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. 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.

✓ Apart from the existing applications, oxypropylation products can be the basis of various polymeric materials, namely polyesters and polyurethanes, other than RPU foams.

✓ 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.

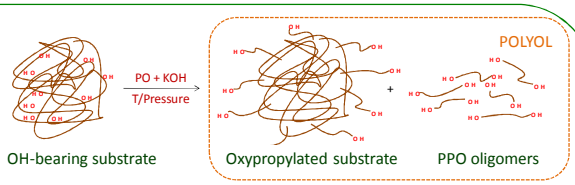


Fig 1 . Illustrative example of oxypropylation reaction.

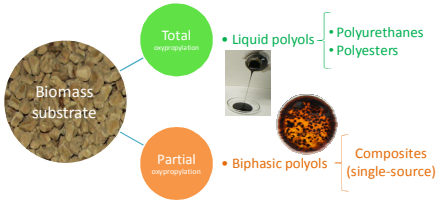


Fig 2 . Polymeric materials derived from the oxypropylated products.

Strategy

✓ Oxypropylated products can be chemically modified following two main strategies:

i. By using **monofunctional** reagents in order to modulate the final polyol properties, namely to lower the hydroxyl functionality;

ii. By using **difunctional** reagents to produce more elaborate macromolecular materials, including networks.

✓ In this work oxypropylated products have been modified by reaction with a mixture containing both monofunctional and difunctional monomers (Table 1) at different proportions. PI/PD and BC/TD molar ratios of 80/20, 50/50 and 20/80 have been used for polyurethane and polyester synthesis, respectively. Figure 3 shows the structure of the final product putting in evidence the effect of using mono- versus difunctional monomers.

✓ The used **biomass substrate** was olive stone (OS) (Azeites Millenium Lda, Mirandela-Portugal) with a main composition (dry basis) of 26.16% of lignin, 37.46% of cellulose, 26.95% of hemicelluloses and 0.44% of ashes [1].

✓ The ensuing **oxypropylated OS** was a viscous polyol with a homopolymer content of 8.7% (w/w) and a hydroxyl number (IOH) of 351.2 mg KOH/g [2].

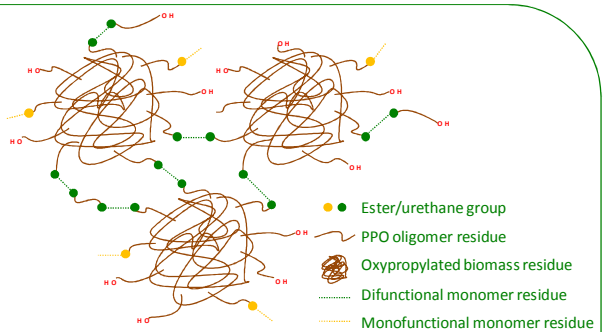
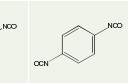
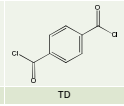


Fig 3 . Structure of the final products after chemical modification.

Tab. 1. Chemical structure of the used monomers.

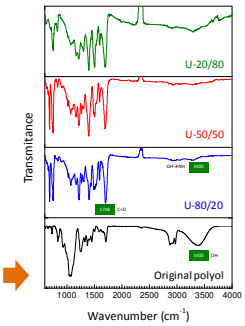
Polyurethane		Polyester	
Phenyl isocyanate	Phenyl diisocyanate	Benzoyl chloride	Terephthalic dichloride
			
PI	PD	BC	TD

Experimental/Results

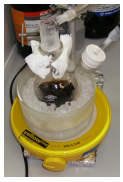
❑ Polyurethanes

Polyurethanes were synthesized in solution (dichloromethane) at T_{amb} under nitrogen atmosphere using DBTDL as catalyst. After the reaction period (6 hours) residual isocyanate has been neutralized with methanol and the final product purified and dried before analysis.

Fig 4 . FTIR-ATR analysis for the polyurethane series.

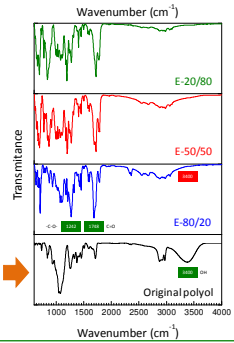


❑ Polyesters



Polyesters were synthesized in solution (dichloromethane) starting in a ice bath until T_{amb} using TEA as catalyst. After the reaction period (1 hour) the final product was purified and dried before analysis.

Fig 5 . FTIR-ATR analysis for the polyester series.



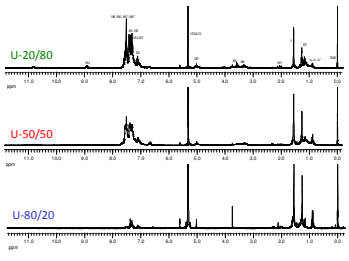
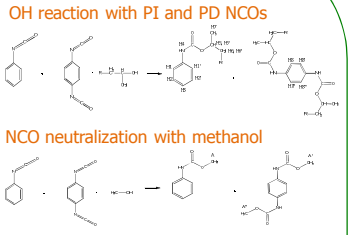


Fig 6 . H-NMR analysis for the urethane series.



Conclusions

✓ A major aspect of this study is the demonstration of the use of a renewable resource (OS) as a precursor for producing new polymeric materials.

✓ New families of both polyesters and polyurethanes were synthesized whose properties varied from viscous liquids to quite rigid solids as the difunctional monomer content increases.

✓ The strategy used in this work provide a way to modulate the final properties of the biobased polymer, namely thermal properties (characterization in course).

References

[1]. M. Matos; M.F. Barreiro; A. Gandini, Ind. Crops Prod. 2010, 32, 7-12.

[2]. M. Matos; M.F. Barreiro; A. Gandini, EPF 2011, 2011.

Acknowledgements

FCT (PTDC/CTM/71491/2006_FCOM-01-0124-FEDER-007156)

Azeites Millenium for providing olive stone