

Production of Polyurethane Foams from Bark Wastes

Lúisa P. Cruz-Lopes, Liliana Rodrigues, Idalina Domingos, José Ferreira, Luís Teixeira de Lemos, Bruno Esteves

Abstract—Currently, the polyurethanes industry is dependent on fossil resources to obtain their basic raw materials (polyols and isocyanate), as these are obtained from petroleum products. The aim of this work was to use biopolyols from liquefied *Pseudotsuga (Pseudotsuga menziesii)* and Turkey oak (*Quercus cerris*) barks for the production of polyurethane foams and optimize the process. Liquefaction was done with glycerol catalyzed by KOH. Foams were produced following different formulations and using biopolyols from both barks. Subsequently, the foams were characterized according to their mechanical properties and the reaction of the foam formation was monitored by FTIR-ATR. The results show that it is possible to produce polyurethane foams using bio-based polyols and the liquefaction conditions are very important because they influence the characteristics of biopolyols and, consequently the characteristics of the foams. However, the process has to be further optimized so that it can obtain better quality foams.

Keywords—Bio-based polyol, mechanical tests, polyurethane foam, *Pseudotsuga* bark, renewable resources, Turkey oak bark.

I. INTRODUCTION

LIQUEFACTION of lignocellulosic materials at low temperatures and pressure is a process that has evolved significantly in the last few years. The main advantage of these processes against traditional liquefaction at high pressure and temperature is that the liquor is composed of larger molecules that can be re-condensed to achieve new products. Some of these products can successfully substitute similar products usually made by less sustainable processes. The reduction of oil reserves and the growing concern about global climate change have led to the development of alternative renewable materials [1], [2]. Biomass, wood in particular, is among the most abundant renewable resources and is a promising resource that can replace oil. Thus, much effort has been made in the conversion of biomass into industrial commercially viable products [3], [4].

Currently, the Polyurethanes Industry is dependent on the fossil resources for the production of its key raw materials (polyols and isocyanates), because these are obtained from petroleum products. However, many studies have been developed in order to replace the petroleum-based polyol for

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other bio-based [5], [6]. Liquefaction of lignocellulosic biomass at atmospheric pressure with polyalcohols is a common method used to obtain biopolyols [5]. Other processes such as the oxypropilation have also been used to obtain polyols for Polyurethanes (PUs) Industry [7].

A wide variety of lignocellulosic biomass such as wood, wheat straw, corn meal and corn stalks have been studied for the production of biopolyols, and these usually feature promising properties for the production of PUFs comparable with the obtained from oil [5]. On the other hand, the main structural units of biomass are cellulose (30-35%), hemicellulose (15-35%) and lignin (20-35%), materials rich in hydroxyl (OH) groups, which make them interesting materials for the production of bio-based, PUs after liquefaction [5]. Commercially, the most relevant PU products are the foams and these are usually classified as flexible, semi-rigid or rigid, depending on their mechanical characteristics and core densities [8].

Currently, PU is the most versatile polymer that exists on the market. PUs are used as flexible or rigid foams. Flexible foams are widely applied in the industrial segment of mattresses, upholstery and automotive seats while rigid PU foams are mainly used as insulating material in construction and in the cooling sector.

In this work, we studied the suitability of using liquefied barks for the production of PU foams.

II. EXPERIMENTAL

A. Sample Preparation

The material used was bark from *Quercus cerris* and *Pseudotsuga menziesii*. The samples were grounded and sieved into four fractions > 40 Mesh, 40-60 Mesh, 60-80 Mesh and < 80 Mesh. The <80 Mesh fraction was selected for the liquefaction reactions.

