Bioblocks: Valorization of Biorefinery Waste

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Abstract

Lignin is considered the second most abundant organic natural compound in the world, representing a promising source of new materials based on renewable resources. The main purpose of this study is produce lignin based polyurethanes adhesives to apply in granulate cork in order to fabricate cork stoppers.

In the first place it was necessary to extract and purify the Kraft lignin from black liquor. The method used was lignin precipitation (pH 2) followed by Soxhlet extraction with n-pentane, washing and drying. For this synthesis the components are: lignin (source -OH), Polymeric Methylene diphenyl diisocyanate (NCO source), 1,4-bicyclo [2,2,2] octane 97% (catalyst) and tetrahydrofuran (solvent).

the influence of the ratio [OH]: [NCO] in the urethane synthesis with or without catalyst was conducted in five different molar ratios (1: 3, 1: 5.1: 9. 1:12, 1:14), with and without a catalyst. It was performed a viscosity study (48h) for different lignin concentrations in pMDI, 5%, 10%, 15%, 20% and 25% (m / v) to study kinetics of polymerization.

Regarding manufacture cork stoppers, they were made using lignin adhesives dissolved in pMDI, with or without catalyst, partial lignin substitution by 0.5% 1% and 3% (m/m) polyethylene glycol. Then to facilitate the lignin incorporation incorporate a bigger was used tetrahydrofuran as solvent.

Cork stopper were evaluated for standard commercial tests such as, visual, boiling and torsion tests. Some of the cork stoppers produced have can be used for commercial applications.

Key-words: Lignin, Adhesives, Biorefinery, Cork Stoppers.

1. Introduction

In order to simultaneously reduce dependence on oil and mitigate climate change, alternatives to existing production chains are necessary. It becomes increasingly clear that biomass have enormous potential to replace fossil resources, and to allow the production of bioenergy, biofuels and biochemicals. Terms such as bioproducts, bioenergy, bio-economy are being increasingly used by the entire scientific community and policy, confirming the growing concern on sustainable growth industries with zero waste and ecological processes (biomass, 2006 of the European Parliament and of the Council 2002 and Ree and Annevelink, 2007).

Black liquor is a complex aqueous solution of various organic compounds such as lignin, polysaccharides, resinous compounds with a low molecular mass, and even inorganic components mostly insoluble salts. A previous study characterized chemical composition of black liquor as can be seen in table 1.

Table 1 – Black Liquor composition.

Licor Negro		
Element	Símbol	% SS
Carbon	C	34-39
Oxygen	O	33-38
Sodium	Na	37-25
Sulfur	S	3-7
Hydrogen	H	3-5
Potassium	K	0,1-2
chlorine	Cl	0,2-2
nitrogen	N	0,002-2

The aim of this research is to study a way of producing lignin based polyurethanes adhesives from Kraft Lignin. This Kraft lignin is extracted from black liquor and used as a raw material in the formulation of adhesive, which is intended to be used in granulated cork in order to manufacture commercial cork stoppers. Lignin can be obtained from the black liquor by various procedures. In this particular case the lignin is extracted by precipitation in acid environment and purified by Soxhlet extraction with n-pentane.

The adhesives manufacture is based on polyurethane production by reaction Kraft lignin with Polymeric Methylene diphenyl diisocyanate (pMDI). This reaction often took place in the absence/presence of 1,4-bicyclo [2,2,2] 97% octane (DABCO) and polyethylene glycol (PEG).

2. Materials and Methods

2.1. Raw-Materials

Black liquor used in this study is derived from hardwood, and it was provided from Portucel Soporcel; Polymeric Methylene diphenyl diisocyanate (pMDI); 1,4-bicyclo [2,2,2] octane 97% (DABCO) from Acrós; Tetrahydrofuran, C_4H_8O from Fisher; Agglomerated Cork provided by Cork Supply.

2.2 Lignin Extraction and Purification

The black liquor was subjected to a filtration process using an aqueous acidic solution with pH 2. Lignin was purified with a Soxhlet extraction, with n-pentane during 6 h, to remove extractives with the purpose of removing lignin extractives. Filtration takes place in a laboratory apparatus like figure 1. Finally the precipitated was washed with acidic solution (ph 2), dried in kept at 4ºC.

