Structure-Property Relationship in High $T_g$ Thermosetting Polyimides

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OBJECTIVE

1) Replace MDA in PMR-15 with 2,2'-substituted benzidine

2) Evaluate the thermo-oxidative stability and mechanical properties of DMBZ-15 against PMR-15.
Glass Transition Temperatures (Tₐ’s) of Polyimide Resins

<table>
<thead>
<tr>
<th>Resins</th>
<th>Tₐ by TMA, (°C)</th>
<th>Tₐ by TMA, (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Non-postcure</td>
<td>Postcure at 316 °C</td>
</tr>
<tr>
<td>PMR-15</td>
<td>276</td>
<td>350</td>
</tr>
<tr>
<td>DMBZ-15</td>
<td>333</td>
<td>391</td>
</tr>
<tr>
<td>PEBZ-16</td>
<td>341</td>
<td>407</td>
</tr>
<tr>
<td>BFBZ-18</td>
<td>370</td>
<td>360, 404</td>
</tr>
<tr>
<td>PHBZ-18</td>
<td>250</td>
<td>348</td>
</tr>
</tbody>
</table>
X-Ray Crystal Structure of 2,2'-Bis(trifluoro)benzidine (BFBZ)

Dihedral Angle $\varphi = 59^\circ$

X-Ray Crystal Structure of 2,2'-Dimethylbenzidine (DMBZ)

Dihedral Angle $\phi = 75^\circ$
Isothermal Aging of Polyimide Resins at 288 °C (550 °F) under 1 atm of Circulating Air

![Graph showing weight loss vs. hours at 288 °C for different polyimide resins.](image)
Thermoplastic Polyimides

Polyimides with Substituted Benzidine

<table>
<thead>
<tr>
<th>Substituent</th>
<th>Tg</th>
<th>TGA</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF₃</td>
<td>290 °C</td>
<td>600 °C</td>
</tr>
<tr>
<td>CH₃</td>
<td>300 °C</td>
<td>500 °C</td>
</tr>
<tr>
<td>Ph</td>
<td>unclear</td>
<td>600 °C</td>
</tr>
</tbody>
</table>

CP-MAS $^{13}$C NMR of DMBZ-15 imidized powder (top) and cross-linked resin (bottom)

**Imidized powder**

a. Benzophenone carbonyl  
b. Nadic imide carbonyl  
c. BTDE imide carbonyl  
d. DMBZ carbon next to nitrogen  
e. Endcap double bond; BTDE next to benzophenone; DMBZ biphenyl link  
f. Other aromatics  
h. Nadic bridge  
i. Other aliphatic nadic peaks  
j. DMBZ methyls

**Cross-linked resin (changes only)**

e. BTDE next to benzophenone; DMBZ biphenyl link  
h. Other nadic aliphatics  
i. Nadic bridge
Compressive Strength of Polyimide Composites

One hot-wet cycle = 93 °C water soak to >1% weight gain,
Dry out at 288 °C to < 0.1% moisture
Degradation Products of DMBZ-15 by TGA-MS
Gas Evolution Profile of DMBZ-15 Polyimide Resins

- CO$_2$
- Phenyl Isocyanate
- Aromatics
- CO
- Water
- Methane
- Water

Absorbance vs. Wavenumber (cm$^{-1}$)
Conclusion

1) PMR polyimides containing substituted benzidines displayed high $T_g$'s (350 – 407 °C), due to hindered rotation of noncoplanar biphenyldiamines

2) Stability of substituents in BTDA-based PMR polyimides: $\text{CH}_3 > \text{Ph} > \text{CF}_3$, in contrast to thermoplastic polyimides: $\text{CF}_3 \sim \text{Ph} > \text{CH}_3$

3) Phenylethynyl endcap is more stable than nadic endcap

3) DMBZ-15 (BTDE/DMBZ/NE) composites exhibited comparable mechanical properties to PMR-15