Effect of aluminum nitride on thermomechanical properties of high performance PEEK

R.K. Goyal a, A.N. Tiwari b, U.P. Mulik a, Y.S. Negi c,*

a Polymer and Materials R&D, Centre for Materials for Electronics Technology, Department of Information Technology, Government of India, Panchwati, Off Pashan Road, Pune 411 008, Maharashtra, India
b Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology, Bombay, Powai, Mumbai 400 076, Maharashtra, India
c Polymer Science and Technology Laboratory, Department of Paper Technology, Indian Institute of Technology, Roorkee, Saharanpur Campus, Saharanpur 247 001, Uttarpradesh, India

Abstract

High performance polymer matrix composites based on poly(ether–ether–ketone) (PEEK) as matrix and aluminum nitride particle (AlN p) as filler were prepared. The effect of AlN p on the storage modulus, loss modulus, mechanical loss factor, and glass transition were investigated. The AlN p reinforcement is more pronounced above glass transition temperature (Tg). Composite containing 70 wt.% AlN p exhibit about 100% increase in storage modulus at 50 °C and about 500% increase at 250 °C, and 19 °C increase in glass transition temperature as compared to pure PEEK. Peak height of tan δ for composites was decreased to one sixth of the pure PEEK. It is probably due to improved crystallinity of PEEK and strong interaction between the AlN p and PEEK matrix. SEM reveals excellent distribution of AlN p in PEEK matrix and good interaction between AlN p and PEEK matrix.

Keywords: A. Polymer-matrix composites (PMCs); B. Thermomechanical; B. Hardness; PEEK

1. Introduction

High performance polymers based composites have been in increasing demand for the last few decades, for their application in high-speed aircraft structures, electronic/microelectronics substrates, and space structural components of space research vehicles due to its high strength, modulus and retention of mechanical properties over a wide temperature range and extreme environmental conditions.

PEEK has advantages over the epoxy resin based composites because of its high fracture toughness and excellent resistance to moisture. PEEK is a high performance semicrystalline polymer due to its outstanding thermal stability, wear resistance, mechanical properties, and excellent resistance to chemicals. It has high melting (Tm), glass transition (Tg) and continuous service temperature. It can be processed by conventional methods such as injection molding, extrusion, compression molding and powder coating techniques. Therefore, PEEK and its composites have been reported for use in aerospace, automotive, structural, high temperature wiring, tribology, and biomedical applications [1–3]. Moreover, a wide range of morphologies from amorphous to different degree of crystallinity could be obtained by control cooling or crystallization method.

Carbon fiber and glass fiber reinforced PEEK composites have been reported extensively for high performance aerospace applications [4–6]. Recently, Sandler et al. studied the thermal and mechanical properties of carbon nanofibre reinforced PEEK [7]. Dynamic mechanical relaxation behaviour of a series of cold crystallized, melt crystallized and carbon fiber reinforced PEEK samples have been
cited in literature [5,8]. Adam and Gaitonde studied thermomechanical properties of PEEK and PEEK/CF composites over a temperature range from 27 °C to −196 °C [9]. Tregub and Harel reported that for a constant CF reinforced PEEK composite, the dynamic modulus, strength and fatigue life are significantly higher than that of sample having lower crystallinity [5].

Recently, nano-Al₂O₃, nano-SiO₂ [10] and hydroxyapatite [3] reinforced PEEK has been reported to be particulate composites. Wang et al. studied wear and friction coefficient of PEEK reinforced with varying weight fractions of SiC, SiO₂, Si₃N₄ and ZrO₂ [11–14]. However, there are no detailed reports about thermomechanical properties of particulate PEEK composites. AlNp is widely used as reinforcing filler in polymer matrices on account of its high thermal conductivity (150–220 W/m K), low CTE (4 × 10⁻⁶ °C), low dielectric constant (8.9) and excellent mechanical properties [15].

