Improvement of Thermal and Mechanical Properties of Polyimide Using Metal Oxide Nanoparticles

Ahmad Raza Ashraf\(\phi\).\$, Zareen Akhter\$\$, Leonardo C. Simon\(\phi\)

\(\phi\) Department of Chemical Engineering, University of Waterloo, Waterloo, Canada

\$ Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan

2016 SPE AUTOMOTIVE COMPOSITES CONFERENCE & EXHIBITION (ACCE)
September 7-9 2016, Novi, Michigan, USA
Overview

Introduction
- What are polyimides?
  - History, structure, properties
- Applications
  - General
  - Automotive

Synthesis
- Polyimide
- Polyimide nanocomposites

Results + Conclusion
- Glass transition temperature
- Storage modulus
- Thermal stability
What are polyimides?

• High performance polymers
• Aromatic polyimides consists of
  1. Heterocyclic imide rings and
  2. Aryl groups
  linked by simple atoms or groups

R = alkyl or phenyl with or without functional groups
History

• The first synthesis of polyimide was performed by Bogert and Renshaw in 1908.

• High-molecular weight aromatic polyimide was synthesized in 1955 by Edward and Robinson.

• Poly(4,4'-oxydiphenylene pyromellitimid) widely known as Kapton® was commercialized in early 1960s.

• After the success of Kapton (Dupont), several other PIs have been synthesized and investigated extensively.

• Commercial examples also include Vespel (Dupont), Upilex (Ube), Meldin (Saint-Gobain).
Polyimides

Outstanding thermal stability

Low dielectric constant

Low moisture absorption

Excellent mechanical properties

Fire and wear resistance

Chemical and radiation resistance

High glass transition temperature

Low dielectric constant

Low moisture absorption

Outstanding thermal stability

Excellent mechanical properties

Fire and wear resistance

Chemical and radiation resistance

High glass transition temperature
Why polyimides are so strong???

Charge Transfer Complex

Thin film insulators in electronic packaging.

Base of flexible white LED strip lights.

H$_2$O$_2$ sensors.

Gas separation membranes.

Lightweight composites of RP46 polyimide and glass fibers are extraordinarily fire-resistant electrical-insulation materials.
Applications in automotive industry

- Aerospace structures as outer protective covering, engine ducts and bushings.

- The bushings, bearing pads and splines in the 10-stage high-pressure compressor of the Rolls-Royce BR710 turbofan engine are made from Vespel polyimide. These parts are exposed to temperatures up to 274 °C yet need no lubrication.
Applications in automotive industry

- Polyimide foams: The winner of NASA's 2007 commercial invention of the year are effective for sound, heat and cold insulation.
  - Effective thermal insulation from -240 °C to +204 °C
  - Inherently fire-resistant
  - Low cost and fast production
  - Can be molded into different shapes.

- Aerospace ethernet cables comprise of aluminized polyimide shield.
  1. Engineered fluoropolymer jacket
  2. Braided shield
  3. Aluminized polyimide shield
  4. FEP filler
  5. Color-coded composite dielectric
Applications in automotive industry

- Thinner, lighter Vespel® SP-21 thrust washers replace all-metal needle bearings in a new 7-speed AT for rear-drive vehicles.

- Variable stator vane bushings made from Vespel CP are used in the high pressure section of the compressor in an aircraft engine. The laminate withstands temperatures in excess of 675°F.
Applications in automotive industry

- DuPont™ Vespel® polyimide bushings offers weight and performance advantages over metal in exhaust gas recirculation (EGR) valves.

- Due to their stiffness, tensile strength & resistance to friction, wear and hot exhaust gases at temperatures up to 220 °C, these bushings have replaced metal components in EGR system used in four and six cylinder stratified-charged petrol engines.
Applications in automotive industry

- BWD oil pressure light switch has polyimide film diaphragm.

- Conductive Kapton is used as mirror & seat heaters, engine warmers of cars, wing, floor and satellite heaters in aerospace. (thermo-llc.com)
Applications in Automotive Industry

- The circuits of BWD throttle position sensors are printed on flexible polyimide film for excellent dimensional stability and for prevention of electrical performance drift.

