FROM OXYPROPYLATED OLIVE STONE TOWARDS NOVEL POLYMERIC MATERIALS

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Introduction

The oxypropylation of OH-bearing substrates constitutes an original approach to the rational exploitation of the biomass. Total oxypropylation of a variety of natural polymers, including chitosan and chitin residues, different types of lignins, cork and more complex structures like sugar beet pulp, converts these solids, often otherwise intractable biomass residues, into liquid polyols thanks to the introduction of oligo(propylene oxide) grafts. The transformation of these polyols into rigid polyurethane (RPU) foams has been to date the main studied application. On the other hand, the partial oxypropylation is presented as a viable approach to prepare composite materials based on a single biomass component, where the outer "sleeve" of the fibres or the granules is plasticized by the oligo(propylene oxide) grafts and hence becomes the matrix, whereas their inner cores are preserved and constitute the reinforcing elements[(1)]. Nevertheless these existing approaches, the oxypropylation products can be the basis of other polymeric materials, namely polyesters and polyurethanes, other than RPU foams. Figure 1 shows a survey of viable synthetic approaches.

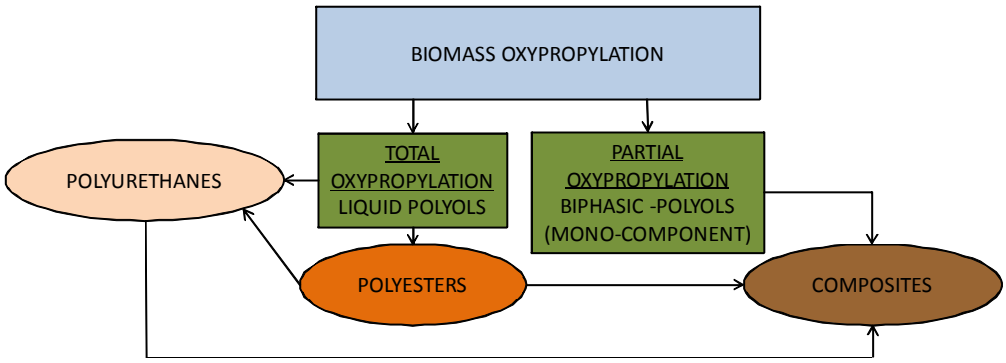

Figure 1. Schematic representation of synthetic pathways to produce polymeric materials from oxypropylated biomass substrates.

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. Given the growing interest in macromolecular materials from renewable resources, it seems clear that research aiming at finding new uses for the OS residue, and indeed for other olive oil industry by-products, is of high relevance and in perfect synchronization with the growing interest on the biorefinery concept.

Following our previous work dealing with the optimization of the OS oxypropylation process [(2,3)], the purpose of this work is to explore the possibility of chemically modify the generated polyols through reactions with isocyanates and acid chlorides to produce polyurethanes and polyesters, respectively. Two different approaches have been used: (1) the use of monofunctional reagents in order to modulate the final polyol properties, namely lowering the functionality and (2) the use of difunctional reagents to produce polymeric networks. The products resulting from the first strategy have potential to be applied in polyurethane synthesis, namely to generate products with elastomeric

properties and those resulting from the second one can constitute, for example, useful matrix for composite materials.

Results and Discussion

Olive stone (OS) was kindly provided by a local industry (Azeites Milénium Lda, Mirandela, Portugal). This granular material has fragments with 2-5 mm average size and low contamination of skin and seeds and was ground using a Restch blade mill equipped with a 0.25 mm mesh sieve. Its main composition on a dry basis (%, w/w) was 31.1% of lignin and 63.8% of holocelluose. The ash content was around 0.7%.

The oxypropylation was carried out in a 300 ml stainless steel PARR autoclave equipped with stirring, heating elements and both pressure and temperature sensors. The desired amount OS, propylene oxide (PO) and catalyst (KOH) were placed in the reactor that was thereafter closed and heated under stirring till 200 ºC. Optimization was done by selecting different OS/PO ratios and KOH contents. Based on the achieved characterization (viscosity, OH index and POP homopolymer content) the more promising polyols have been selected for chemical modification.

In a first approach, ester and urethane modifications have been performed with aliphatic and aromatic monofunctional reagents. The conversion of part or all of the OH groups of the polyols into much less polar moieties brought about significant changes in the properties of the ensuing materials, which were thoroughly characterized. Thereafter, difunctional reagents were employed to transform the polyols into polyester and polyurethane networks, whose properties were again assessed as a function of the type of reaction (different modes of esterification and condensation with diisocyanates), the specific structure of the reagent (aliphatic vs. aromatic) and the extent of OH conversion (stoichiometry). The characterization of these new materials involved FTIR and NMR spectroscopy, DSC and GPC.

Conclusion

The major importance of this work is the demonstration of the use of a renewable resource, OS residue, which was recovered from the sludges of a two-phase olive oil process, as a precursor for producing new polymeric materials. This residue was successfully converted into viscous polyols, through a straightforward process that requires no solvent and generates no by-products (oxypropylation), and thereafter chemically modified into polyurethanes and polyesters. This work will proceed by introducing different techniques, namely microwave-assisted technology, which is recognized as a powerful tool for synthesis purposes.

Acknowledges

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References

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