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BIO-BASED ALIPHATIC POLYESTERS FROM ALIPHATIC DIACIDS AND BICYCLIC ALDITOLS: A COMPARATIVE STUDY

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Due to the diminishing of fossil fuel resources, the research for the replacement of petrochemical by renewable polymers is increasing in these last years [1,2]. One of the platforms to produce these renewable polymers is that based on carbohydrates because these compounds are abundant in nature and after modification they can be used as building blocks for producing different types of polycondensates, such as polyesters among others [3,4].

In this work we have prepared and compared the thermal and mechanical properties of aliphatic polyesters made from aliphatic diacids with different polymethylene chain lengths (2, 4, 6, 8) and three bicyclic sugar derived diols namely, dianhydro-1,4:3,6-D-glucitol (also known as isosorbide, Is), and two bicyclic diazetalized hexitols, 2,4:3,5-di-*O*-methylene-D-mannitol (Manx-diol) and -D-glucitol (Glux-diol) derived from D-mannose and D-glucose respectively (Fig. 1) [5].

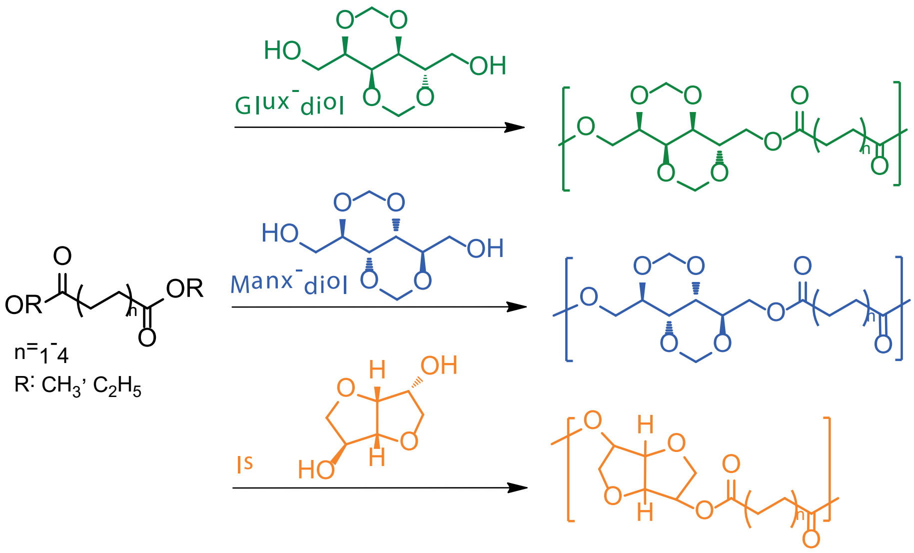

Fig.1. Synthetic route leading to the aliphatic polyesters

These polyesters were synthesized by two step melt polycondensation process from the dicarboxylic dimethyl or diethyl esters and sugar-based diols at temperatures that varied from 160ºC and 220 ºC, depending on which diester and diol were used.

The chemical structure of them was ascertained by both ^{1}H and ^{13}C NMR spectroscopy. They were obtained with high yields and molecular weights within the 47,000-26,000 range with dispersity degrees oscillating between 2.1-2.8 (Table 1). The thermal stability of these polyesters studied by TGA under nitrogen atmosphere showed that all of them were thermally stable up to around 250-350 ºC with lower onset and maximum rate decomposition temperatures for polyesters made from succinic acid (Table 1).

DSC studies showed that some polyesters made from Glux-diol and Is with long aliphatic diesters were semicrystalline. For all series of polyesters, the glass transition temperature decreases with the length of the polymethylene segment of the diester unit and the highest values were obtained for the series of homopolyesters made from Glux-diol units (Table 1).

Table 1. Characteristics of aliphatic homopolyesters

Polyester	M_w[a] (g·mol^{-1})	Đ[a]	T_g[b] (°C)	T_m[c] (°C)	ΔH_m[c] (J·mol^{-1})	^oT_d[d] (°C)	$^{max}T_d$[d] (°C)
PGluxSuc[e]	26800	2.2	103	-	-	264	390
PGluxAdi	41300	2.1	72	-	-	380	419
PGluxSub	46500	2.2	57	133	21.2	366	424
PGluxSeb	34400	2.1	45	117	30.3	382	429
PManxSuc[f]	30800	2.8	68	-	-	320	405
PManxAdi	29000	2.8	29	-	-	368	422
PManxSub	41600	2.6	26	-	-	370	420
PManxSeb	36200	2.7	22	-	-	375	420
PIsSuc	26200	2.7	79	-	-	334	392
PIsAdi	27400	2.7	20	-	-	386	423
PIsSub	38400	2.3	18	-	-	389	429
PIsSeb	34000	2.6	5	52	20.9	389	429

[a]Weight-average molecular weight an dispersity measured by GPC; [b]Glass-transition temperature measured by DSC; [c]Melting temperature and enthalpy measured by DSC; [d]Onset (5%) and maximum decomposition temperatures measured by TGA; [e]Data taken from the literature [6]; [f]Data taken from the literature [7];

The mechanical properties were evaluated from strain-stress tests. They were found to be influenced by the crystallinity and the T_g of the sample. Amorphous polyesters with low T_g values, such as PManxAdi or PIsSeb behave as ductile materials with low modulus, and amorphous polyesters with high T_g values, such as PGluxAdi or crystalline polyesters, such as PGluxSub and PGluxSeb displayed rather good mechanical properties with Young's moduli between 1.1 and 1,5 GPa, tensile strengths in the 30-50 MPa range and elongations to break about 3-5%.

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