B. Liquefaction Reaction

Liquefaction was held on a double shirt reactor with heated oil using glycerol as solvent catalysed by KOH. A ratio of 1:10 cork/solvent was used and 6% of potassium hydroxide was added based on the solvent mass. In order to achieve a better liquefaction percentage, the mixture was pre-stirred to obtain a more homogenous preparation. After closing the reactor, the automatic stirrer was placed at ± 70 rpm. The liquefaction reaction was held at 200 °C (temperature of the oil in the jacket) for 1 hour. The solvents, catalyst and bark were inserted inside the reactor when the oil achieved the desired temperature. To filter the residues methanol was used to solubilize the liquefied material. A pump and a Buckner Funnel with a paper filter were used to separate the solid residues that resulted from the liquefaction.

C. PU Foam Production

Polyurethane foams produced with *Pseudotuga* (PPUF) and *Quercus Cerris* polyols (CPUF) were prepared by mixing for 30 s the polyol in combination with catalyst, surfactant and blowing agent in accordance to Table I. Finally, the polymeric isocyanate was added and the resulting mixture was vigorously shaken until the foam starts to grow. The foams were left to stabilize during 24 hours at room temperature. The homogenization was made in a propylene beaker with a IKA Ost Basic mixer with rotating blades at 700 rpm.

TABLE I
REAGENTS AMOUNT FOR FOAM PRODUCTION

Samples	Isocyanate (g)	Catalyzer (g)	Expansion agent (g)	
Isocyanate variation	6	0.4	0.01	
	7			
	8			
	9	0.4		
	6			
	7			
Catalyzer variation	8	0.16	0.01	
		0.4		
		0.6		
	0.8	0.4		
	0.4			
	0.6			
Expansion agent Variation	8	0.4	0.01	
			0.2	
			0.01	
	CPUF	8	0.4	0.01
				0.2
				0.2

D. PU Foam Testing

Mechanical tests of PPUF and CPUF were made accordance to ISO 844:2007 in a Universal Test Machine.

E. FTIR-ATR

The identification of the main functional groups in the PU foams produced were made by FTIR-ATR. The spectra were taken in a spectrophotometer FTIR PerkinElmer UATR Two, with a resolution of 4.0 cm⁻¹ and 72 scans recorded medium infrared region, in the range 4000-400 cm⁻¹.

III. RESULTS AND DISCUSSION

A. Isocyanate Variation

Table II shows the results obtained for the PPUF and CPUF, using different quantities of isocyanate.

Overall, the compressive strength and modulus of compression (elasticity) are greater for higher quantities of isocyanate, although there is a decrease when 9 g of isocyanate is added. These results are in agreement with results presented by [9], [10] which claim that increased amounts of isocyanate lead to better mechanical properties but if the amount of isocyanate is large and the number of NCO groups exceeds the OH groups, this will lead to the reaction of

isocyanate with urethanes and urea forming allophanes and biurets decreasing the mechanical properties of foam [11].

The foams produced exhibit densities between 56 g/dm³ and 83 g/dm³ what lies within the range of densities obtained in similar studies done by [1] with densities between 57-79 g/dm³ for PU foams made from the liquefaction of bark of *Quercus suber* (Cork). Other studies present smaller densities around 30 g/dm³ with foams derived from corn polyols [12]. The compression strength of the produced foams ranged between 2 and 33 kPa that are also in the range of the foams produced with cork derived polyols by [1].

TABLE II
MECHANICAL PROPERTIES OF FOAMS WITH DIFFERENT ISOCYANATE CONTENT

Samples	Isocyanate (g)	Density (g/dm ³)	Compression Modulus (kPa)	Compression Strength (10%) (kPa)
PPUF	6	62.85	142.36	2.17
	7	82.99	213.60	2.41
	8	57.64	227.88	21.19
	9	55.99	120.01	13.54
	7	65.91	499.43	32.68
	8	36.20	103.45	8.68
CPUF	9	48.44	378.90	31.06

B. Catalyzer Variation

Table III presents the results obtained for the PPUF and for the CPUF, in which the amount of catalyst was changed. Overall the compression module and strength increases with the increase of the catalyst. The density differences could be related to the heterogeneity of PUFs. Two competing reactions occur during foam production; the gelation reaction between the polyol and the isocyanate and the expansion reaction between water and isocyanate [13], [14]. The amount of catalyst is important because, without catalyst reactions speed is too slow. However there needs to be a right balance between the rate of expansion and reaction of gelation because if the expansion is too rapid the foam may collapse if, on the other hand, the gelation reaction exceeds the expansion reaction, this can lead to shrinkage of the foam [7]. The best mechanical properties were obtained when 0.6 g of catalyst were employed.