DMA is a widely used technique to detect weak glass transitions easily and precisely due to its higher sensitivity as compared to DSC. Hence, it is widely used to investigate relaxation of polymer segments [16], polymer miscibility [17] and thermal degradation behaviour [18] in polymer blends and polymer composites.

The objective of this study is to investigate the effect of AlNp on thermomechanical properties such as storage modulus (E’), mechanical loss factor (tan δ), and loss modulus (E”) and glass transition temperature of high performance composites based on PEEK as matrix. The AlNp loading was varied from 0 to 70 wt.% in PEEK matrix.

2. Experimental

2.1. Materials

A high quality PEEK (grade 5300PF) donated by Gharda Chemicals Ltd. Panoli, Gujarat, India under the trade name GATONE™ PEEK was used as matrix in the present study. The Aluminum nitride particulate (AlNp) purchased from Aldrich Chemical Company was used as reinforcement without surface treatment. An ethanol from Merck was used for homogenizing the AlNp and PEEK mixture. The mean particle size of the PEEK and AlNp was 25 µm and 5 µm, respectively.

2.2. Sample preparation

Various compositions of PEEK reinforced with 0–70 wt.% AlNp were prepared using the method described in our previous paper [1]. Dried powder of AlNp and PEEK were well premixed through magnetic stirring using an ethanol and the resultant slurry was dried in oven at 120 °C to remove the excess alcohol. The pure PEEK (controlled) and composite samples were prepared by using a laboratory hot press under a pressure of 15 MPa at a temperature of 350 °C. Composite samples were coded by PK–AN–X, where PK, AN, and X denotes PEEK, AlNp, and wt.% of AlNp, respectively.

For SEM study, small pieces were cut parallel to the axial direction of the molded disks and mounted in a block of denture base polymer resin (DPI-RR cold cure). The obtained sample surfaces were manually ground and polished with successive finer grades of sand papers followed by cloth (mounted on wheel) polishing using water/alumina suspension to remove scratches developed during sand polishing. Thus, obtained samples were called as polished samples in the present study. Selected polished samples were also 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 and were called as etched samples.

2.3. Microstructure analysis

Morphology of AlNp/PEEK composite samples was studied using SEM (Philips XL-30) with an accelerating voltage of 10–20 kV. The polished and etched samples were coated with a thin layer of gold using gold sputter coater [Polaron SC 7610].

2.4. Density

Experimental density of the pure PEEK and PEEK composites was measured by a method adopted in earlier paper [1].

2.5. Thermogravimetric analysis (TGA)

The thermal stability and the wt.% of char yield for pure PEEK and AlNp/PEEK composites were performed on a TGA (Mettler–Toledo 851 e). The samples were heated from room temperature to 1000 °C at the heating rate of 10 °C/min in nitrogen atmosphere.

2.6. Dynamic mechanical analysis (DMA)

DMA was carried out in three point bending mode using a Perkin–Elmer DMA 7 e dynamic mechanical analyzer at a heating rate of 5 °C/min and a deformation frequency of 1 Hz. The samples of size 15–17 mm in length, 3–4 mm in width were cut from the molded disks. All the samples were polished to get the thickness of 1.82 mm. The samples annealed in a vacuum oven for 2 h at 260 °C were mounted in the DMA and the test was carried out for the temperature range 30–250 °C in argon atmosphere under static load of 550 mN and a dynamic load of 500 mN. Before starting the cycle, the samples were held for 5 min at 30 °C to stabilize the position of the knife.

3. Results and discussion

Various compositions of high performance PEEK reinforced with varying weight % of AlNp, were prepared, characterized and discussed in detail in this section.
3.1. Scanning electron microscope

The morphological and particles distribution in PEEK matrix was studied using SEM. Fig. 1a and b shows the morphology of pure PEEK and AlN\textsubscript{p} powder, respectively. As shown in Fig. 1a, PEEK has irregular particles of rod like shape of length ranging from 10 to 50 \( \mu \text{m} \). Fig. 1b shows irregular angular shaped AlN\textsubscript{p}. Size of the AlN\textsubscript{p} ranged from 1 to 10 \( \mu \text{m} \). Fig. 1c–d shows the SEM of the fractured surface of the PKAN-30 sample at a magnification of 500 and 2000. It can be seen that AlN\textsubscript{p} are uniformly distributed in the PEEK matrix.