- The Dayton audio D250P-8 compression driver features polyimide diaphragm for smooth character and rich detailed sound.
Synthesis of polyimide

**Step 1**
1. DMAc
2. 25°C
3. 24 hrs stirring

**Polyamic acid**

**Step 2**
Thermal Imidization
- 70°C (18hr),
- 120°C, 150°C, 200°C, 250°C, 280°C (1hr each)

**Polyimide**

**BTDA** = 3,3’,4,4’-benzophenonetetracarboxylic dianhydride
**MDA** = 4,4’-methylenedianiline
Synthesis of polyimide/nanocomposites

1. MDA + DMAc
2. Sonication
3. MDA/DMAc/NPs
4. BTDA
5. Stirring
6. Polyamic acid/ Nanocomposite
7. Thermal Imidization (25 - 280 °C)
8. Polyimide/Nanocomposite
Review: Interaction of nanoparticles with polyamic acid

Interaction between nanoparticles and polyimide

Polyimide/Al₂O₃ Nanocomposites

Glass transition temperature (Tg)

- Pure polyimide (BM) displayed glass transition temperature (Tg) at 272 °C.
- Incorporation of Al₂O₃ nanoparticles increased the Tg of polyimide matrix.
- Trend was continued with increasing concentration of nanoparticles.
- At 9% loading of nanoparticles Tg was increased from 272 °C to 337 °C.

BM = polyimide (BTDA + MDA)
Polyimide/Al₂O₃ Nanocomposites

- Modulus of pure polyimide (BM) is above 1 GPa up to 250 °C.
- It decreased sharply around glass transition temperature (Tg = 272 °C).
- Al₂O₃ nanoparticles improved the modulus.
- Modulus value at 50 °C increased from 1.60 GPa to 2.56 GPa at 9% loading of nanoparticles.

BM = polyimide (BTDA + MDA)
## Polyimide/Al$_2$O$_3$ Nanocomposites

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Tg (°C)</th>
<th>Modulus$^{50}$ (GPa)</th>
<th>Modulus$^{150}$ (GPa)</th>
<th>Modulus$^{250}$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BM</td>
<td>272</td>
<td>1.60</td>
<td>1.21</td>
<td>0.88</td>
</tr>
<tr>
<td>BM-Al$_2$O$_3$-3%</td>
<td>300</td>
<td>1.95</td>
<td>1.48</td>
<td>1.08</td>
</tr>
<tr>
<td>BM-Al$_2$O$_3$-5%</td>
<td>316</td>
<td>2.20</td>
<td>1.67</td>
<td>1.21</td>
</tr>
<tr>
<td>BM-Al$_2$O$_3$-7%</td>
<td>325</td>
<td>2.46</td>
<td>1.70</td>
<td>1.24</td>
</tr>
<tr>
<td>BM-Al$_2$O$_3$-9%</td>
<td>337</td>
<td>2.56</td>
<td>2.01</td>
<td>1.64</td>
</tr>
</tbody>
</table>

Tg = Glass transition temperature  
Modulus$^{50}$ = Modulus at 50 °C  
Modulus$^{150}$ = Modulus at 150 °C  
Modulus$^{250}$ = Modulus at 250 °C
Polyimide/Al$_2$O$_3$ Nanocomposites

Thermal Stability

- Decomposition started after 450 °C.
- Temperature of 5% weight loss is above 540 °C.
- Shape of curve suggests one step degradation mechanism.
- Nanoparticles incorporation improved the thermal stability of polyimide.

$N_2$, Ramp at 20 °C/min to 800 °C
BM = polyimide (BTDA + MDA)
### Polyimide/Al₂O₃ Nanocomposites

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T_1$ (°C)</th>
<th>$T_5$ (°C)</th>
<th>$T_{10}$ (°C)</th>
<th>$R_{800}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BM</td>
<td>449</td>
<td>542</td>
<td>572</td>
<td>61</td>
</tr>
<tr>
<td>BM-Al₂O₃-3%</td>
<td>451</td>
<td>545</td>
<td>575</td>
<td>63</td>
</tr>
<tr>
<td>BM-Al₂O₃-5%</td>
<td>453</td>
<td>545</td>
<td>575</td>
<td>64</td>
</tr>
<tr>
<td>BM-Al₂O₃-7%</td>
<td>453</td>
<td>545</td>
<td>576</td>
<td>65</td>
</tr>
<tr>
<td>BM-Al₂O₃-9%</td>
<td>453</td>
<td>552</td>
<td>580</td>
<td>68</td>
</tr>
</tbody>
</table>

