Low Viscosity Imides Based on Asymmetric Oxydiphthalic Anhydride

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A series of low-melt viscosity imide resins were prepared from asymmetric oxydiphthalic dianhydride (a-ODPA) and 4-phenylethynylphthalic anhydride as the endcap, along with 3,4′-oxydianiline (3,4′-ODA), 3,4′-methylenedianiline (3,4′-MDA), 3,3′-methylenedianiline (3,3′-MDA) and 3,3′-diaminobenzophenone (3,3′-DABP), using a solvent-free melt process. These imide oligomers display low-melt viscosities (2-15 poise) at 260-280 °C, which made them amenable to low-cost resin transfer molding (RTM) process. The a-ODPA based RTM resins exhibit glass transition temperatures (Tg’s) in the range of 265-330 °C after postcure at 343 °C. The mechanical properties of these polyimide/carbon fiber composites fabricated by RTM will be discussed.
Low-Melt Viscosity Imides Based on Asymmetric Oxydiphthallic Anhydride

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High Temperature Polyimide Composites
Materials and Processing

♦ PMR-15, PMR-II-50, AFR-PE4, PETI-5 composites all require solvent-based prepregs for processing. 

  *time consuming, costly and hazardous*

♦ Process polymer composites via RTM, VARTM

  *produce 30% cost saving & 12% weight saving*

♦ New low-melt viscosity (10-30 poise) imide resins:
  • amenable to low-cost RTM process
  • advance PMC temperature capability to 260-315°C beyond state-of-the-art RTM resins, such as epoxy (177 °C) & BMI (232 °C)
Synthesis of RTM Resins (NASA Glenn)

RTM370
(Tg =370°C)

RTM350
(Tg =350°C)

RTM330
(Tg =330°C)

Advantages of polyimide resins containing a-BPDA vs s-BPDA

- Lower melt viscosities
- Higher Tg’s
Open-Hole Compression Strength of RTM370, RTM350, RTM330 vs BMI-5270-1

- **RTM370**
- **RTM350**
- **RTM330**
- **BMI-5270-1**

**Conditions:**
- 23 °C (74 °F)
- 288 °C (550 °F)
- 315 °C (600 °F)
Open-Hole Compression Modulus of RTM370, RTM350, RTM330 vs BMI-5270-1

<table>
<thead>
<tr>
<th>Temperature</th>
<th>RTM370</th>
<th>RTM350</th>
<th>RTM330</th>
<th>BMI-5270-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>23 °C</td>
<td>50 GPa</td>
<td>45 GPa</td>
<td>40 GPa</td>
<td>50 GPa</td>
</tr>
<tr>
<td>288 °C</td>
<td>55 GPa</td>
<td>50 GPa</td>
<td>45 GPa</td>
<td>60 GPa</td>
</tr>
<tr>
<td>315 °C</td>
<td>60 GPa</td>
<td>55 GPa</td>
<td>50 GPa</td>
<td>70 GPa</td>
</tr>
</tbody>
</table>
Short Beam Shear Strength of RTM370, RTM350 & RTM330 vs BMI-5270-1

- RTM370
- RTM350
- RTM330
- BMI-5270-1

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>RTM370</th>
<th>RTM350</th>
<th>RTM330</th>
<th>BMI-5270-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>288</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>315</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- 23 °C: 74 °F
- 288 °C: 550 °F
- 315 °C: 600 °F

Short Beam Shear Strength (MPa)
New Effort in RTM Resins

- Prepare novel imide resins with low-melt viscosities (10-30 poise) that are amenable to RTM or VARTM processes.

- Process new imide resins by RTM or VARTM into composite panels and evaluated mechanical properties and durability at 550-600 °F.
Low-melt Viscosity Imide Resins Based on a-ODPA

\[ \text{a-ODPA} \quad \overset{\text{X} = \text{O, CH}_2, \text{C=O}}{\longrightarrow} \quad \text{Imidized Oligomers} \]

\[ \overset{\text{Melted}}{\longrightarrow} \quad \text{PEPA} \]
Physical Properties of Imide Oligomers/Resins
Based on a-ODPA / 4-PEPA