Moreover, polished samples of PKAN-30, PKAN-60 and PKAN-70 were also examined at a magnification of 500 and are shown in Fig. 2a–c, respectively. All these samples showed the uniform distribution of AlN\textsubscript{p} in PEEK matrix. There were no large aggregates of AlN\textsubscript{p} in PEEK matrix, which is expected due to good processing condition and interaction between AlN\textsubscript{p} and PEEK matrix.

As shown in Table 1, composite samples PKAN-60 and PKAN-70 showed experimental density lesser than theoretical density by 5.46% and 7.69%, respectively. To verify the presence of porosity these samples were examined at a magnification of 5000. The sample PKAN-50 showed negligible (0.7%) difference between experimental density and theoretical density. So we have not examined at a magnification of 5000. As shown in Fig. 2d–e, the porosity of sub-micron size was found, which resulted in experimental density of PKAN-60 and PKAN-70 lesser than theoretical density.

The interfacial interaction between AlN\textsubscript{p} and the PEEK were also studied by etching PEEK composite samples containing lower AlN\textsubscript{p} concentration i.e., composite PKAN-10, and higher AlN\textsubscript{p} concentration i.e., composite PKAN-50. We can see from Fig. 3a–b that the AlN\textsubscript{p} are having less angular irregularity than that of pure AlN\textsubscript{p} as shown in Fig. 1b, which may be due to polymer coating on AlN\textsubscript{p} and good interaction between AlN\textsubscript{p} and the PEEK during processing. The boundary between the AlN\textsubscript{p} and PEEK is indistinct.

3.2. Density

Table 1 shows the theoretical and experimental density of the AlN\textsubscript{p} filled PEEK. It can be seen that the composite density increased with AlN\textsubscript{p} content due to higher density of AlN\textsubscript{p} compared to PEEK. The experimental density is higher than that of theoretical density below 50 wt.% AlN\textsubscript{p} reinforced PEEK, which may be attributed to porosity free samples and increased crystallinity of PEEK as a result of strong nucleation effect of AlN\textsubscript{p} [1]. However, the experimental density of the PEEK containing above 50 wt.% AlN\textsubscript{p} is lower by more than 5% than that of theoretical density, which may be due to the presence of sub-micron size porosity in the samples as confirmed by SEM micrographs. As more and more AlN\textsubscript{p} is added inter-particle distance is decreased and aggregation of particles formation takes place. These aggregates hinder the infiltration of molten polymer, which results in porosity in the samples.

Fig. 1. SEM micrographs of (a) PEEK powder, 2000x; (b) AlN\textsubscript{p} powder, 4000x; (c) fractured PKAN-30, magnification: 500x; and (d) fractured PKAN-30, magnification: 2000x.
3.3. Thermogravimetric analysis (TGA)

The thermal stability and the % char yield of the pure PEEK and AlN<sub>p</sub>/PEEK composites are shown in Table 2. The temperature at 10 wt.% loss (T<sub>10</sub>) was taken as the decomposition temperature and tabulated in Table 2. It can be seen from the Table 2 that pure PEEK has T<sub>10</sub> at 570°C. It is observed that as the percentage of AlN<sub>p</sub> increases in PEEK the thermal stability of composite is increased to 590°C for PEEK with 50 wt.% AlN<sub>p</sub>. On further addition of AlN<sub>p</sub> i.e., the thermal stability of PEEK

