Search for novel biobased materials within the OLIVPOL project

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Introduction

The design of polymers from renewable resources is receiving an increasing attention highlighting the use of cheap and biodegradable starting materials in order to reduce petroleum dependence and the negative impact on the environment [1]. Olive stone (OS) is an agro-industrial residue (by-product of the olive oil extraction process) that, due to its high heating power (heat of combustion of 4.1 Kcal/kg), finds application mostly in thermal processes being used for power generation in the electricity sector and for space calefaction in residential and commercial buildings [2]. Within the field of materials technology, the examples calling upon OS are particularly scarce and mainly devoted to its direct use as reinforcing agent or filler in polymer composites [3, 4]. More recently, and in the context of the project OLIVPOL, our research group has been involved in the OS chemical modification by oxypropylation in view of producing novel biobased polyols [5] that could be further used as precursors to other interesting materials such as polyurethanes and polyesters (Fig. 1).

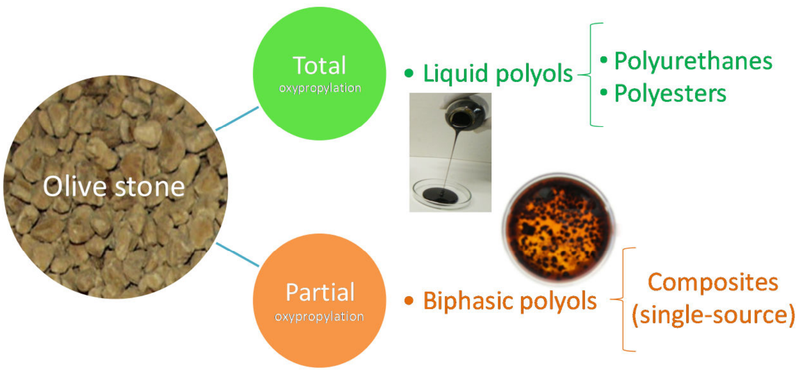

Fig. 1 *An integrated view of the generated products within the OLIVPOL project.*

Experimental

Olive stone (OS) was provided by a local industry (Azeites Milénium Lda, Mirandela, Portugal) in the form of a granular material comprising fragments with 2-5 mm average size and low contamination of skin and seeds. Its main composition on a dry basis (%, w/w) was 26.2% of lignin, 37.5% of cellulose, 27% of hemicelluloses and 0.44% of ashes. OS (both pristine and ground) was oxypropylated in a 300 ml stainless steel PARR autoclave. Briefly, OS, propylene oxide (PO) and catalyst (KOH) were placed in the reactor that was heated to 200 ºC under stirring. Optimization was achieved by selecting different OS/PO (w/v) ratios (10/20, 10/30, 10/40 e 10/50) and KOH contents (w/w) (1, 3, 5 and 10 %). The ensuing polyols were characterized by measuring their viscosity, OH index and PPO homopolymer content. Based on these results, the more promising formulations were chosen to proceed with chemical exploitation to produce polyurethanes and polyesters. High hydroxyl content polyols (351.2 and 389.2 mg KOH/g) proceeding from formulations using an OS/PO molar ratio of 10/20 and KOH contents of 1 and 3%, respectively, were found quite adequate for these polymerization processes.

In a first approach, ester and urethane modifications were performed with aliphatic and aromatic monofunctional reagents. Thereafter, difunctional reagents were employed to transform the polyols into the corresponding polyester and polyurethane networks. Finally, the effect on properties was inspected by using mixtures containing both monofunctional and difunctional reagents. Phenyl isocyanate/1,4-phenyl diisocyanate (PI/PD) and benzoyl chloride/tereftaloyl dichloride (BC/TD) at molar ratios of 80/20, 50/50 and 20/80 were used for these polyurethane and polyester syntheses, respectively. The final products were characterized by FTIR and NMR spectroscopy and DSC, and the reaction kinetics was accessed by FTIR monitoring. The different materials thus obtained changed from highly viscous liquids (when monofunctional monomer prevailed) to rigid solids (when the opposite occurred).

In a complementary study, using model samples of rigid polyurethane foams synthesized with oxypropylated lignins (a component of OS), the biodegradation potential of the generated materials was also demonstrated [6].

Conclusions

The most relevant aspect of the OLIVPOL project is the use of a renewable resource, OS, which is recovered from the sludge of a two-phase olive oil production process, as precursor to new polymers, which opens new avenues of its exploitation, in addition to burning. The OS residue was in fact successfully converted into viscous polyols, as such, or containing reinforcing stone cores, by total or partial oxypropylation, respectively. Moreover, the synthesis of new macromolecular materials using the oxypropylated products, such as polyesters and polyurethanes, demonstrated a promising approach to the production of original value-added products based on renewable resources.

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