Thermomechanical Properties of Nanosilica Reinforced PEEK Composites

Y. H. Lai \textsuperscript{a}, M. C. Kuo \textsuperscript{a, b}, J. C. Huang \textsuperscript{a*}, M. Chen \textsuperscript{a}

\textsuperscript{a} Institute of Materials Science and Engineering; Center for Nanoscience and Nanotechnology, National Sun Yat-Sen University, Kaohsiung, Taiwan 804, R. O. China

\textsuperscript{b} Department of Polymer Materials, Kun Shan University, Tainan, Taiwan 700, R. O. China

* Corresponding author: jacobc@mail.nsysu.edu.tw

Keywords: Nanocomposites, PEEK, Silica, Thermal properties, Surface modification.

Abstract. The nano-sized silica particulates reinforced poly(ether ether ketone) (PEEK) composites were fabricated by means of simple compression molding technique. The nano-sized silica, measuring 30 nm in size, was firstly modified by surface-pretreatment with stearic acid. The thermomechanical properties of the resulting PEEK/SiO\textsubscript{2} nanocomposites were measured using dynamic mechanical analysis (DMA) and thermal mechanical analysis (TMA). The TMA results show that the coefficient of thermal expansion (CTE) becomes lowered when the content of the nanosilica increases. Furthermore, the CTE of the modified-silica filled PEEK nanocomposites shows higher CTE values, as compared with those of the unmodified counterparts. The dynamic modulus of the PEEK nanocomposites shows over 40% increment at elevated temperatures from 100-250°C, indicating the apparent improvement of elevated temperature mechanical properties.

Introduction

The inclusion of inorganic fillers into polymers for commercial applications is primarily aimed at the cost reduction and stiffness improvement [1,2]. It is well known that the polymer composites can be fabricated by the incorporation of inorganic reinforcements into the polymer matrix. The properties of the resulting polymer composites depend on the characteristics, the dimensions, and the shapes of the inorganic fillers, and also on the interfacial bonding strength. It is proposed that with decreasing filler dimension or increasing filler content could significantly improve the specific area of the filler, and in turn it would greatly and effectively improve the transfer of the load between the fillers and the polymer matrix [3]. The inorganic nanofillers, ranging from 1 to 50 nm, were successfully incorporated into the polymeric matrix to strengthen and improve the ductile polymer to be more stiff and resistant for abrasion [4-7].

PEEK is a high-performance engineering plastics with high glass transition (143°C) and melting temperatures (343°C) [8]. Nanoparticle-filled PEEK composites have been successfully fabricated by means of compression molding process [4-7]. The promising high performance nanocomposites reveal a significant improvement in the tribological characteristics, resulting in considerably decreased frictional coefficient and wear rate [4-6]. Moreover, the PEEK polymer filled with nano-sized silica or alumina particles measuring 15-30 nm has demonstrated an improvement of elastic modulus and tensile strength by 20-50% [7].

The inclusion of the ceramic nanofiller into the more flexible and lower thermal resistance polymer can substantially improve its stiffness and thermal stability [7,9-10]. The nano-sized silica or alumina particles without any chemical modification were incorporated into the PEEK polymer. It appears that there are occasional clustering occurrences for two to five nano particles to cluster or align together, the majority of the nano particles were seen to disperse semi-homogeneously in the PEEK matrix [11].

However, the nano-sized silica or alumina particles filled PEEK composites appear to be somewhat agglomeration or clustering in the nanofiller phase [7,11]. It is well known that the dispersion of the nanofiller in the polymer matrix can be improved with the aids of surface
modification by chemical reaction or non-reactive modifier [12-14].

In this study, the stearic acid was applied to modify the hydrophilic surface of the silica nanoparticles for the reason that better-dispersed silica nanoparticles in the PEEK polymer could be resulted in. In order to estimate the effects of this modification on the thermomechanical properties of the PEEK matrix, the linear coefficient of thermal expansion (CTE), storage modulus ($E'$), loss modulus ($E''$), and $\tan\delta = (E''/E')$ of the composites are determined using the thermomechanical analysis (TMA) and dynamic mechanical analysis (DMA) techniques.