$T_1$ = Temperature at 1% weight loss  
$T_5$ = Temperature at 5% weight loss  
$T_{10}$ = Temperature at 10% weight loss  
$R_{800}$ = Residue at 800 °C
Polyimide/Al₂O₃ Nanocomposites

Isothermal study at 400 °C for 30 minutes

- Polyimides can withstand elevated temperatures for a certain period of time.
- Pure polyimide (BM) showed only 2.5% weight loss after 30 minutes of isothermal treatment at 400 °C.
- This was further reduced to 1.9% at 9% loading of Al₂O₃
- Improvement in thermal stability in case of Polyimide/Al₂O₃ composites is evident from decrease in weight loss.

BM = polyimide (BTDA + MDA)

Air, Ramp at 50 °C/min to 400 °C
<table>
<thead>
<tr>
<th>Polymer</th>
<th>$W_{15}$ (%)</th>
<th>$W_{25}$ (%)</th>
<th>$W_{35}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BM</td>
<td>97.81</td>
<td>97.61</td>
<td>97.47</td>
</tr>
<tr>
<td>BM-Al$_2$O$_3$-3%</td>
<td>98.26</td>
<td>98.05</td>
<td>97.91</td>
</tr>
<tr>
<td>BM-Al$_2$O$_3$-5%</td>
<td>98.32</td>
<td>98.12</td>
<td>97.97</td>
</tr>
<tr>
<td>BM-Al$_2$O$_3$-7%</td>
<td>98.38</td>
<td>98.17</td>
<td>98.02</td>
</tr>
<tr>
<td>BM-Al$_2$O$_3$-9%</td>
<td>98.46</td>
<td>98.25</td>
<td>98.12</td>
</tr>
</tbody>
</table>

$W_{15}$ = Weight percent after 15 minutes  
$W_{25}$ = Weight percent after 25 minutes  
$W_{35}$ = Weight percent after 35 minutes
**Polyimide/ZnO Nanocomposites**

**Glass transition temperature (Tg)**

- Pure polyimide displayed glass transition temperature (Tg) at 272 °C.
- Incorporation of ZnO nanoparticles increased the Tg of polyimide matrix.
- Shape of curve at 9% loading suggests different levels of interactions between nanoparticles and polyimide matrix.
- At 9% loading, Tg was increased from 272 °C to 360 °C.

BM = polyimide (BTDA + MDA)
Polyimide/ZnO Nanocomposites

Storage Modulus

- Modulus of pure polyimide (BM) above 1 GPa up to 250 °C.
- It decreased sharply around glass transition temperature (Tg = 272 °C).
- ZnO nanoparticles improved the modulus of parent polyimide matrix both at start and around Tg.
- Modulus value at 50 °C was increased from 1.60 GPa to 2.32 GPa at 9% loading of nanoparticles.

BM = polyimide (BTDA + MDA)
### Polyimide/ZnO Nanocomposites

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Tg (°C)</th>
<th>Modulus(^{50}) ((10^9))</th>
<th>Modulus(^{150}) ((10^9))</th>
<th>Modulus(^{250}) ((10^9))</th>
</tr>
</thead>
<tbody>
<tr>
<td>BM</td>
<td>272</td>
<td>1.60</td>
<td>1.21</td>
<td>0.88</td>
</tr>
<tr>
<td>BM-ZnO-3%</td>
<td>280</td>
<td>1.73</td>
<td>1.30</td>
<td>1.06</td>
</tr>
<tr>
<td>BM-ZnO-5%</td>
<td>319</td>
<td>1.87</td>
<td>1.39</td>
<td>1.08</td>
</tr>
<tr>
<td>BM-ZnO-7%</td>
<td>327</td>
<td>2.14</td>
<td>1.47</td>
<td>1.08</td>
</tr>
<tr>
<td>BM-ZnO-9%</td>
<td>360</td>
<td>2.32</td>
<td>1.70</td>
<td>1.26</td>
</tr>
</tbody>
</table>

