The Oxypropylation of Olive Stone and the Use of the Ensuing Polyols for the Synthesis of Novel Polyesters and Polyurethanes Based on Renewable Resources

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Objectives

- The purpose of this investigation was the search of a more useful and promising way to exploit olive stone (OS), an abundant and renewable Mediterranean natural material;
- In a first step we have undertaken an optimization study of the OS oxypropylation (transformation of the natural solid into a viscous polyol);
- In an second step the more promising polyols were selected for chemical modifications involving ester and urethane formation.

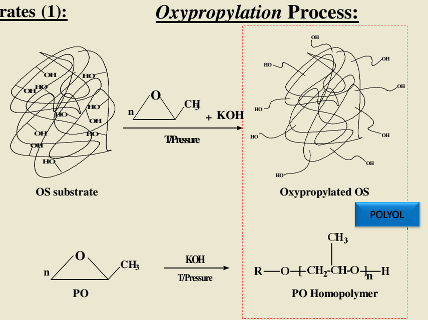
Introduction

Oxypropylation can be applied to various OH bearing substrates (1):

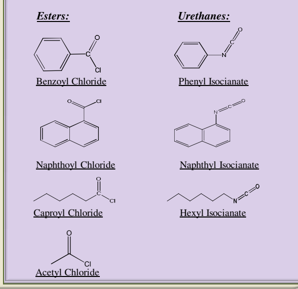
Oxypropylation

- **Total Oxypropylation**
  - Chitin and Chitosan
  - Different types of Lignins
  - Cork
  - Sugar beet pulp
  - Olive Stone powder
- **Partial Oxypropylation**
  - Cellulose fibres
  - Starch granules
  - Olive Stone Grains

***Oxypropylation* Process:**



Monomers for the synthesis of Esters and Urethanes:

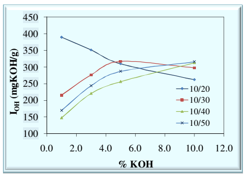


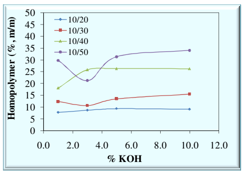
Results

Oxypropylation: optimization study

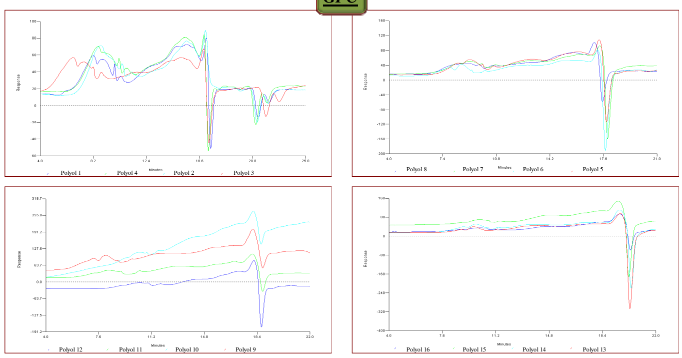
Polyol	OS/PO (w/v, g/ml)	Cat./(Cat.+OS) (%, m/m)	Homopolymer %, (m/m)	Final Residue (%, m/m)	I_{OH} (mg KOH/g)	Viscosity (μ) (25°C, Pa.s)
1	10/20	1,0	7,8	0,1	**389,2**	n.m.
2		3,0	8,7	0,1	**351,2**	n.m.
3		5,0	9,3	≈ 0	**309,5**	350,0
4		10,0	9,1	≈ 0	**261,6**	230,6
5	10/30	1,0	12,3	1,1	**215,3**	n.m.
6		3,0	10,6	1,0	**276,0**	584,6
7		5,0	13,5	≈ 0	**316,6**	360,6
8		10,0	15,6	≈ 0	**297,2**	100,3
9	10/40	1,0	18,1	≈ 0	**147,3**	n.m.
10		3,0	25,8	≈ 0	**220,5**	75,7
11		5,0	26,3	≈ 0	**256,1**	74,9
12		10,0	26,3	≈ 0	**312,9**	11,6
13	10/50	1,0	29,7	≈ 0	**169,6**	77,1
14		3,0	21,2	≈ 0	**243,7**	41,9
15		5,0	31,3	≈ 0	**286,9**	12,4
16		10,0	34,0	≈ 0	**315,8**	7,1

n.m. – not measured





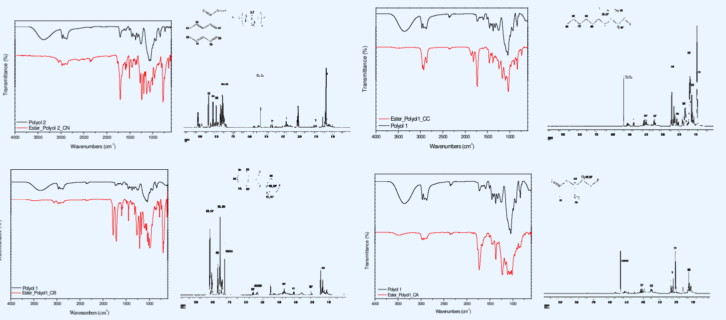
GPC



Synthesis of Esters:

Aromatic:

Aliphatic:

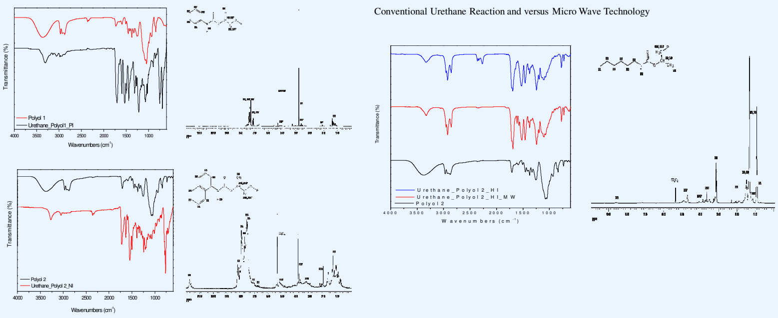


Synthesis of Urethanes:

Aromatic:

Aliphatic:

Conventional Urethane Reaction and versus Micro Wave Technology



Conclusions

- Based on the optimization study, polyols 1 and 2 were chosen due to its higher I_{OH} and lower homopolymer contents;
- The chosen polyols were modified into esters and urethanes. These chemical modifications using monofunctional reactants are useful to modulate the final polyol properties, namely functionality;
- Microwave-assisted technology, which is recognized as a powerful tool for green synthetic purposes, was successfully applied to produce polyurethanes.

References

(1) Gandini, A., Belgacem, N. M., 2008. Monomers Polymers and Composites from Renewable Resources. Amsterdam: Elsevier..

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