKAO-10. However, it increased with the further addition of Al_2O_3 . At a higher loading, because of a decrease in the interparticle distance, the filler was more effective for restricting the mobility of the polymer chain; hence, T_g increased to 157°C for PKAO-60. Nevertheless, T_g of the composite indeed increased to a higher temperature with the filler content when the interface was strong between the filler and matrix. The interfacial adhesion strength depended on the mechanical interlocking, which in turn depended on the shape of the fillers and surface morphology of the matrix. In this study, because of the flat, platelet-shaped Al_2O_3 particles, there may not have been good mechanical interlocking, so this resulted in poor interfacial adhesion between the Al_2O_3 particles and PEEK matrix. Therefore, in this study, the expected increase in T_g was not observed, whereas an increase of 19°C in T_g was observed for an irregularly shaped AlN/PEEK composite system.²²

The interfacial adhesion between the Al_2O_3 particles and PEEK could be estimated with the Kubat parameter (A),¹² which was calculated with eq. (2):

$$A = \{[\tan \delta_c / (V_m \tan \delta_m)] - 1\} \quad (2)$$

where $\tan \delta_c$ is the mechanical loss factor of the composites, $\tan \delta_m$ is the mechanical loss factor of the matrix, and V_m is the volume fraction of the matrix.

The values of the Kubat parameter for all the composites are summarized in Table III. It has been reported that a Kubat parameter approaching 0 corresponds to strong interfacial bonding between the filler and matrix in composites. Table III shows that PKAO-10 and PKAO-30 had negligible values of the Kubat parameter, exhibiting strong interfacial adhesion between the filler and PEEK matrix, which in turn reduced the particle–particle interaction. However, as the Al_2O_3 content increased above 30 wt % in the PEEK matrix, the Kubat parameter also increased, and this indicated that interfacial adhesion decreased. This may have been due to the decrease in the interparticle distance between the Al_2O_3 particles in the PEEK matrix.

Figure 7 shows E'' of the PEEK composites as a function of temperature. The E'' curve of PEEK shifted upward for the studied temperature with the Al_2O_3 content. The increase in E'' for PKAO-10 and PKAO-30 was negligible. However, E'' considerably increased for composites PKAO-40, PKAO-50, and PKAO-60 because of the poor interfacial adhesion. The SEM micrograph of PKAO-40 shows particle–particle interactions and a distinct boundary between the filler and polymer, which caused heat dissipation by particle–polymer and particle–particle friction; hence, E'' was expected to increase with the Al_2O_3 content. The effect of the filler was prominent both above and below T_g . The T_g value associated with the temperature at the E'' peak was shifted toward a lower temperature by $1\text{--}3^\circ\text{C}$ versus that of pure PEEK. This supports the data of T_g determined from the $\tan \delta$ curve. The broadening of the E'' peak of the composites was observed with Al_2O_3 . E'' increased considerably with Al_2O_3 , especially for PEEK reinforced with more than 30 wt % Al_2O_3 . This may have been due to poor interfacial adhesion between Al_2O_3 and the PEEK matrix.

CONCLUSIONS

High-performance PEEK matrix composites reinforced with Al_2O_3 were successfully prepared, and the resultant properties can be summarized as follows:

1. The incorporation of Al_2O_3 into the PEEK matrix led to a significant increase in E' , particularly at high temperatures.
2. T_g was not very much influenced by the volume fraction of Al_2O_3 in the PEEK matrix.
3. The E'' curve shifted upward with an increase in Al_2O_3 . The peak value of E'' nearly doubled for 33 vol % Al_2O_3 reinforced PEEK.
4. The thermal stability of the composites was improved with Al_2O_3 addition to the PEEK matrix.

We can conclude that these futuristic composite materials may be promising materials for high-temperature applications.

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