### Table 1

<table>
<thead>
<tr>
<th>Sample code</th>
<th>% AlN&lt;sub&gt;p&lt;/sub&gt; in PEEK</th>
<th>Theoretical density (g/cm&lt;sup&gt;3&lt;/sup&gt;)</th>
<th>Experimental density (g/cm&lt;sup&gt;3&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PKAN-0</td>
<td>0</td>
<td>1.2900</td>
<td>1.3036</td>
</tr>
<tr>
<td>PKAN-10</td>
<td>10</td>
<td>1.3730</td>
<td>1.3988</td>
</tr>
<tr>
<td>PKAN-30</td>
<td>30</td>
<td>1.5756</td>
<td>1.5947</td>
</tr>
<tr>
<td>PKAN-50</td>
<td>50</td>
<td>1.8485</td>
<td>1.8355</td>
</tr>
<tr>
<td>PKAN-60</td>
<td>60</td>
<td>2.0238</td>
<td>1.9134</td>
</tr>
<tr>
<td>PKAN-70</td>
<td>70</td>
<td>2.2357</td>
<td>2.0638</td>
</tr>
</tbody>
</table>

Fig. 2. SEM micrographs of polished (a) PKAN-30, magnification: 500x; (b) PKAN-60, magnification: 500x; (c) PKAN-70, magnification: 500x; (d) PKAN-60, magnification: 5000x; and (e) PKAN-70, magnification: 5000x.

Fig. 3. SEM micrographs of etched sample of (a) PKAN-10, magnification: 1000x; (b) PKAN-50, magnification: 10,000x.
with 70 wt.% AlN\(p\) is decreased to 582 °C but it is still higher than that of pure PEEK. On addition of more and more AlN\(p\), due to the decrease in inter-particle distance, particles aggregation forms which results in decreased interfacial area between the AlN\(p\) and PEEK matrix. Therefore, thermal stability is reduced after 50 wt.% loading. The increase in thermal stability could be due to the strong interaction or interfacial bonding between the AlN\(p\) and the PEEK matrix.

It can be seen from the Table 2 that the char yield at 1000 °C was increased from 48% for the pure PEEK to 83% for PEEK reinforced with 70 wt.% AlN\(p\). The improvement in char yield may be attributed to combined effect of increase in AlN\(p\) content in composite, which is thermally stable and excellent thermal conducting, and good interaction between AlN\(p\) and PEEK matrix.

3.4. Dynamic mechanical analysis (DMA)

The dynamic mechanical properties such as storage modulus and mechanical loss factor (tan\(\delta\)) of pure PEEK are shown in Fig. 4. It can be seen from the figure that the glass transition temperature (\(T_g\)), reported as the temperature at peak of tan\(\delta\), occurs at 155 °C corresponding to \(\alpha\) transition, which is very close to the reported value [19]. The storage modulus falls rapidly at the \(\alpha\) transition of the PEEK.

Fig. 5 shows that the storage modulus of composites exhibited a plateau zone below 130 °C due to the high performance properties of the PEEK, followed by sharp decrease. As expected, the storage modulus is increased with filler loading. Moreover, with rise in temperature the reinforcing effect of AlN\(p\) is increased significantly above the \(T_g\). This is similar to the previous study of CNF/PEEK, where addition of CNF increases modulus below and above \(T_g\) [7]. However, this is in contrast to short carbon fiber reinforced PEEK (SCFR–PEEK) composite where intense increase in modulus was observed below \(T_g\) afterwards decreased rapidly as in pure PEEK [20].

Table 3 shows the storage modulus of PEEK composites at different temperature. The storage modulus of PKAN-70 composite is increased by 95% to 3.38 GPa as compared to 1.73 GPa for pure PEEK at 50 °C and by about 480% at 250 °C. The modulus is increased due to the high modulus of AlN\(p\) (308 GPa) and from good interaction between the AlN\(p\) and the matrix, which restrict the segmental motion of the PEEK. Thus results in effective transfer of load from the matrix to the AlN\(p\). The increase in modulus corresponds to the high thermal conductivity of the composite as heat conduct better in a stiffer material due to higher acoustic velocity [21]. It is interesting to find that the increase in modulus of PKAN-50 is about 51% at 50 °C and by about 209% at 250 °C, which is comparable to the increase in modulus of 30 wt.% short carbon fiber reinforced PEEK. In present study the significant improvement in storage modulus at 50 wt.% AlN\(p\) content might be attributed to the uniformly dispersed AlN\(p\) in matrix and irregular shaped AlN\(p\), which increased interfacial area between AlN\(p\) and PEEK matrix [22].

