Performance Aromatic-Aliphatic Polyimides

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Two types of aromatic-aliphatic polyimides have been synthesized: polyaddition polyimides, from the Michael reaction between 4,4'-diaminobenzylbismaleimide and ethylenediol (diethyleneglycol respectively) and solution polycondensation polyimides, from the reaction of 5-(2,5-dioxotetrahydrofururyl)-3-methyl-3-cyclohexenyl-1,2-dicarboxylic acid anhydride (epiclon) with 4,4'-diaminodibenzyl [1,4-bis(p-amino phenoxy)benzene respectively]. All monomers and polymers were characterized by conventional methods, and the physical properties of the polymers, including solubility, thermal, optical, electrical or mechanical properties were discussed.

Keywords: bismaleimides, Michael reaction, epiclon, aliphatic polyimides

Polyimides (PIs) are a class of representative high-performance polymers possessing the imide and aromatic groups in the main chains. They are extensively used in microelectronics such as interlayer dielectrics, protective coatings and adhesives, due to their thermostadative stability, high mechanical strength, excellent electrical properties and high radiation resistance [1]. From these, bismaleimides (BMIs) represent a special class of thermoSET compounds. Bismaleimide based structural polymers have attracted much attention as linear polymers or matrix resin due to their good adhesive properties, high thermal stability, and the possibility to form network structures without loss of volatiles [2] especially for fiber-reinforced composites, in electronic industry and aerospace technology [3]. The maleic double bonds in BMIs can undergo facile thermal addition polymerization to result in highly crosslinked and brittle polyimides [4,5]. For practical applications, the use of chain-extended prepolymer is expected to reduce the inherent brittleness of BMIs because of the higher molecular weight between crosslinks [6]. One such chain-extended copolymerization can develop a Michael addition reaction of a nucleophile to the electrophile maleimide double bond. BMIs and bisnucleophiles have been exploited in the synthesis of a variety of linear polyimides. In particular, bisthioles, diamines and diols have been used to extend bismaleimides, resulting in poly(imido-sulfide)s [7], poly(aspartamide)s [8] and poly(imido-ether)s [9]. The fully aromatic polyimides having excellent physical properties often face processing problems because of their limited solubilities and high Tg. A great deal of research effort on soluble polyimide has been focused on alicyclic polyimides that retain high mechanical and thermal properties together with good transparency and low dielectric constant. Epiclon, which is a cycloaliphatic anhydride with flexible and asymmetrical structure, has been used as raw material for polyimides resins to enhance the solubility and to render other new properties [10]. The literature of this field presents different polyimides that combine into the same macromolecule, i.e., units, aromatic rings, asymmetrical groups and flexible bonds (such as epiclon moieties) and develop new expected properties for microelectronic applications [11]. The use of the alicyclic monomers may be a good compromise between processability and thermal properties of polyimides.

The present the paper presents the synthesis and characterization of two imide type compounds: poly(imido-ether)s from the Michael polyaddition reaction between an aromatic bismaleimide and aliphatic diols and alicyclic polyimides from solution polycondensation between a cycloaliphatic dianhydride and aromatic diamines.

Experimental part

Measurements

Infrared spectra were recorded with a Specord M-80 Spectrophotometer from KBr pellets. The 1H-NMR spectra were recorded on a JEOL C-60 MHz Spectrometer for polymer solution in deuterated dimethylsulfoxide (DMSO-d6) using tetramethylsilane (TMS) as internal standard. Thermogravimetric analyses (TGA) were performed on a MOM derivatograph (Hungary) in air, at a heating rate of 12°C/min. The initial decomposition temperature (IDT) is characterized as the temperature at which the sample achieves a wt 5% loss. The glass transition temperatures (Tg) of the polymers were determined with a Mettler differential scanning calorimeter DSC 12E at a heating rate of 12°C/min under nitrogen atmosphere. Mecanical properties were determined with a Schopper MZ Gip testing machine. The numerical average molecular weights (Mn) of the copolymers was determined by gel permeation chromatography using a PL-EMD 950 Evaporative Mass Detector equipped with 2 x PLgel 5 μm MIXED-C, 300 . 7.5 mm columns. The atomic force microscopy measurements (AFM) were performed in air at room temperature, with the SemiContact Technique, in the Phase Contrast Mode, with the commercially available NSG10/Au Silicon cantilevers. The manufacturer’s values for the probe tip radius were of 10 nm, and the typical force constant was 11.5 N/m. In the tapping mode, the cantilever assembly was oscillated at a frequency of 524.5 kHz.