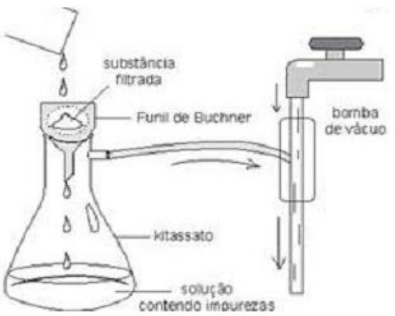

Figure 1 – Filtration apparatus.

Figure 2 – Soxhlet apparatus.

2.3. Adhesives Preparation

2.3.1 Polymerization Reaction

Polyurethane adhesives were prepared by mixing two components, lignin and an isocyanate, in this case pMDI. The tests were carried out with mixtures which the molar ratio OH: NCO varied (table 2), in the absence and presence of catalyst. This molar ratio was determined, assuming that in 100 g of pMDI there are 30 g of NCO and in100 g of lignin are 10 g of OH groups. The polymerization reactions takes 2h at 70°C with without catalyst (0.5%, 1% and 2% (m / m)).

Table 2 – OH:NCO molar ratios.

Rácios NCO:OH
1:3
1:5
1:9
1:12
1:14

Table 3 – Lignin/pMDI solutions (w/v).

Solutions % (m/v)
5
10
15
20
25

2.3.2. Viscosity Tests

Firstly was dissolved the maximum concentration of lignin in pMDI 20% (w/v). Lignin was stirred during 3 h in pMDI. Next the solution was centrifuged to ensure that all lignin was dissolved. The solutions produced are shown in table 3.

Finally, these solutions were stirred overnight. Viscosity was measured with a rotational viscometer (figure 3) to measure viscosity by spindle rotating. The viscosity measures were done in triplicate in the same conditions, same spindle speed and temperature of 25 ° C for each adhesive.

2.3.3. Cork Stoppers Manufacturing

For each cork stopper it was used a ratio of 8 grams of granules per 2 grams of adhesive. The mold and the press used were specifically designed and manufactured in 310 steel, allowing manufacture of corks with 29 mm diameter and 45 mm length. The mold was heated (45 min. at 100 ° C and 15 min. at 60 ° C) to promote the polycondensation.

Figure 3 – Viscosity equipment.

Figure 4 – Cork Stoppers Mold and Press.

2.4. Quality Evaluation Corks

2.4.1 Visual

Cork stoppers can modify their shape during the process. For that reason after unmold the stopper it is necessary to evaluate in order to check consistency, compression and the effectiveness of spreading the adhesive by temperature effect.

2.4.2 Boiling Test

These test consist basically in making the cork stopper immersing in boiling clean water at 100°C over 1 hour (figure 5). Then the stopper is allowed to dry in the oven overnight at a temperature of 40 ° C.

2.5. Torsion Test

A torsion test consists in an applied force through rotation of a particular body or material to be characterized. The equipment (figure 6) used has a revolving head and the other fixed, and the cork stopper to be tested is placed between them. It is necessary to measure the diameter of the cork stopper and insert the value in the equipment. On the rotating head is applied the torsion force by a mobile metal arm that the equipment has which promote a twist on cork stoppers axis. This equipment provides several important parameters such as the maximum force, displacement, torsion angle and finally to shear stress.

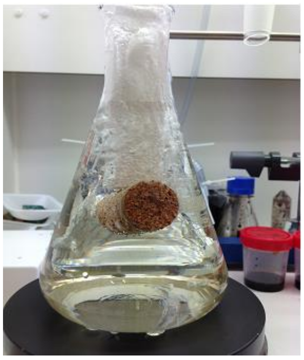

Figure 5 – Boiling Test

Figure 6 – Torsion Test Equipment.