Fig. 6 shows that the mechanical loss factor (tan\(\delta\) transition) shifts to higher temperature and becomes broader with AlN\(p\) content. The \(T_g\) of the composites is increased by 19 °C from 155 °C for pure PEEK to 174 °C for

<table>
<thead>
<tr>
<th>Sample code</th>
<th>(T_{10}) (°C)</th>
<th>Char yield (%) at 1000 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PKAN-0</td>
<td>570</td>
<td>48</td>
</tr>
<tr>
<td>PKAN-10</td>
<td>578</td>
<td>54</td>
</tr>
<tr>
<td>PKAN-30</td>
<td>588</td>
<td>65</td>
</tr>
<tr>
<td>PKAN-50</td>
<td>590</td>
<td>73</td>
</tr>
<tr>
<td>PKAN-60</td>
<td>580</td>
<td>76</td>
</tr>
<tr>
<td>PKAN-70</td>
<td>582</td>
<td>83</td>
</tr>
</tbody>
</table>

Fig. 4. Storage modulus and mechanical loss factor versus temperature for pure PEEK.
Fig. 5. Storage modulus versus temperature for PEEK composites (a) PKAN-0, (b) PKAN-10, (c) PKAN-30, (d) PKAN-50, (e) PKAN-60, and (f) PKAN-70.

Table 3
Storage modulus at different temperatures and glass transition temperature of PEEK composites

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Storage modulus (GPa) at different temperatures (°C)</th>
<th>$T_{g,tan}$ (°C)</th>
<th>$T_{g,LM}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50  100  150  200  250</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PKAN - 0</td>
<td>1.73 1.69 0.72 0.30 0.22</td>
<td>155</td>
<td>145</td>
</tr>
<tr>
<td>PKAN-10</td>
<td>1.86 1.80 0.97 0.42 0.28</td>
<td>159</td>
<td>146</td>
</tr>
<tr>
<td>PKAN-30</td>
<td>1.88 1.84 1.30 0.585 0.38</td>
<td>165</td>
<td>153</td>
</tr>
<tr>
<td>PKAN-50</td>
<td>2.61 2.58 1.78 1.04 0.68</td>
<td>166</td>
<td>150</td>
</tr>
<tr>
<td>PKAN-60</td>
<td>2.98 2.98 2.35 1.51 1.06</td>
<td>174</td>
<td>162</td>
</tr>
<tr>
<td>PKAN-70</td>
<td>3.38 (95)$^a$ 3.38 (100) 2.74 (280) 1.88 (527) 1.28 (480)</td>
<td>164</td>
<td>164</td>
</tr>
</tbody>
</table>

$T_{g,tan}$: Glass transition temperature reported as temperature at tan δ peak.

$T_{g,LM}$: Glass transition temperature reported as temperature at loss modulus peak.

$^a$ Values in brackets show % increase over pure PEEK.

Fig. 6. Mechanical loss factor (Tan δ) versus temperature for PEEK composites (a) PKAN-0, (b) PKAN-10, (c) PKAN-30, (d) PKAN-50, and (e) PKAN-60, (f) PKAN-70.
PKAN-60. However, at higher loading i.e., at 70 wt.% due to the presence of porosity as confirmed by density and SEM, the glass transition of PKAN-70 composite was lowered than that of the composites reinforced with lower AlN_p content. However, it is still higher than that of pure PEEK. This supports the results of PEEK reinforced with 30 wt.% short carbon fiber where increase in T_g from 148 to 159 °C was observed [20]. However, these results are in contrast to CNF/PEEK [7] and PPTA treated mica/PAEK [23] composite, where shift in T_g was not observed. This may be due to poor interaction between two components. Therefore, poor interaction is not enough to affect the macromolecular mobility of polymer chains. In present study shift of T_g towards higher temperature may be due to the good interaction between the AlN_p and the matrix and increase in crystallinity [8,19] as observed in previous study [1].