Materials

Maleic anhydride (Aldrich) was sublimed before use. Acetic anhydride, 5-(2,5-dioxotetrahydrofururyl)-3-methyl-3-cyclohexenyl-1,2-dicarboxylic acid anhydride (epiclon), ethylenediol, diethyleneglycol, 4,4’-diaminodibenzyl, and 1,4-bis(p- amino phenoxy)benzene, provided by different commercial sources, were used as received. Solvents such as acetone, methanol, N-vinyl-2-pyrolidone (NVP), from

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different commercial sources, were purified by the usual methods [14].

Monomer synthesis

\(N,N' \cdot 4,4'\)-dibenzylbismaleimide (BMI) was synthesized by Searle reaction between maleic anhydride and 4,4'‐diaminodibenzyl according to the literature [15]. Yield: 79.3%; mp: 232-234°C. Elem. Anal., calcld. for C\(_{22}\)H\(_{16}\)O\(_4\)N\(_2\) (372) C: 70.96%; H: 4.30%; N: 7.52% found: C, 69.99%; H, 4.65%; N, 7.12%. IR (KBr disc): 3100 cm\(^{-1}\) (=C-H), 1770, 1720 cm\(^{-1}\) (imide I), 1400 cm\(^{-1}\) (imide II), 1150 cm\(^{-1}\) (imide III), 690 cm\(^{-1}\) (imide IV), 1605 cm\(^{-1}\) (arom. ring). \(\text{H-NMR (DMSO-d}_6\): } \delta = 7.3-7.96 \text{ (m, 8 H, aromatic), 7.16 (s, 4 H, -CH).}

Polymers synthesis

Polyimides PI\(_1\). The synthetic procedure to obtain these oligomers was a Michael polyaddition reaction between the \(N,N' \cdot 4,4'\)-dibenzylbismaleimide and 1.2-ethanediol (diethyleneglycol respectively) in a 2:1 molar ratio BMI:diol (scheme 1A). The reactions were performed at 105°C, for 12-14 h, under nitrogen atmosphere, in dry NMP, (40% monomers concentration solution), using 2-mercapto-benzothiazole as catalyst. The reaction mixture was subsequently poured into water. The precipitate was collected by filtration and washed several times with water and methanol. The products were dried at 60°C for 5 h in a vacuum oven.

Polyimides PI\(_2\) were obtained by solution polycondensation reaction of equimolar amounts of 5-(2,5-dioxotetrahydrofurfuryl)-3-methyl-3-cyclohexenyl-1,2-dicarboxylic acid anhydride (epiclon) and 4,4'-diaminodibenzy or 1,4-bis(p-aminophenoxy)benzene, respectively, in NMP, under anhydrous conditions and nitrogen atmosphere (scheme 1B). The first step was run at room temperature by adding the solid dianhydride to the solution of diamine in NMP, under stirring in inert atmosphere. The resulting viscous solution of polyamic acid (stirred at room temperature for 3-4 h) was then heated at 185-200°C for 2-3 h, so that the cyclization to imide structure took place. The water resulting from the cyclization process was eliminated with a slow stream of nitrogen. Small parts of polymer solutions have been cast onto glass plates to check the film forming ability. The rest of solution was poured into water to precipitate the solid polymer.

Prepregs Manufacture

The resulting oligomers PI\(_1\) have been used to prepare prepregs by impregnation of glass fabrics via solvent/solution techniques. The prepregs have been obtained firstly by impregnation of a glass tissue (with Finish Z-6040 and thickness 0.18-0.20 mm) with the corresponding polymer varnish (50% solid copolymers in NMP or DMF). They hold 40-42 wt. % copolymer and 3-3.5% volatiles after 15 min. of drying at 120°C. The resulting prepregs have been pressed under 2.5 MPa at 180°C for 1h and then thermally treated at 200°C for 48 h.

Results and discussions

In order to obtain a favourable balance between processability and physical characteristics, the monomer structures were selected such as flexible, angular units, ortho-catenation, cycloaliphatic or asymmetrical groups to be introduced within the polymer backbone as to inhibit inter-chain interactions and to promote better solubility. Two types of aromatic-aliphatic polyimides have been synthesized: polyaddition polyimides, PI\(_1\), and polycondensation polyimides, PI\(_2\). The synthetic chemistry for these structures is outlined in scheme 1.

Scheme 1. Synthesis of the polyimides PI\(_1\) and PI\(_2\)
The polyimides PI1 have been obtained by Michael polyaddition reactions between N,N'-4,4'- dibenzylbismaleimide (BMI) and 1,2-ethanediol and diethylene glycol respectively. The polyimides PI2 have been obtained by solution polycondensation between a cycloaliphatic dianhydride, 5-(2,5-dioxotetrahydrofururyl)-3-methyl-3-cyclohexenyl-1,2-dicarboxylic acid anhydride, and 4,4'-diaminodibenzyl or 4-bis(p-aminophenoxy) benzene, followed by thermal ring closure of the resulting polyamidic acids (PAA). The chemical structures of the obtained polymers were supported with the analytical results of elemental analysis and of IR and 1H-NMR spectroscopy.