TABLE III
MECHANICAL PROPERTIES OF FOAMS WITH DIFFERENT CATALYST CONTENT

Samples	Catalyst(g)	Density (g/dm ³)	Compression Modulus (kPa)	Compression Strength (10%) (kPa)
PPUF	0.16	40.88	40.42	7.24
	0.4	57.64	227.88	21.19
	0.6	45.63	282.17	13.47
CPUF	0.4	36.20	103.45	8.68
	0.6	81.95	920.02	49.16

C. Expansion Agent Variation

Table IV shows the results obtained for the PPUF and CPUF, where the amount of blowing agent was changed. The results obtained for the PPUF show that with the increase in mass of blowing agent, there is a decreased in the compression module and compression strength, while for the CPUF, it is

the opposite these differences may be related to the biopolyol used. More tests are being made in order to test the different properties in accordance to the polyol origin.

TABLE IV
MECHANICAL PROPERTIES OF FOAMS WITH DIFFERENT EXPANSION AGENT CONTENT

Samples	Expansion agent (g)	Density (g/dm ³)	Compression Modulus (kPa)	Compression Strength (10%) (kPa)
PPUF	0.01	57.64	227.88	21.19
	0.2	64.15	190.05	11.02
CPUF	0.01	36.20	103.45	8.68
	0.2	45.73	281.32	18.02

D. FTIR-ATR

Fig. 1 presents the FTIR-ATR spectra for the foams produced from Pseudotsuga polyols with different concentrations of isocyanate. According to [7], the most important frequencies relating PU foams are, the band around 3200–3450 cm⁻¹ attributed not only to OH groups but also to symmetric and asymmetric stretching vibrations of the N-H of the urethane and urea groups that result from a reaction occurring between water and isocyanate. The bands between 2950 and 2850 cm⁻¹ are also important since they relate to the asymmetric and symmetric stretching vibrations of C-H. The peak that corresponds to the stretching vibration of the NCO group in isocyanate is found near 2250 cm⁻¹. The isocyanate peak is absent for the low amount of isocyanate used (6g) which indicates that all of the compound was consumed in the reaction. With higher isocyanate amounts the peak around 2250 cm⁻¹ appears which mean that there was unreacted isocyanate in these reactions.

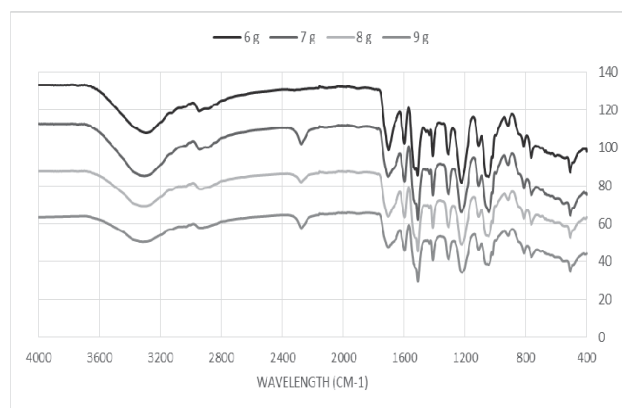


Fig. 1 FTIR-ATR spectra for Pseudotsuga bark foams with different concentrations of isocyanate

Fig. 2 presents the FTIR-ATR spectra for the foams produced from Turkey oak bark polyols with different concentrations of isocyanate. Similar to the Pseudotsuga foams spectra, the peak around 2250 cm⁻¹ is visible for amounts higher than 7 g although it is very small when 8 g were added. There were no significant differences in the spectra between Pseudotsuga bark foams and Turkey oak bark foams.