<table>
<thead>
<tr>
<th>Dianhydride</th>
<th>Diamine</th>
<th>Oligomer Min. η [@280°C] by Brookfield (^1) (Poise)</th>
<th>Oligomer Min. Complex [η](^\text{[η]})@260°C(^2) (Poise)</th>
<th>Cured Resin (T_g) (°C) NPC(^3) By TMA</th>
<th>Cured Resin (T_g) (°C) PC(^4)@650°F By TMA(^5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-ODPA</td>
<td>3,4’-ODA</td>
<td>3.5</td>
<td>15.0</td>
<td>296</td>
<td>329</td>
</tr>
<tr>
<td>a-ODPA</td>
<td>3,4’-MDA</td>
<td>4.0</td>
<td>14.0</td>
<td>270</td>
<td>294</td>
</tr>
<tr>
<td>a-ODPA</td>
<td>3,3’-MDA</td>
<td>2.5</td>
<td>3.0</td>
<td>273</td>
<td>266</td>
</tr>
<tr>
<td>a-ODPA</td>
<td>3,3’-DABP</td>
<td>3.0</td>
<td>4.0</td>
<td>270</td>
<td>297</td>
</tr>
</tbody>
</table>

\(^1\) Absolute viscosity measured by Brookfield Viscometer at 280 °C.
\(^2\) Complex viscosity measured by Aries Rheometer, using parallel plates.
\(^3\) NPC = No Post cure
\(^4\) PC = Post cured at 343 °C (650 °F) for 16 hrs.
\(^5\) TMA = Thermal mechanical analysis heated at 10 °C/min, using expansion mode.
Physical Properties of Imide Oligomers/Resins Based on *a-BPDA* and 4-PEPA

<table>
<thead>
<tr>
<th>Resin</th>
<th>Diamine</th>
<th>Oligomer Min. η @280 °C by Brookfield ¹ (Poise)</th>
<th>Oligomer Min. Complex [η]* @280°C ² (Poise)</th>
<th>Cured Resin T₉(°C) NPC ³ byTMA</th>
<th>Cured Resin T₉(°C) PC⁴@ 650°F By TMA⁵</th>
</tr>
</thead>
<tbody>
<tr>
<td>RTM370</td>
<td>3,4′-ODA</td>
<td>14</td>
<td>11</td>
<td>342</td>
<td>370</td>
</tr>
<tr>
<td>RTM350</td>
<td>3,4′-MDA</td>
<td>7.4</td>
<td>20</td>
<td>338</td>
<td>350</td>
</tr>
<tr>
<td>RTM330</td>
<td>3,3′-MDA</td>
<td>1.5</td>
<td>10</td>
<td>288</td>
<td>330</td>
</tr>
</tbody>
</table>

¹ Absolute viscosity measured by Brookfield Viscometer at 280 °C.
² Complex viscosity measured by Aries Rheometer, using parallel plates.
³ NPC = No Postcure
⁴ PC = Postcured at 343 °C (650 °F) for 16 hrs.
⁵ TMA = Thermal mechanical analysis heated at 10 °C/min, using expansion mode.
Rheology of a-ODPA/3,4′-ODA/PEPA Imide Resins at 260 °C Hold

Advantages:
Maintained low-melt viscosity (4-15 poise) at 260 °C
Rheology of a-ODPA/3,3′-DABP/PEPA Imide Resins at 260 °C Hold

Advantages:
Maintained low-melt viscosity (4-15 poise) at 260 °C
Conclusions

♦ a-ODPA based RTM imide resins exhibit low melt viscosities at 260 °C comparable to a-BPDA based resins at 280 °C (10 fold)

♦ a-ODPA based RTM imide resins exhibit lower T_g’s (40- 65 °C lower) than a-BPDA based RTM imide resins

Reason: Additional flexible –O– linkage versus Steric hindrance of biphenyl unit
Continued Efforts

♦ Fabricate composite panels from a-ODPA imide resins by RTM at 260 °C and VARTM, if feasible

♦ Evaluate Mechanical properties of a-ODPA/PEPA based imide composites
Acknowledgements

Funding Sources:

♦ Air Force Office of Scientific Research Grant to Clark Atlanta University Program manager: Dr. Charles Lee

♦ NASA Supersonic Program Program manager: Dale Hopkin