

NEW POLYURETHANES FROM OXYPROPYLATED OLIVE STONE

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Abstract

The oxypropylation of OH-bearing substrates constitutes an original approach to the rational exploitation of certain biomass macromolecules. The oxypropylation of a variety of natural polymers (chitin, chitosan, lignin, etc.) converts these solid substrates into a liquid product, thanks to the introduction of oligo(propylene oxide) grafts. If reaction conditions are chosen in order to promote extensive grafting (total oxypropylation) a viscous polyol results, whereas if reaction is limited to the outer "sleeve" of the fibers or the granules (partial oxypropylation) a biphasic polyol suitable to prepare single-source composites, is generated.

The purpose of this work is to explore the possibility of chemically modifying the generated polyols through reactions with isocyanates to produce polyurethanes, other than rigid polyurethane foams. This could be achieved by the chemical modification of the oxypropylation products (condensation with isocyanates) by using mono and difunctional reagents to modulate properties and/or produce useful polymer networks. The biomass substrate used here was olive stone (OS) (Azeites Millenium Lda, Mirandela-Portugal) with a mean composition (dry basis) of 26% of lignin, 37.5% of cellulose, 27% of hemicelluloses and 0.5% of ashes. The ensuing oxypropylated OS was a viscous polyol with a homopolymer content of 9% (w/w) and a hydroxyl number (IOH) of 351 mg KOH/g.

These oxypropylated products were then modified by reacting them with a mixture containing both monofunctional and difunctional monomers in different proportions. Phenyl isocyanate (PI) and 1,4-phenyl diisocyanate (PD) were used at PI/PD molar ratios of 80/20, 50/50 and 20/80. The polyurethanes were synthesized in dichloromethane solution at room temperature under a nitrogen atmosphere, using DBTDL as catalyst. After a reaction period of 6 hours, the residual isocyanate functions were neutralized with methanol and the final product purified and dried before analysis. The characterization of the ensuing polyurethanes involved FTIR and NMR spectroscopy and DSC. Additionally, kinetic data were accessed by FTIR in transmittance mode by mimicking the used formulations.

FTIR results indicated an effective incorporation of PI and PD through chemical reaction with the polyol hydroxyl groups, by the disappearance of the band assigned to them (3430 cm⁻¹), together with the appearance of both urethane carbonyl (1720 cm⁻¹) and free N-H (3290 cm⁻¹) bands. As the PI/PD molar ratio decreased, i.e. as the content of the difunctional monomer increased, residual hydroxyls were detected, indicating an incomplete conversion. Nevertheless, their T_g shifted towards higher values, thus corroborating an increase in crosslinking density, associated with the reduction in network chain mobility. These processes produced the expected change from a highly viscous liquid (PI/PD=80/20) to rigid solids (PI/PD=50/50 and 20/80).

A major aspect of this study is the demonstration of the use of a renewable resource (OS) as a precursor for producing novel interesting macromolecular materials. The strategy used in this work provided a way to modulate the final thermal and mechanical properties, among others, of these biobased polymers.