3. Experimental Results and Discussion

3.1. Lignin Extraction and Purification

The Kraft lignin was extracted with a 48.5% yield in an acidic solution, slightly higher than those reported in the literature for this method, which lie in the range of 33-40% (Jaaskelainen et al., 2003) (Gellerstedt et al., 1994). The lignin obtained is free from polysaccharides, because the bonds between lignin and sugars are readily hydrolyzed in acidic environment. However lignin structure can be modified, in particular by cleavage of ether linkages in an acid environment, leading to depolymerization phenomenon (Duarte et al., 1996) and increased content of groups (OH) free phenolic. The purification of the lignin was performed using a soxhlet extraction, using n-pentane as a solvent. (Hussin M. et al. 2013) (Mohammed et al. 2011) (Wanrosli et al. 2007). During extraction solvent, n-pentane gets a yellowish color, indicating that in fact extractives are being removed. The extracted and purified lignin is shown in figure 7.

Figure 7 – Extracted and purified Kraft Lignin.

3.2. Adhesives

3.2.1. Adhesives Preparation

It is known that reactive groups NCO:OH molar ratio strongly influence the adhesive properties particularly the polymer molecular weight, resulting from the reaction between monomers. It was tested the following racios-1:3; 1:5; 1:9; 1:11 and 1:14, with and without catalyst at 70ºC for 2 h. The adhesive viscosity increases when the catalyst is added to the mixture lignin-pMDI. This observation is verified for 1% and 2% of catalyst. According the experiment carried out, the ratio 1: 5 to 1: 9 with 1% catalyst (m / m) are the ones where is verified a change in viscosity. The others adhesives exhibit a similar behavior regardless formulation. However, it is known in literature that the maximum molecular weight is obtained when the two reactive groups are in equimolar amounts. Thus, a small excess of the reagents dramatically decreases the molecular weight (Ionescu, A. M 2005).

3.2.2 Viscosity Tests

The tests were performed in three consecutive days every two hours, and then the same tests were repeated in two other days performing viscosity measures hour by hour, in order to define reaction kinetics. Different concentrations of lignin in pMDI were prepared subject to stirring overnight. The next day the stirring was stopped, followed by centrifugation. Supernatant was removed and utilized in mixtures with pMDI, and subjected to measurement of viscosity. The graphs presented in this topic are intended to realize the influence of concentration on the viscosity and the development of viscosity over time. Graphic representations are based on the viscosity average obtained for each concentration over time on the same day.

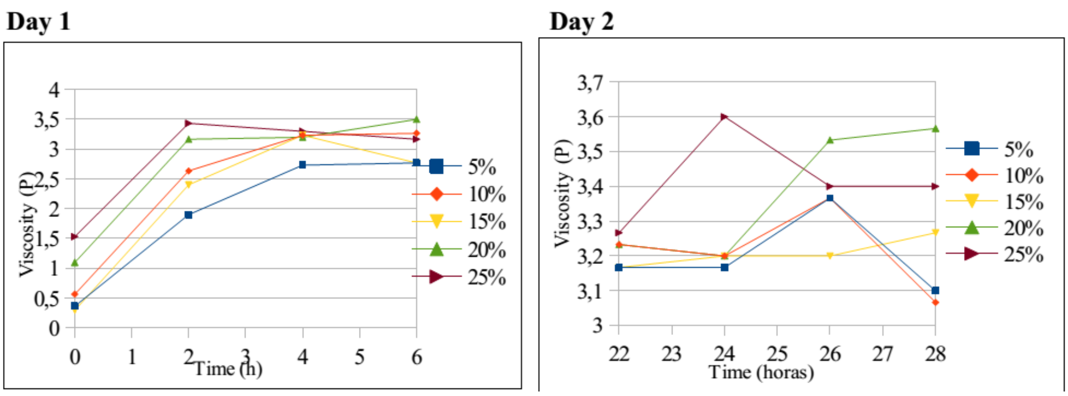

Figure 8 – Graphic representation of the average viscosity during day 1 and 2.

3.3. Cork Stoppers Manufacture

The manufacture of cork stoppers was done sequentially and immediately after the application of granulate. The stoppers manufactured are:

• Cork Stoppers without solvent: stoppers were made with and without catalyst, and others in which the lignin is partly replaced by a diol.

• Cork Stoppers with solvent: stoppers were made with a solvent, with the intention of having a greater lignin amount.

