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Thermal and Dielectric Properties of High Performance Polymer/ZnO Nanocomposites

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Abstract. Zinc oxide (ZnO) filled high performance poly(aryletherketon) (PAEK) matrix nanocomposites were studied for the application in electronic applications. The nanocomposites were prepared using planetary ball milling process followed by hot pressing. Experimental density of the nanocomposites was close to those of theoretical density indicating porosity free samples. Scanning electron microscopy showed excellent dispersion of nano sized (< 100 nm) ZnO particles into the PAEK matrix. X-ray diffraction (XRD) confirmed that the size of ZnO crystallites is about 58 nm. Thermogravimetry analyzer (TGA) showed significant increase in thermal stability and char yield of the nanocomposites with increasing ZnO content in the matrix. The dielectric constants of the nanocomposites increased significantly compared to those of pure PAEK.

1. Introduction
Polymer matrix composites with discontinuous fillers (or dispersants) are widely used for the applications like die attachment, electrically and thermally conductive, adhesives encapsulations and thermal interface materials. It is well known that polymers are easily processable and need low processing temperatures. However, compared to ceramics they have lower electrical and thermal conductivity, lower stiffness, and higher coefficient of thermal expansion (CTE). The field of nanotechnology is one of the most popular areas for current research and development. At present, easily availability of nanomaterials offers the promise of developing polymer matrix nanocomposites (PNCs) with tailored thermal, mechanical and electrical properties for a particular application. PNCs are polymer matrix composites (PMCs) containing fillers with at least one dimension in the range of 1 nm to 100 nm. There are several ceramic particles like Al\textsubscript{2}O\textsubscript{3}, AlN, SiO\textsubscript{2}, BN, ZnO etc \cite{1-5}, which have been added into the polymer matrices such as ultra high molecular weight polyethylene (UHMWPE) \cite{4}, Polyvinyl alcohol \cite{5}, emeraldine base polymer \cite{6}, Low density polyethylene \cite{7}, Polycaprolactone \cite{8}, Polyester imide \cite{9}, Polyamide–imide \cite{10}, Silicon rubber \cite{11}, Polymethylmethacrylate \cite{12-13}, Nylon-6 \cite{14}, Polypropylene \cite{15}, Polystyrene \cite{16}, Polyimide \cite{17}. It was reported that the addition of ZnO into the polymer matrix increases the thermal stability, dielectric properties, and wear resistance of the composites.

Polyaryletherketone (PAEK) is a high temperature semi-crystalline thermoplastics polymer which has high glass transition and melting point. In addition, it shows very good impact strength at low temperatures, high mechanical fatigue strength, and a very low tendency to creep as well as good sliding and wear properties. The chemical resistance is also very good \cite{18}. Despite its good mechanical, tribological and chemical properties, hardly any work on the PAEK based composites is reported in the literature. In view of above, the aim of this study is to study the effect of addition of ZnO nanopowder on the dielectric constant and thermal stability of the PAEK matrix.
2. Experimental procedure

2.1 Materials

PAEK powder was donated by Gharda Chemicals Ltd., Thane (Mumbai), India. The ZnO nanopowder was purchased from M/s Sigma Aldrich Chemicals Ltd., USA. According to manufacturer, its particle size is < 100 nm.

2.2 Preparation of PAEK/ZnO nanocomposites

The different weight percentages (0 to 30 wt. %) of ZnO were added into the PAEK matrix using planetary ball milling with 5 h mixing time. The ball to powder ratio was about 10:1. Mixed powder was taken out from the mill after 5 h and dried in a vacuum oven at 180 ºC for 4 h. The weighted powder was filled into the tool steel die for hot pressing. The samples were hot pressed at 350 ºC under 45 MPa pressure. The thickness and diameter of the samples were 1.5 mm and 13 mm, respectively. Since, properties of nanocomposites vary with volume fraction of reinforcing particles, volume fraction of ZnO was determined using equation 1.

\[
V_f = \frac{W_f}{W_f + W_m(\rho_f/\rho_m)}
\]  

(1)

where, \(V_f\) is the volume fraction, \(W_f\) is the weight fraction, and \(\rho_f\) is the density of ZnO particles. \(W_m\) and \(\rho_m\) are the weight fraction and density of PAEK matrix, respectively. The wt. % and corresponding vol. % of the ZnO into the nanocomposites is shown in Table 1.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>% ZnO in the PAEK matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC-0*</td>
<td>0</td>
</tr>
<tr>
<td>NC-5</td>
<td>5</td>
</tr>
<tr>
<td>NC-10</td>
<td>10</td>
</tr>
<tr>
<td>NC-20</td>
<td>20</td>
</tr>
<tr>
<td>NC-30</td>
<td>30</td>
</tr>
</tbody>
</table>

* NC-X, where X represents wt% ZnO added into the PAEK matrix.