Experimental

The PEEK powders (grade Victrex 450P, diameter ~2-3 mm) were purchased from the ICI Company, USA, and were further ground into fine powders measuring 50 µm. The density of PEEK polymer is 1.30 Mg/m$^3$. The fumed silica nanoparticles with diameter ~30 nm and purity ~99.9% were purchased from the Plasmachem Gmbh Company, Germany/Russian. The SiO$_2$ particles are irregular in shape with an aspect ratio near 1, and the density of the silica is 2.65 g/cm$^3$.

PEEK nanocomposites were fabricated by means of compression molding at 400°C under a load of 60 MPa. Prior to compression molding, the fine PEEK powders were completely mixed with the stearic acid modified silica nanoparticles through ultrasonic vibration in alcohol medium, and then the well dispersed sol was dried at 80°C to remove the excess alcohol. PEEK nanocomposites with filler contents of 2.5, 5.0, 7.5, and 10.0 wt% were prepared through this compression mold method.

Glass transition temperatures ($T_g$), storage modulus, loss modulus, and $\tan\delta$ of the resulting PEEK nanocomposites were measured using a dynamic mechanical analyzer (Perkin-Elmer Pyris Diamond DMA). A bending mode testing was applied during the DMA scans, and the scanning range was from 30 to 250°C at a heating rate of 2°C/min and at a frequency of 1 Hz under nitrogen atmosphere. Coefficient of thermal expansion was measured by using a thermomechanical analyzer (Perkin-Elmer Diamond TMA). The thickness of the specimen was 1 ~ 2 mm, and the scanning range was from 30 to 250°C at a heating rate of 2°C/min and at a fixed load of 0.05 N under nitrogen atmosphere.

Results and Discussions

TMA measurements

The PEEK nanocomposites with 30 nm silica incorporation were successfully fabricated through hot-press method. The photograph of the resulting PEEK nanocomposite is shown in Fig. 1. The dimension of the resulting PEEK composite is about 120 mm $\times$ 120 mm $\times$ 2 mm (length $\times$ width $\times$ thickness).

![Fig. 1 The 30 nm nano-silica filled PEEK/SiO$_2$ composite.](image)

It is well known that the CTE and $T_g$ of materials can be estimated using the TMA technique. As expected, CTE is the criterion for the dimensional stability of materials. The effect of the nanofiller incorporation on the dimensional stability and $T_g$ of the resulting PEEK composites, as a function of nano-silica volume fraction, is established, and the results are shown in Fig. 2 and Table 1. Both the composites with surface modified (M) and unmodified (U) are examined and compared.
As shown in Table 1, the inclusion of the nano-silica would decrease significantly the rubbery CTE ($\alpha_R$), as the filler content increases, irrespective of the modified or unmodified cases. It is known that the specific heat of the silica is much higher than that of the PEEK polymer. It is expected that the incorporation of the nano-sized silica could significantly increase the overall specific heat of the PEEK composite: the nano-silica particles possessing large specific areas would greatly absorb the heat transferred from the PEEK matrix, and in turn greatly suppress the thermal expansion of the plastic PEEK polymer when the temperature is higher than $T_g$. The other reason for the reduction of $\alpha_R$ might be due to hindrance of the silica nanoparticles toward the expansion of PEEK chain segments themselves when the temperature is over $T_g$. The slight decrease in $\alpha_G$ for composites with a lower amount of silica is also a result of the lower CTE value of the ceramic characteristics of silica. But when the nano-silica volume fraction is higher and the particle clustering becomes more severe, this effect becomes less and less evident.

Furthermore, PEEK composites reinforced with modified-silica exhibit higher CTE values, as compared with those of the unmodified counterparts. It might account for the reason that the PEEK
polymer filled with modified silica shows more uniform nanoparticle dispersions and smaller filler domains, as a consequence, the free volume of this PEEK composite would be larger than that of the PEEK polymer filled with the unmodified silica. It is known that the free volume of the amorphous polymer should be greatly responsible for the CTE value: the larger the free volume should result in higher CTE value, as expected. The value of $T_g$ obtained from the TMA measurement reveals no significant difference, and this result is in accordance with that obtained from the following DMA method.

