

## Polyurethane Foams from Liquefied *Eucalyptus globulus* Branches

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Currently, polyurethane (PU) production is completely dependent upon fossil oil, as the two primary reagents necessary for PU production, polyol and isocyanate, are derived from fossil fuels. Eucalyptus branches are waste products for most forest management companies. In this work, polyols obtained by the liquefaction of eucalyptus branches were used for foam production. The influence of the isocyanate, catalyst, surfactant, and blowing agent contents on the foam properties was studied. Overall the amount of each chemical used in the production of PU foams had a noticeable effect on the density and compressive properties. The amount of water (blowing agent) had the strongest effect and decreased the density and compressive properties because of higher foam expansion. The other chemicals increased or decreased the density and compressive stress depending on the amount used. The density of the produced foams ranged from 36 kg/m<sup>3</sup> to 108 kg/m<sup>3</sup>, the compressive stress ranged from 15 kPa to 149 kPa, and the Young's modulus ranged from 64 kPa to 2100 kPa. The results showed that it is possible to convert these forest residues into PU foams with properties somewhat similar to those of commercial foams, although with a lower compressive strength.

*Keywords:* Compressive properties; Eucalyptus branches; Liquefaction; Optimization; Polyurethane foams

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### INTRODUCTION

The first polyurethanes (PUs) were synthesized by professor Otto Bayer in 1937 in preparation for the second World War to replace latex rubber polymers used in tires (Thomson 2005). Now, PUs are present in most products that are used daily, from insulating materials to medical implants (Mahmood *et al.* 2016). Polyurethanes are versatile polymers used in the furniture industry, automotive industry (*e.g.*, bumpers, seats, and upholstery), and in construction (acoustic and thermal insulation) (Hu *et al.* 2012; Cinelli *et al.* 2013).

Polyurethanes are copolymers containing blocks of polyesters or polyethers with a low molecular weight that are covalently bound by one or more urethane groups (Thomson 2005). Currently, PU production is completely dependent upon fossil oil, as the two primary reagents necessary for PU production, polyol and isocyanate, are derived from this fossil fuel (Hu *et al.* 2012; Gama *et al.* 2015b). Oil shortages, as well as the high price of raw materials, has prompted the search for renewable materials for the manufacture of polymers. Polyols from biomass liquefaction contain a large number of hydroxyl groups and have the potential to successfully replace polyols from petroleum in the synthesis of

PU foams. In recent years, several studies have focused on the production of PU foams from several types of liquefied biomass, including cornmeal (Wang *et al.* 2008), cork (Gama *et al.* 2015a; Esteves *et al.* 2017b), sugar bagasse (Hakim *et al.* 2011), wood (Ertaş *et al.* 2014), coffee grains (Soares *et al.* 2014), soy wool (Hu *et al.* 2012), wheat straw (Chen and Lu 2009), and cork-rich barks from *Pseudotsuga menziesii* and *Quercus cerris* (Cruz-Lopes *et al.* 2016; Esteves *et al.* 2017a).

The formation of a PU foam involves several reagents, which are an isocyanate, polyol, blowing agent, catalyst, and surfactant. Each of these reagents has a specific function in several chemical reactions that occur during foam formation. The most common isocyanates used for the production of rigid PU foams are aromatic isocyanates, like toluene di-isocyanate and polymeric diphenyl-methane di-isocyanate (MDI) (Mahmood *et al.* 2016). The catalysts used in the production of PU foams are mostly tertiary amines and organometallic compounds (bismuth, iron, mercury, and cobalt). Tertiary amines catalyze the reaction of isocyanate and water, while organometallic catalysts promote the reaction of isocyanate and polyol (Yan *et al.* 2008). Some catalysts, such as 4-diazabicyclo [2, 2, 2] octane, operate specifically in the formation of urethane (gelling) (Mahmood *et al.* 2016). Expansion agents may be classified as physical blowing agents, which vaporize (*e.g.*, n-pentane), or as chemical blowing agents, such as water, which actively intervenes in the formation of PU foams. More specifically, water reacts with isocyanates and forms unstable carbamic acid, which breaks down into carbon dioxide (Mahmood *et al.* 2016). There are several other compounds that can act as blowing agents, including dichloromethane (Soares *et al.* 2014; Gama *et al.* 2015a) and ethylene glycol (da Silva *et al.* 2013). The choice of reagent influences not only the size and number of cells in the foam, which affects the mechanical properties, but also the thermal conductivity and acoustics (Soares *et al.* 2014). In the process of PU foaming, the surfactant has several functions, which include emulsifying the liquid components, stabilizing the cell structure, adjusting the size, and preventing cell collapse (Mahmood *et al.* 2016). The most common surfactants in PU foam formation are silicon-based.