Tg = Glass transition temperature  
Modulus\(^{50}\) = Modulus at 50 °C  
Modulus\(^{150}\) = Modulus at 150 °C  
Modulus\(^{250}\) = Modulus at 250 °C
N$_2$, Ramp at 20 °C/min to 800 °C

BM = polyimide (BTDA + MDA)

- ZnO nanoparticles decreased the thermal stability of polyimide.
- $T_5$ was lowered to 460 °C from 542 °C.
- ZnO concentration has no effect on thermal behavior.
- Shape of curve suggests one step degradation mechanism for pure polyimide and two steps for polyimide/ZnO.
### Polyimide/ZnO Nanocomposites

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T_1$ (°C)</th>
<th>$T_5$ (°C)</th>
<th>$T_{10}$ (°C)</th>
<th>$R_{800}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BM</td>
<td>449</td>
<td>542</td>
<td>572</td>
<td>61</td>
</tr>
<tr>
<td>BM-ZnO-3%</td>
<td>393</td>
<td>459</td>
<td>504</td>
<td>62</td>
</tr>
<tr>
<td>BM-ZnO-5%</td>
<td>404</td>
<td>465</td>
<td>513</td>
<td>63</td>
</tr>
<tr>
<td>BM-ZnO-7%</td>
<td>404</td>
<td>468</td>
<td>517</td>
<td>63</td>
</tr>
<tr>
<td>BM-ZnO-9%</td>
<td>390</td>
<td>465</td>
<td>514</td>
<td>67</td>
</tr>
</tbody>
</table>

$T_1$ = Temperature at 1% weight loss  
$T_5$ = Temperature at 5% weight loss  
$T_{10}$ = Temperature at 10% weight loss  
$R_{800}$ = Residue at 800 °C
Comparison between PI/Al\textsubscript{2}O\textsubscript{3} and PI/ZnO

Glass transition temperature (Tg)

- Both types of nanoparticles increased glass transition temperature (Tg).
- At 9% loading, ZnO nanoparticles are more effective in increasing glass transition temperature than Al\textsubscript{2}O\textsubscript{3} counterparts.
Comparison between PI/Al₂O₃ and PI/ZnO

Storage Modulus ($E'$) at 50 °C

- Nanoparticles increased modulus.
- Addition of Al₂O₃ changes is more effective than ZnO to improve $E'$. 
Comparison between PI/Al$_2$O$_3$ and PI/ZnO

- Al$_2$O$_3$ nanoparticles improved the thermal stability at 5% weight loss.
- ZnO decreased thermal stability.
Conclusions

- Nanoparticles can further improve modulus, glass transition temperature and thermal stability, thus with potential to provide further benefit in automotive applications.

- Thermogravimetric analysis (TGA) showed substantial thermal stability, thermal decomposition started after 450 °C in some cases.

- Isothermal studies with TGA showed that polyimides are capable to withstand at elevated temperatures for longer period of time.
Conclusions

- Incorporation of Al$_2$O$_3$ and ZnO nanoparticles increased the glass transition temperature and modulus of polyimide.

- At 9% loading, ZnO nanoparticles increased glass transition temperature more than Al$_2$O$_3$, but Al$_2$O$_3$ provided better modulus.

- Polyimide/Al$_2$O$_3$ nanocomposites had higher thermal stability than polyimide alone.
Acknowledgments

- **University of Waterloo, Waterloo, Canada** (NSERC Discovery Grant and experimental facilities)

- **Quaid-i-Azam University, Islamabad, Pakistan** (experimental facilities)

- **Higher Education Commission of Pakistan** for funding of **Ahmad Raza Ashraf** under International Research Support Initiative Program (for research visit as graduate student at University of Waterloo, Canada) and Indigenous PhD Fellowship Program at Quaid-i-Azam University, Islamabad, Pakistan.

Thank you!