The IR spectra of the resulting products showed characteristic absorptions bands for the imide structure at: 1785-1770 cm⁻¹ and at 1720-1710 cm⁻¹ (imide I) bands which are commonly attributed to the symmetrical and asymmetrical stretching vibrations of carbonyl groups of imide groups. The absorptions at 1395-1380 cm⁻¹ (imide II) due to C-N stretching in imide ring, at 1175-1180 cm⁻¹ (imide III) and 680-670 cm⁻¹ (imide IV) possibly due to imide ring deformation, are also present. Other absorptions bands in the range of 1030-1040 cm⁻¹ and 1175-1300 cm⁻¹ respectively, were attributed to the aliphatic and aromatic ether bridges, while others at about 3000-2850 cm⁻¹ were due to symmetrical and asymmetrical stretching vibrations of aliphatic groups. Figure 1 shows the IR spectra of BMI, PI1-a and PI2-b.

The 1H-NMR spectra also confirm the expected structures. Table 1 presents spectral 1H-NMR data for the both imide type polymers, PI1 and PI2.

The thermal stability was evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The resulting polyimides begin to decompose above 270°C and show 10% wt loss in the range of 315-368°C (Table 2). Based on the similar structures one can assume that the degradation process could begin in the aliphatic segment of the backbone and then propagates to the entire structure [16]. The glass transition temperature (Tg) that could be considered as the temperature at which a polymer undergoes extensive cooperative segmental motion along the backbone, is affected by different intra- and intermolecular interactions including hydrogen bonding, electrostatic and ionic forces, chain packing efficiency and chain stiffness. The presence of the flexible ether linkages in the polymer structure decreases the energy of internal rotation, lowering the Tg (PI2-b table 2) [17].室温溶解度测试实验是通过使用不同的溶剂：NMP，DMF，THF，DMSO，DMAc，CHCl₃，acetone，methanol，toluene，benzene。所有产品的溶解度在电子供体溶剂中如NMP，DMF，DMSO，DMAc，THF，是可溶的。这些产品具有在分子结构中的灵活键合和序列，以及通过氢键、静电和离子力而产生的异质性和空间阻碍，防止了分子链的紧密包装，并且使分子形状远非刚性轴 [18]。模型分子用于 PI2 的片段（通过研究的聚合物）

<table>
<thead>
<tr>
<th>Sample</th>
<th>1H-NMR spectral data</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI1-a</td>
<td>6.87-7.90 (m, 12H, arom); 4.67-4.70 (t, 2H, methine - succinimide ring); 2.95-3.07 (d, 4H, methylene -, succinimide ring) 2.87 (s, 4H, ethylene, BMI bridge) 3.83 (m, 4H, aliphatic - diol moiety)</td>
</tr>
<tr>
<td>PI1-b</td>
<td>7.05 - 7.86 (m, 12H, arom); 4.67 -4.73 (t, 2H, methyne - succinimide ring) 2.94-3.02 (d, 4H, methylene -, succinimide ring) 2.87 (s, 4H, ethylene -, BMI bridge) 3.58 - 3.81 (m, 8H, aliphatic- diol moiety)</td>
</tr>
<tr>
<td>PI2-a</td>
<td>6.92 - 8.02 (m, 12H, arom); 1.97 - 4.10 (m, 11H, aliphatic - epicon moiety) 2.88 (s, 4H, ethylene -diamine moiety)</td>
</tr>
<tr>
<td>PI2-b</td>
<td>6.87 - 8.23 (m, 18H, arom); 1.95 - 4.05 (m, 11H, aliphatic - epicon moiety)</td>
</tr>
</tbody>
</table>

* Multiplicity: s = singlet; m = multiplet; t = triplet; d = doublet. Solvent DMSO-d₆, internal reference TMS.
Hyperchem program, version 4.0 (19) confirm these structures as flexible macromolecular chains in comparison with all aromatic polyimides which are usually rigid linear polymers (fig. 2).

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The polyimide-ether)s, PI1, have been used to prepare prepregs. The composites have shown a good flexural strength in the range 363-382 MPa (table 3), values similar to those of other related bismaleimide/glass fabric composites [20-23].