2.3 Characterization

2.3.1 Density Measurement

The theoretical density \(\rho_{th}\) of the nanocomposites was calculated using rule of mixture as shown in equation (2). The densities of ZnO and PAEK were considered as 5.61 g/cc and 1.29 g/cc, respectively.

\[
\rho_{th} = \rho_f V_f + \rho_m V_m
\]  

(2)

Where, \(V_m\) is the volume fraction of matrix. The experimental density \(\rho_{ex}\) was determined by Archimedes Principle using equation (3).

\[
\rho_{ex} = \frac{W_{air}}{W_{air} - W_{liq}} \times \rho_{liq}
\]  

(3)

where, \(W_{air}\) and \(W_{liq}\) are the weight of samples in air and liquid medium (ethanol), respectively. The density \(\rho_{liq}\) of ethanol is (0.79 g/cc).
2.3.2 X-Ray Diffraction (XRD)
XRD pattern of the pure ZnO nano-sized powder was recorded on Philips X’Pert PANalytical PW 3040/60. Ni filtered Cu kα radiation (λ = 1.54) generated at 40 kV and 30 mA was used for diffraction angle (2θ) ranging from 10º to 90º. Analysis was carried out at room temperature.

2.3.3 Scanning Electron Microscopy (SEM)
SEM (JOEL: JSM-6360A) was carried out to examine the dispersion of ZnO nanoparticles in the PAEK matrix. Before SEM, 30 wt% ZnO nanocomposites sample was fractured in liquid nitrogen for about 15 minutes. Sample surface was coated with a thin layer of platinum using sputter coater (JEC 60) to avoid its charging.

2.3.4 Dielectric properties
The dielectric constant was obtained from the measurement of capacitance (C) using Precision Impedance Analyzer (Wayne Kerr Electronics 6515B, UK) at frequency ranges from 1 kHz to 15 MHz at room temperature. The dielectric constant (ε) was evaluated using equation (4),

$$\varepsilon = \frac{C \times t}{S \times \varepsilon_0}$$

where, S is the surface area, C is the capacitance and t is the thickness of sample. The $\varepsilon_0$ is the permittivity of free space (8.854 × 10^{-12} F/m) i.e. real part. The dielectric loss tangent/dissipation factor which is the ratio of dielectric loss to dielectric constant was obtained directly from the instrument. Before measurements silver paste was applied on both sides of the samples.

2.3.5 Thermal properties
Thermogravimetry analysis (TGA) was done to find out thermal stability and char yield of the nanocomposites using TGA (Perkin Elmer TGA 4000). The samples were heated from 50 °C to 1000 °C at a heating rate 10 °C/min in N₂ atmosphere. The temperatures of 10 wt% and 30 wt% loss were represented as the degradation temperature of T_{10} and T_{30}, respectively. The maximum decomposition temperature (T_{max}) was taken as the temperature corresponding to maximum of the peak obtained from the first order derivative curve of TGA (i.e. DTG). The % char yield was determined at temperature of 1000 °C.

3. Results and discussion
3.1 Density of nanocomposites
Figure 1 shows the experimental and theoretical density of nanocomposites as a function of ZnO content. It is observed that the density of the samples increased from 1.29 g/cc for pure PAEK to 1.68 g/cc for 30 wt% (9.0 vol.%) ZnO nanocomposite. It is due to higher density (i.e. 5.61 g/cc) of pure ZnO. The experimental density of the nanocomposite containing 5 wt% (~ 1.19 vol.%) ZnO is slightly higher than that of theoretical density. This may be due to the nucleating effect of ZnO nanoparticles which probably increases the crystallinity of the matrix. Thereafter, the experimental density of the nanocomposites is close to those of theoretical density of the samples.
3.2 X-Ray Diffraction (XRD)

