Polyimide nanocomposites with functionalized SiO$_2$ nanoparticles: Enhanced processability, thermal and mechanical properties

Young-Jae Kim,$^a$ Jong-Heon Kim,$^b$ Shin-Woo Ha,$^{a,c}$ Dongil Kwon,$^b$ Jin-Kyu Lee$^a$

$^a$Department of Chemistry, Seoul National University, Seoul 151-747, Korea

$^b$Department of Materials Science and Engineering, Seoul National University, Seoul 151-744, Korea

$^c$Present address: Department of Medicine, Emory University, Atlanta, GA 30322, USA

Figure. S1 Size distributions of (a) SiO$_2$ in EtOH, (b) DETAS-SiO$_2$ in EtOH, (c) as-prepared P-SiO$_2$ in NMP, and (d) P-SiO$_2$ in NMP after being stored for one year.
Figure. S2 TEM images of unmodified SiO$_2$-PI nanocomposites. The TEM images were obtained by spin-coating SiO$_2$-PAA solution onto a TEM grid, followed by thermal imidization.

Figure. S3 FT-IR spectra of (a) unmodified silica nanoparticles, (b) DETAS-SiO$_2$, and (c) P-SiO$_2$. 
Figure. S4 Solid $^{13}$C CP/MAS NMR spectra of (a) DETAS-SiO$_2$ and (b) P-SiO$_2$.

Table S1. Calculated molar ratio of organic groups on SiO$_2$ nanoparticles by TGA.

<table>
<thead>
<tr>
<th></th>
<th>Weight percent (wt%)</th>
<th>Molecular weight (g/mol)</th>
<th>Relative amount from 100 g sample (mol)</th>
<th>Mole percent of organic groups (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>87.4</td>
<td>60 (for fully condensed SiO$_2$)</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>DETAS on the DETAS-SiO$_2$</td>
<td>5.6</td>
<td>265.43 (for DETAS)</td>
<td>$2.1 \times 10^{-2}$</td>
<td>1.4</td>
</tr>
<tr>
<td>Phthalic anhydride on the P-SiO$_2$</td>
<td>7</td>
<td>148.12 (for phtalic anhydride)</td>
<td>$4.7 \times 10^{-2}$</td>
<td>3.1</td>
</tr>
</tbody>
</table>
Figure. S5 TEM images of 40 wt% SiO$_2$-PI nanocomposites. The TEM images were obtained by spin-coating SiO$_2$-PAA solution onto a TEM grid, followed by thermal imidization.

Figure. S6 Thermal expansion of neat PI film and SiO$_2$-PI nanocomposite films with various SiO$_2$ contents.
Calculation details

The mathematical equation\(^1\) is described as follows:

\[ \alpha_c = \alpha_f \phi_f + \alpha_m \phi_m \]

where the subscripts \(c, m, f\) represent nanocomposites, polymer, and filler phase, respectively. \(\alpha\) and \(\phi\) are coefficient of thermal expansion and the volume fraction of the constituents. The coefficient of thermal expansion for polyimide and SiO\(_2\) are 33.9 and 0.55 \((10^{-6}/°C)\), respectively.

Table S2. The experimental and calculated value of coefficients of thermal expansion of polyimide and SiO\(_2\)-polyimide nanocomposites

<table>
<thead>
<tr>
<th>wt. %</th>
<th>vol. %</th>
<th>Experimental value ((10^{-6}/°C))</th>
<th>Calculated value ((10^{-6}/°C))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PI</td>
<td>-</td>
<td>33.9</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>2.2</td>
<td>30.8</td>
<td>33.1</td>
</tr>
<tr>
<td>10</td>
<td>4.6</td>
<td>30.6</td>
<td>32.2</td>
</tr>
<tr>
<td>20</td>
<td>9.8</td>
<td>27.8</td>
<td>30.2</td>
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