The NMP solutions of the polyimides PI2, having a concentration of 10%, were cast onto glass substrates and dried to yield thin transparent films. Figures 3 and 4 show the bi- and three-dimensional structure, respectively, for the film PI2-b, studied to examine the surface morphology and to measure its surface topography by Atomic Force Microscopy.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mn (g/mol)</th>
<th>IDT * (°C)</th>
<th>T10 °C (°C)</th>
<th>Tg °C (°C)</th>
<th>IDT °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI1-a</td>
<td>-</td>
<td>290</td>
<td>315</td>
<td>-</td>
<td>312</td>
</tr>
<tr>
<td>PI1-b</td>
<td>-</td>
<td>295</td>
<td>320</td>
<td>-</td>
<td>323</td>
</tr>
<tr>
<td>PI2-a</td>
<td>70000</td>
<td>270</td>
<td>325</td>
<td>240</td>
<td>-</td>
</tr>
<tr>
<td>PI2-b</td>
<td>75000</td>
<td>280</td>
<td>368</td>
<td>230</td>
<td>-</td>
</tr>
</tbody>
</table>

* Initial decomposition temperature = temperature of 5% weight loss;
* Temperature of 10% weight loss (oligomers)
* Glass transition temperature; * cure: 200°C / 3h

Table 2

<table>
<thead>
<tr>
<th>Property b</th>
<th>Sample (MPa)</th>
<th>Sample (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flexural Strength (RT/dry)</td>
<td>382</td>
<td>363</td>
</tr>
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</table>

*a Cure cycle: 180 °C / 1h + 200 °C / 48h
*b Property measured using 2 mm composites: glass fabric Finish Z-6040/resin content 42% by weight.

Table 3

MECHANICAL PROPERTIES OF COMPOSITES POLY(IMIDE-ETHER)5/GLASS FABRICS*
The surface morphology and roughness of the polyimide film could be mainly the result of polymer chains characteristics that govern aggregation and molecular ordering during drying and thermal imidization processes. Transparency in the visible region was evaluated by averaging the transmittances in the range from 400 to 780 nm in the UV-VIS spectrum. The PI2 films exhibited characteristic signal as from 450 nm (fig.5).

The refractive index, $n$, is a fundamental physical property of a substance and is the most important property of any optical system that uses refraction. The refractive indices of the polymer solutions are considered as additive functions of the solvent ($w_{\text{DMF}}$) and polymer ($w_{\text{polymer}}$) compositions (equation 1).

$$n_{\text{solution}} = n_{\text{DMF}} w_{\text{DMF}} + n_{\text{polymer}} w_{\text{polymer}}$$

The refractive index values of the resulting polyimides PI2 were determined based on the refractive index for N,N-dimethylformamide (DMF) and the refractive index measurements of the polymer solutions, using an Abbe refractometer, with an experimental error of approx. $\pm 4\%$ (table 4) [24]. The number average molecular weights $M_n$ for polyimides were determined by gel permeation chromatography (GPC) measurements in DMF, on a PL EMD-950 evaporative light scattering detector apparatus (table 2).

The dielectric constant, $\varepsilon$, is used to describe a material’s ability to store the charge, when used as a capacitor device. Materials with dielectric constants below 4.0, provide effective electrical barrier properties and this behavior has led them to be referred as “dielectrics” [24, 25]. The magnitude of the dielectric constant is dependent on the ability of the polarizable units in a polymer to orient fast enough to keep up with the oscillations of an alternating electric field. The contribution of each polarization mode to the dielectric constant is expressed in equation (2).

$$\varepsilon = \varepsilon_{\text{electronic}} + \varepsilon_{\text{atomic}} + \varepsilon_{\text{dipolar}}$$

At optical frequencies (approx. $10^{15}$Hz), only the lowest mass species, the electrons, are efficiently polarized. Dielectric constant at optical frequency, $\varepsilon_{\text{electronic}}$, when only electronic polarization occurs, was determined using Maxwell’s relationship, that implies knowledge of the refractive indices of the studied polymers, $n$, according to eq. (3):

$$\varepsilon_{\text{electronic}} = n^2$$

Table 4 presents the experimental data for the refractive index and optical dielectric constant of the polyimides PI2.

The polyimides PI2 showed low optical dielectric constants reflecting the influence of the different binding structures. The control of the balance between the optical and electrical properties is very important in the polyimide materials applications.

**Conclusions**

Soluble polyimides containing flexible ether bridges and asymmetrical structural moieties were prepared by Michael polyaddition reaction or by solution poly-condensation at high temperature. The polyimides showed high thermal stability with decomposition temperature above 270°C and glass transition temperatures in the range of 230-240°C. The oligomers PI1 based on bismaleimides were used to obtain new composites which presented flexural strength values (363÷382 MPa) comparable to that of the other related bismaleimide –diamine/glass fabric composites. The polyimides PI2, soluble in polar aprotic solvents, could be cast into thin films from such solutions. The PI2-b film showed a root-mean-square (rms) roughness of 1.52319 nm over an area of (1 × 1)μm² (AFM measurements). The epilcon based polymers demonstrated small refractive index values (1.747, 1.679) small optical dielectric constants (3.052, 2.819) and characteristic absorptions as from 450 nm in the visible region. The optical properties of these compounds in connection with their electrical and strong adhesion, recommend them as dielectric interlayers in the fabrication of semiconductor chips and multichip packaging structures.

**References**


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