Polycondensation 2010 Meeting

Book of Abstracts

5-8 September 2010
Rolduc Abbey, The Netherlands
Poly(ethylene terephthalate) terpolymers containing 1,4-cyclohexanedinemethanol and isosorbide

R. Quintana, A. Martinez de Ildaruya, A. Alla, S. Muñoz Guerra

Universitat Politècnica de Catalunya, ETSEIB, Chemical Engineering Department, Av. Diagonal 647, 08028 Barcelona, Spain. E-mail: antxon.martinez.de.ildaruya@upc.edu

Introduction
Poly(ethylene terephthalate) (PET) is a thermoplastic polyester widely used in the field of textile and packaging industry [1,2]. However, due to its constitutional regularity it has a high tendency to crystallize which is an inconvenient for those applications in which a high transparency is required. To overcome this limitation, we have synthesized and characterized new terpolymers derived from PET that incorporate varying amounts of 1,4-cyclohexanedinemethanol (CHDM) and D-isosorbide, a biobased monomer.

Materials and methods
PECIsT terpolymers were obtained by a two step melt polycondensation procedure, from terephthalic acid, ethylene glycol, and variable amounts of CHDM and isosorbide on a Karl Kurt Juchheim stainless steel reactor. The molecular weights were determined on a Waters GPC system. NMR spectra were recorded on a Bruker AMX-300 from samples dissolved in CDCl₃. Thermal properties were evaluated on a PerkinElmer DSC Pyris 1 calibrated with indium and zinc at heating/cooling rates of 10 °C·min⁻¹ under nitrogen circulation. Thermogravimetric analysis (TGA) were carried out on a PerkinElmer TGA-8 thermobalance at a heating rate of 10 °C·min⁻¹ under a nitrogen atmosphere.

Results and discussion
The structure of PECIsT terpolymers is shown in Figure 1. They were obtained with fairly high molecular weights and intrinsic viscosities ranged between 0.55-0.7 dL·g⁻¹ (Table 1).

![Figure 1: Chemical structure of PECIsT terpolymers](image)

The composition of the PECIsT terpolymers, determined from ¹H NMR spectra showed that small amounts of isosorbide were lost in the polycondensation, and that all of them contain small amounts (less than 3%) of diethylene glycol units as a consequence of the occurrence of etherification side reactions.

<table>
<thead>
<tr>
<th>Polyester</th>
<th>Final composition E/C/Is</th>
<th>Molecular weights [η] (dL·g⁻¹)</th>
<th>Mw (g·mol⁻¹)</th>
<th>PD</th>
<th>Tₙ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE₇₀C₃₀T</td>
<td>71.4/28.6/0</td>
<td>0.70</td>
<td>32400</td>
<td>2.3</td>
<td>81</td>
</tr>
<tr>
<td>PE₇₀C₃₂/S₁₂T</td>
<td>73/23.4/3.6</td>
<td>0.64</td>
<td>30600</td>
<td>2.3</td>
<td>84</td>
</tr>
<tr>
<td>PE₇₀C₃₀/₁₉₀T</td>
<td>74.3/19.2/6.5</td>
<td>0.63</td>
<td>30100</td>
<td>2.5</td>
<td>88</td>
</tr>
<tr>
<td>PE₇₀C₁₅/S₁₅T</td>
<td>75.6/14.4/10</td>
<td>0.61</td>
<td>25900</td>
<td>2.4</td>
<td>91</td>
</tr>
<tr>
<td>PE₇₀I₃₀T</td>
<td>76.9/0/23.1</td>
<td>0.55</td>
<td>26600</td>
<td>2.4</td>
<td>105</td>
</tr>
</tbody>
</table>

147
Figure 2: $^1$H and $^{13}$C NMR spectra of PE$_{70}$C$_{15}$Is$_{15}$T terpolyester

Figure 2 shows both $^1$H and $^{13}$C NMR spectra of PE$_{70}$C$_{15}$Is$_{15}$T with indication of peak assignments. Signals due to nonprotonated aromatic carbons showed splitting due to sequence effects at the level of dyads (left inset in Figure 2). By integration of these signals the number average sequence length and the degree of randomness were calculated. It was determined that all terpolymers synthesized have a random distribution of comonomers in the polymer chain.

Finally the thermal properties were evaluated. Terpolymers with 70 or 80 mol % of E units were observed to be almost amorphous for any content in C or Is units. Additionally it was observed that the $T_g$ of the terpolyester increased with the content of Is units in the copolymer (Table 1). All terpolymers showed good thermal stability as determined by TGA measurements.

Conclusion

New PET derived terpolymers have been synthesized by incorporation of CHDM and the biobased monomer isosorbide. It was observed that this incorporation repressed the crystallinity, increased the $T_g$, improved the processability.

Acknowledgments

The authors would like to thank CICYT (MAT2006-13209-C02-02 and MAT2009-14053-C02-01) and La Seda de Barcelona S.A for the financial support received.

References