It is well known that in particulate polymer composites, particles are surrounded by two regions; first by tightly bounded polymer or constrained polymer chain also called mesophase, and second, by loosely bounded polymer chains or unconstrained polymer chain i.e., regions of a continuous phase of polymer having restricted mobility. As the average interparticle distance decreases with the incorpora-

![Fig. 7. Peak height of tan delta versus AlN_p loading for PEEK composites.](image1)

![Fig. 8. Loss modulus versus temperature for PEEK composites (a) PKAN-0, (b) PKAN-10 (c) PKAN-30, (d) PKAN-50, (e) PKAN-60, and (f) PKAN-70.](image2)
ation of more filler particles, the loosely bound polymer gradually transformed to the tightly bound polymer. Hence, the volume fraction of loosely bound polymer decreases, thus leading to an increase in $T_g$ [24]. Presence of crystallinity also leads to a considerable increase in the breadth of the relaxation as compared to the initially amorphous specimen, and a corresponding decrease in intensity [8].

The peak height of the tan$\delta$ and area under the tan$\delta$ curve of the composites is decreased substantially with AlN$_p$ content. Fig. 7 shows peak values of tan$\delta$ for PEEK composites versus AlN$_p$ loading. The peak value of tan$\delta$ of PEEK (0.17) is reduced to one sixth of the pure PEEK for PKAN-70 composite. In contrast to SCFR–PEEK composite where peak height is increased considerably. The peak height and area under the tan$\delta$ curve is decreased probably due to the combined effect of (i) the reduced fraction of PEEK in composite, (ii) restricted fraction of the PEEK segments in the vicinity of AlN$_p$, (iii) increase in crystallinity, which decreases the amorphous phase of polymer involved in the glass transition [8,19], and (iv) good dispersion of AlN$_p$ in PEEK, which results in strong interaction between AlN$_p$ and the PEEK matrix [25].

Fig. 8 shows the loss modulus of PEEK and composites versus temperature with different filler content. It can be seen from the figure that the loss modulus and peak values of loss modulus decreases with AlN$_p$ content. The temperature at loss modulus peak or glass transition temperature ($T_g$, LM) was shifted towards higher temperature compared to PEEK. This supports the data of temperature of peak value of tan$\delta$ curve. Broadening of the loss modulus of composites was also observed as in tan$\delta$ versus temperature curve. Decrease in loss modulus with AlN$_p$ may be due to strong interaction or physical bonding between AlN$_p$ and PEEK matrix.

4. Conclusions

We have prepared the high performance PEEK composites incorporating AlN$_p$ up to 70 wt.%. Storage modulus is increased about 500% at 250 $^\circ$C. Glass transition temperature is increased by 19 $^\circ$C. Peak height and area under the tan$\delta$ curve is reduced. We believe that strong interaction between the AlN$_p$ and PEEK and improvement in crystallinity play an important role in determining the properties of storage modulus, tan$\delta$ and glass transition. Thermal stability of the composites is also improved. Hence, we can conclude that these futuristic composite materials may be the promising materials for high temperature applications.

Acknowledgements

RKG greatly acknowledges to the Executive Director of C-MET for permitting him for Ph.D. from IIT Bombay/C-MET, Pune. We thanks to Dr. P.D. Trivedi, Polymer Division, Gharda Chemicals, India for providing good quality PEEK powder. We would also like to thank to Dr. D.P. Amalnerkar and Dr. T. Seth for their help. We also acknowledge with thanks to Professor (Mrs.) I.K. Varma for giving fruitful suggestions and encouragement in this research area.

References

