Synthesis and characterization of polyimides for FPC applications

J. H. Yoon, Y. U. Bae and T. H. Yoon *

Department of Materials Science and Engineering, Gwangju Institute of
Science & Technology, Gwangju, Korea

Introduction

As the microelectronic devices become smaller and lighter, flexible printed circuit boards (FPC) have received great attention ever before. Among the materials for FPC, polyimides are the promising candidate due to their excellent thermal, mechanical and electrical properties, high dimensional stability, and good chemical resistance [1]. In FPC, polyimides have to have CTE of 17 ppm since that of Cu is 17 ppm and excellent adhesive property (80g/mil), besides high Tg (>230°C), good thermal stability (>500°C), low water absorption and good solubility [2-3]. Consequently, research has been focusing on the preparation of novel polyimides with low CTE and good adhesion without sacrificing good thermal properties as well as solubility.

In order to lower CTE, one has to increase rigidity of polyimide backbone by utilizing rigid-rod type monomers. But these monomers would decrease solubility and processability [4-6], resulting in poor adhesion. Consequently, (polyimide-acid) instead of polyimide has been widely utilized, which is converted to polyimide by thermal imidization, leading to large volume shrinkage and thus large residual stress. Another inherent drawback of polyimide for FPC is relatively poor adhesion property.

In this study, therefore, we attempted to prepare polyimides from mono-substituted PMDA-based rigid-rod type diamides and diamines such as mDAPO and pDA to prepare soluble polyimide precursors with CTE of 17 ppm and good adhesion property besides excellent thermal, mechanical and good solubility.

Experimental

The monomers such as PMDA, 3FPPMDA, and mDAPO were synthesized as reported previously, while pDA was purchased from Aldrich and utilized after sublimation. The polyimides were prepared via a conventional two-step process: polyimide-acid, followed by solution imidization by refluxing in NMP with 2,4-DCB (Scheme 1).

In order to lower CTE of polyimides, pDA was added by varying the molar ratio of mDAPO/pDA. The polyimides were designed to have a molecular weight of 20,000 g/mol and characterized by FT-IR, NMR, DSC and TGA. In addition, intrinsic viscosity and coefficient of thermal expansion (CTE) were also measured. Adhesion property was evaluated via peel test with the samples prepared from polyimide coated Cu foils.

Scheme 1. Synthetic scheme of polyimides

Results and Discussion

The polyimides prepared from PMDA and 3FPPMDA with mDAPO/pDA were characterized by FT-IR and NMR, demonstrating successful polymer synthesis. These polyimides were only soluble in NMP or DMAc among the solvents tested (Table 1). Despite rigid backbone structure, good solubility can be attributed to triphenylamide segments and non-co-planar characteristics of mDAPO. The intrinsic viscosities evaluated in NMP were in the range of 0.21-0.25 dL/g, demonstrating successful polymerization considering of the controlled molecular weight of 25,000 g/mol.

The polyimide of PMDA-mDAPO provided Tg of 322°C, which increased as pDA increased, providing Tg of 348°C with 40% pDA. Compared to this, 3FPPMDA-based polyimides showed Tg of 319°C, which increased to 350°C at 50% pDA, respectively. These polyimides also exhibited excellent thermal stability in air, providing thermal degradation temperature of 500°C or higher in air at 10°C/min.

CTE value of PMDA-mDAPO based polyimide was 26 ppm and decreased to 17.3 ppm at 40% pDA, while 3FPPMDA-mDAPO polyimides provided CTE of 29 and 16 ppm at 0% and 60% pDA respectively. As expected, CTE decreased as pDA increased.

Table 1. Solubility of mono-substituted PMDA-mDAPO polyimides

<table>
<thead>
<tr>
<th>mDAPO/pDA</th>
<th>NMP</th>
<th>DMAc</th>
<th>CHCl₃</th>
<th>TCB</th>
<th>THF</th>
<th>Volume Acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMDA</td>
<td>100</td>
<td>S</td>
<td>S</td>
<td>P</td>
<td>P</td>
<td>S I P I I I I</td>
</tr>
<tr>
<td>70/30</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>P</td>
<td>P</td>
<td>S I P I I I I</td>
</tr>
<tr>
<td>60/40</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>I</td>
<td>I</td>
<td>S I P I I I I</td>
</tr>
<tr>
<td>50/50</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>P</td>
<td>S I P I I I I</td>
</tr>
<tr>
<td>40/60</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>P</td>
<td>S I P I I I I</td>
</tr>
</tbody>
</table>

*Polyimide similar to Tg for 24hrs (100°C)
**S: Soluble, P: Partially soluble, I: Insoluble

Table 2. Characteristics of mono-substituted PMDA-mDAPO polyimides

<table>
<thead>
<tr>
<th>mDAPO/pDA</th>
<th>Tg (°C)</th>
<th>Tg (°C)</th>
<th>CTE (ppm)</th>
<th>Tg (°C)</th>
<th>Residue (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMDA</td>
<td>322</td>
<td>322</td>
<td>24.0</td>
<td>522</td>
<td>32</td>
</tr>
<tr>
<td>70/30</td>
<td>348</td>
<td>337</td>
<td>20.9</td>
<td>515</td>
<td>30</td>
</tr>
<tr>
<td>60/40</td>
<td>348</td>
<td>340</td>
<td>17.3</td>
<td>514</td>
<td>27</td>
</tr>
<tr>
<td>50/50</td>
<td>348</td>
<td>340</td>
<td>17.3</td>
<td>514</td>
<td>27</td>
</tr>
<tr>
<td>40/60</td>
<td>348</td>
<td>340</td>
<td>17.3</td>
<td>514</td>
<td>27</td>
</tr>
</tbody>
</table>

*a: 25°C in NMP; b: by DSC and test 100°C/min; c: by DSC 90°C/min, d: by TGA, 50°C/min, e: by TGA, 10°C/min; f: by TGA at 500°C, 10°C/min in air

Conclusions

1. Polymides of PMDA-mDAPO/pDA and 3FPPMDA-mDAPO/pDA were successfully synthesized with molecular weight of 25,000 g/mol.
2. The polyimides exhibited high Tg, excellent thermal stability in air and good solubility in NMP and DMAc.
3. The CTE of 17 ppm was obtained by adding pDA of 40% (PMDA-mDAPO/pDA) and 60% (3FPPMDA-mDAPO/pDA).

References