Figure 2 shows diffraction intensity versus diffraction angular position ($2\theta$) in the range 30-70º for the major crystallographic reflection for the ZnO nano powder. Pure ZnO powder shows sharp Bragg peaks at $31.837^\circ$, $34.502^\circ$, $36.334^\circ$, $47.650^\circ$, $56.726^\circ$, $63.012^\circ$ and $68.114^\circ$ corresponding to diffraction planes of (010), (002), (011), (012), (110), (013) and (112) indicating that it has an hexagonally wurtzite crystal structure [13]. The crystallite size of ZnO nanopowder was calculated using Scherrer’s equation (Equation. 5),

$$\text{Crystallite size} = \frac{k \times \lambda}{\beta \times \cos \theta} \quad (5)$$

where, $k$ is the shape factor (for cubic materials, it is 0.9), $\lambda$ is the Cu $k\alpha$ wavelength of X-ray, $\beta$ is the full width at half maxima and $\theta$ is the Bragg’s angle. The powder size was about 58 nm.
3.3 Scanning electron microscopy (SEM)
Figure 3(a) shows the SEM image of pure ZnO nanopowder. It can be seen that the size of ZnO particle is smaller than 100 nm and some aggregates are also seen. Figure 3(b) shows SEM image 30 wt% ZnO filled PAEK nanocomposite (NC-30) at a magnification of ×10,000. It can be clearly seen that the ZnO nanoparticles are almost uniformly dispersed in the matrix. However, ZnO aggregates were also observed at some location due to its hydrophilic nature [9] and higher specific surface area.

3.4 Dielectric Properties
Figure 4 shows the dielectric constant of PAEK/ZnO nanocomposites. For a given frequency, dielectric constant of nanocomposites increases with increasing ZnO content in the matrix. It is well known that ZnO is a polar ceramic. When a high frequency AC field is applied, the ZnO particle is in a quick and strong polarization and hence it results in higher dielectric constant for the nanocomposites [7]. Figure 5 shows the dissipation factor of the nanocomposites. It decreases for the nanocomposites containing up to 10 wt% ZnO, thereafter it increases with increasing ZnO content in the matrix.

3.5 Thermogravimetry analysis (TGA)
Figure 6(a) shows the residual weight of the nanocomposites as a function of temperature. It is observed that pure PAEK has a degradation temperature (T$_{10}$) of 567 ºC. It was observed that the T$_{10}$ of the nanocomposites increases significantly with increasing ZnO content and also the char yield at 1000 ºC increased significantly from 53 % for pure PAEK (NC-0) to 67.5 % for NC-30 nanocomposites. Therefore, the incorporation of ZnO in polymer matrix improved the thermal stability of the nanocomposites. The increase in thermal stability could be due to strong interaction and/or interfacial bonding between the matrix and ZnO nanoparticles, which hindered the segmented movement of the PAEK [9]. Figure 6(b) shows the derivative curve of the nanocomposites as a function of temperature.
Figure 3 SEM images of (a) pure ZnO nanopowder, inset shows high magnification image (b) 30 wt. % ZnO (NC-30) filled PAEK nanocomposites.
Figure 4 Dielectric constant versus vol% ZnO content for PAEK/ZnO nanocomposites

Figure 5 Dissipation factor versus vol.% ZnO content for PAEK/ZnO nanocomposites
When major weight loss begins, there is a sharp increase in the derivative which then reaches a maximum rate of weight loss. After the maximum, the derivative curves tend to level off somewhat. It shows that the maximum decomposition of the nanocomposites increases from 579 °C for the pure matrix to 592 °C for NC-30.

Figure 6 (a) TGA curves and (b) DTG curves for the PAEK/ZnO nanocomposites under nitrogen atmosphere
4. Conclusion

High performance PAEK/ZnO nanocomposites were successfully prepared using planetary ball mill followed by hot pressing. XRD shows that ZnO powder has hexagonal crystal structure and its crystallite size is about 58 nm. SEM shows good dispersion of ZnO nanoparticles into the matrix. Dielectric constant and the thermal stability of the nanocomposites increased significantly with increasing content of ZnO in the matrix.

5. Acknowledgement

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