Structure-Property Relationship in High \( T_g \) Thermosetting Polyimides

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OBJECTIVE

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

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

<table>
<thead>
<tr>
<th>Resins</th>
<th>T_g by TMA(^a), (°C)</th>
<th>T_g by TMA, (°C) Postcure(^b) at 316 °C</th>
</tr>
</thead>
<tbody>
<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(^c), 404(^d)</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
Thermoplastic Polyimides

\[
\text{Polyimides with Substituted Benzidine} \quad \begin{array}{ll}
X = \text{CF}_3 & T_g = 290 \, ^\circ\text{C} \\
X = \text{CH}_3 & T_g = 300 \, ^\circ\text{C} \\
X = \text{Ph} & T_g = \text{unclear}
\end{array}
\]

TGA / N\textsubscript{2} (5\% Wt Loss)

\[
600 \, ^\circ\text{C} \\
500 \, ^\circ\text{C} \\
600 \, ^\circ\text{C}
\]

Frank W. Harris, S.L.C. Hsu, c.C. Tso, Polymer Preprints, 31(1), 342 (1990)
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
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