**DMA measurements**

![Graph showing storage modulus and tan δ for different filler content.]

Fig. 3  The (a) storage modulus and (b) tan δ of the modified-silica filled PEEK nanocomposites. The peak temperature of the tan δ can be defined as the glass transition temperature.

Table 2  Storage modulus ($E'$) and $T_g$ for the 30 nm unmodified-silica (U) and modified-silica (M) filled PEEK composites. The $T_g$ values obtained from DMA method are based on the peak temperature of tan δ curve.

<table>
<thead>
<tr>
<th>Sample</th>
<th>U/M</th>
<th>Storage modulus ($E'$) (GPa)</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>30°C</td>
<td>50°C</td>
</tr>
<tr>
<td>Pure PEEK</td>
<td>--</td>
<td>2.66</td>
<td>2.59</td>
</tr>
<tr>
<td>SiO$_2$ 2.5 wt%</td>
<td>U</td>
<td>3.19</td>
<td>3.10</td>
</tr>
<tr>
<td>M</td>
<td>3.26</td>
<td>3.19</td>
<td>3.08</td>
</tr>
<tr>
<td>SiO$_2$ 5 wt%</td>
<td>U</td>
<td>3.43</td>
<td>3.35</td>
</tr>
<tr>
<td>M</td>
<td>3.48</td>
<td>3.41</td>
<td>3.30</td>
</tr>
<tr>
<td>SiO$_2$ 7.5 wt%</td>
<td>U</td>
<td>3.49</td>
<td>3.43</td>
</tr>
<tr>
<td>M</td>
<td>3.50</td>
<td>3.42</td>
<td>3.31</td>
</tr>
<tr>
<td>SiO$_2$ 10 wt%</td>
<td>U</td>
<td>3.62</td>
<td>3.54</td>
</tr>
<tr>
<td>M</td>
<td>3.72</td>
<td>3.64</td>
<td>3.49</td>
</tr>
</tbody>
</table>

Dynamic mechanical analysis for the unmodified-silica and modified-silica filled PEEK nanocomposites were conducted to examine the effect of the inorganic nanoparticles on the thermomechanical properties of the PEEK polymer. In Fig. 3, the storage modulus ($E'$) and tan δ of the PEEK nanocomposites are shown. Addition of the inorganic filler would increase the level of the $E'$ in the glassy region, with the highest value observed for the filler content of 10 wt%. It appears that the dispersion of the silica nanoparticles in the PEEK matrix seems to be acceptable, so
that the modulus of the organic PEEK polymer can be improved with increasing inorganic filler content.

As for the enhancement on the storage modulus associated with the surface pretreatment, as shown in Table 2, the $E'$ values for the PEEK polymer filled with the modified silica appear to be slightly higher than those of the unmodified counterparts, suggesting that better dispersion of the nano-sized silica could reduce its domain size and make greater improvement on the modulus of the PEEK matrix.

Summary

1. The inclusion of the nano-sized silica particles into the PEEK matrix could significantly decrease the CTE values at temperatures greater than $T_g$, demonstrating the improvement on the dimensional stability of the resulting PEEK nanocomposites.
2. The PEEK nanocomposite filled with the modified-silica would result in higher CTE values as compared with those of the unmodified counterparts, indicating that the more uniform filler dispersions and smaller filler domains in the PEEK matrix could bring about a high level of polymer free volume.
3. The inclusion of nano-sized silica particles could significantly increase the storage modulus of the resulting PEEK composites. However, it shows minimum effect on the $T_g$ value.
4. The PEEK nanocomposite filled with the modified silica would show higher storage modulus values as compared with those of the unmodified counterparts, also suggesting that the better dispersion of the nano-sized silica could reduce the polymer domain size and make greater improvement on the modulus of the PEEK matrix.

Acknowledgements

The authors would like to gratefully acknowledge the sponsorship from National Science Council of Taiwan, ROC, under the project no. NSC 93-2216-E-110-005.

References