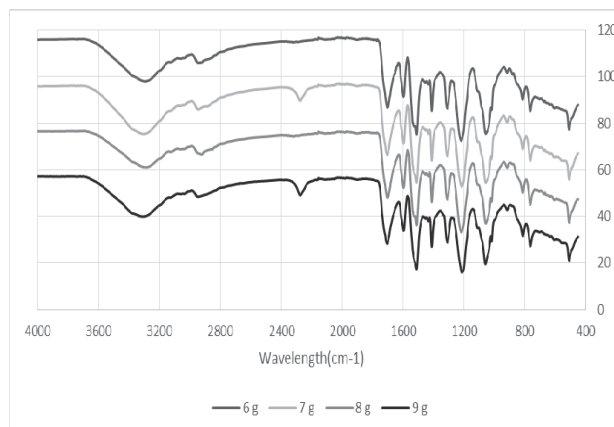


Fig. 2 FTIR-ATR spectra for turkey oak bark foams with different concentrations of isocyanate

Fig. 3 presents the FTIR-ATR spectra for the foams produced from Turkey oak bark polyols with different concentrations of catalyst. The lowest amount of catalyst (0.16g) is clearly not enough to promote a good foam formation since which can be seen by the high intensity of the isocyanate peak showing that there was a significant amount of unreacted compound. Generally, a higher amount catalyst has a lower isocyanate peak. Similar results were reported by [7].

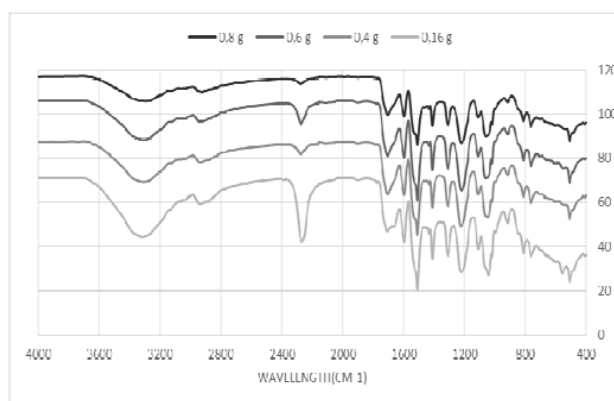


Fig. 3 FTIR-ATR spectra for Pseudotsuga bark foams with different concentrations of catalyst

Fig. 4 presents the FTIR-ATR spectra for the foams produced from Turkey oak bark polyols with different concentrations of catalyst. In relation to Turkey oak foams spectra the isocyanate peak is almost undistinguished showing that most of the isocyanate reacted.

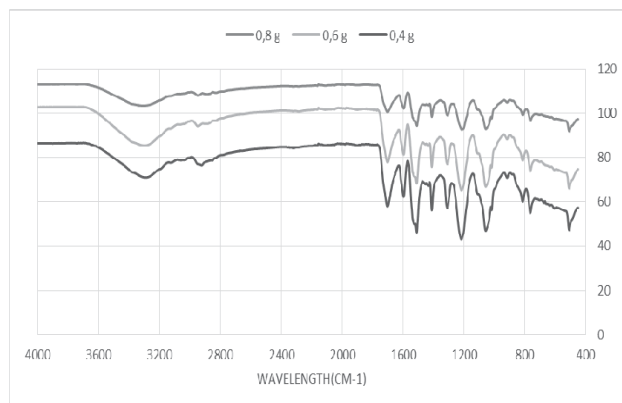


Fig. 4 FTIR-ATR spectra for turkey oak bark foams with different concentrations of catalyst

IV. CONCLUSION

In conclusion, it was possible to obtain good quality foams with both *Pseudotsuga* and Turkey oak barks. Overall the compressive strength and compressive modulus are greater for higher quantities of isocyanate and catalyst. The best mechanical properties were obtained with 8 g of isocyanate and 0.6 g catalyst. FTIR-ART tests show that there has to be an optimization of the formulation in order to obtain the best foams with the minimum reagents. New tests are underway to achieve foams with better mechanical properties.

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