3.4 Visual and Boiling Tests

Cork stoppers with defects that could compromise the cork were rejected for torsion testing. All stoppers except for two retained their shape. The stopper contained only cork agglomerate, when enter in contact with water, disintegrated, and the stopper solvent, 80% (m / m) lignin in the pMDI after 1 h showed changes in their shape, having been stretched.

3.5 Torsion Tests

It is intended to determine the cork's ability to distort when subjected to a certain torsion force.. The stoppers without solvent were subjected to torsion testing. The results are presented in table 4, and the stoppers suitable for wine market are in blue.

Table 4 – Torsion values.

Rolhas	*DIC* (mm)	*F* (daN)	*Deslocamento* (mm)	*Ângulo de Torção* (º)	*Tensão de Corte* (daN/cm^2)
Cortiça	26,08	3,1	15,60	57	5,3
Standard	25,72	2,6	45,40	76	6,0
pMDI	26,00	2,5	11,10	54	4,1
20:0	25,31	2,4	41,90	74	5,7
17:3	**25,96**	**8,2**	**25,40**	**63**	**15,6**
14:6	**25,98**	**7,9**	**31,10**	**67**	**15,8**
11:9	**26,04**	**8,2**	**28,50**	**65**	**15,9**
20:0 DABCO 1%	**26,00**	**8,3**	**33,40**	**68**	**16,9**
17:3 DABCO 1%	25,16	2,4	35,90	70	5,5
14:6 DABCO 1%	25,70	1,6	28,90	65	3,2
11:9 DABCO 1%	25,92	3,5	29,40	66	6,9
20:0 PEG 0,5%	25,90	2,8	37,30	71	6,0
17:3 PEG 0,5%	**25,74**	**8,2**	**26,80**	**64**	**16,2**
14:6 PEG 0,5%	**25,63**	**8,3**	**25,90**	**63**	**16,5**
20:0 PEG 1%	**25,92**	**9,9**	**25,50**	**63**	**19,0**
17:3 PEG 1%	**26,04**	**5,5**	**6,30**	**50**	**8,4**
14:6 PEG 1 %	**25,85**	**9,7**	**41,90**	**74**	**21,5**
11:9 PEG 1%	**26,03**	**9,4**	**23,50**	**62**	**17,4**
20:0 PEG 3%	**25,82**	**9,6**	**25,90**	**63**	**18,7**
14:6 PEG 3 %	**25,87**	**10,7**	**25,40**	**63**	**20,6**

4. Conclusions

In this study it was intended to develop adhesives based on Kraft lignin, from PortucelSoporcel, to apply in cork agglomerates. This principle is based on the availability of raw materials on the one hand, and on the other to contribute to a more sustainable technology. The Kraft lignin was extracted from black liquor, with a yield around 48.5%, quite acceptable when compared with literature values. The Kraft process degrades lignin, so we will have a lignin with low molecular weight. Molecular weight is a indicative property of the polymerization degree. After lignin extraction it was possible synthesize polyurethane adhesives. The first step was monitoring the polymerization reaction between the two monomers (lignin and pMDI), by varying the concentration [OH]: [NCO]. From various ratios tested the one who seems that maximize the size of the polymer chain, is 1: 5 with the catalyst at 1% (m / m). In a second phase, the evolution of the viscosity was analyzed over time for adhesives. The results are not very clear but generally increase with viscosity over time, and lignin concentration. Thus it can be said that the increase lignin amount helps increase the polyurethane chain. The adhesives viscosities stabilize for values between 3.3-3.6 P. Different adhesives were used for stoppers manufacture, and all of them were subjected to the same visual subjected to the same stopper to visual, boiling and torsion tests. Stoppers resisted boiling test, maintaining its shape and structure. In the mechanical tests, torsion, the critical parameter proved to be maximum force, since almost has a torsion angle greater than 40º. Regards maximum force, the values are not tested stoppers conclusive. The sample amount is not sufficient to standardize the adhesives behavior with confidence. However it is noted that the PEG use hardens the stoppers, harmful parameter for stoppers production.

5. References

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