Hu *et al.* (2014) reviewed polyols intended for PU production that were from the liquefaction of various types of liquefied biomass, such as agricultural waste, pulp, and bio-refineries wastes, as well as from hardwoods and softwoods. It was reported that different OH index and acid number values were achieved depending on the type of biomass. For example, the OH index for liquefied wood ranged from 200 mg KOH/g to 435 mg KOH/g and the acid number ranged from 12 mg KOH/g to 38 mg KOH/g, while the maximum values that could be reach for the studied biomass were 540 mg KOH/g and 41 mg KOH/g for the OH index and acid number, respectively. Similar results have been reported with OH indices between 193 mg KOH/g and 440 mg KOH/g for liquefied wood, cork, pine, poplar, and eucalyptus bark (Ertaş *et al.* 2014; Mateus *et al.* 2015, 2017a,b).

The OH index of a produced polyol depends heavily on the solvent used during liquefaction because these polyols already have a high OH index. This has been shown before by Zheng *et al.* (2011), who attained OH indices for polyols from liquefied pine wood of 700 mg KOH/g with a mixture of polyethylene glycol and glycerol and 280 mg KOH/g when using only polyethylene glycol. The OH index is dependent not only upon the solvents used during liquefaction, but also their impurities content (Kunaver *et al.* 2010).

One of the most important properties of PU foams is their behavior during compression. The compression curves for PU foams generally have three distinct regions. The first represents the linear elasticity of the material; in this region, deformation is

directly proportional to the applied force and the cell walls bend. The Young's modulus can be determined by the slope of the line in this region (Gama *et al.* 2015a). The second region represents the plastic deformation zone, where the foam deforms because of the collapse of the cells. The third region represents the densification of the material and consequently hardening of the foam.

This work intended to determine the possibility of efficiently converting eucalyptus branches into a liquefied material for the production of more environmentally benign PU foams. The polyols obtained from the liquefaction of eucalyptus branches were used for the production of foams with different isocyanate, catalyst, surfactant, and blowing agent quantities to optimize the process.

## EXPERIMENTAL

### Materials

The eucalyptus branches used in this study were waste products from the company Pedrosa & Irmãos (Leiria, Portugal), which is a forest management company. *Eucalyptus globulus* branches were milled in a knife mill, which was followed by sieving and drying at 105 °C. The less than 80 mesh (< 0.180 mm) fraction was used for the tests. The catalyst used was Polycat 34® (Evonik, Essen, Germany), which is a tertiary amine catalyst that primarily promotes the urethane reaction in rigid foam formulations. The surfactant and isocyanate used were, respectively, Tegostab B8404®, which is a non-hydrolysable polyether-polydimethylsiloxane copolymer, and MDI Voranate M229®, both of which were acquired from Dow Chemical Company (Michigan, USA).

### Methods

#### *Liquefaction*

The liquefaction process was conducted in a double shirt reactor (600 mL) heated with oil at 180 °C for 120 min. The samples (10 g) were liquefied using a mixture of glycerol and ethylene glycol as solvents with a sample to solvents ratio of 1:10; the liquefaction process was catalyzed with 3% sulfuric acid (based on sample dry mass). The liquefied samples were then dissolved in methanol and filtered. The insoluble residue was determined gravimetrically. Two different glycerol to ethylene glycol ratios were tested, one of which was glycerol rich (GR) with a 1:1 ratio and the other one glycerol poor (GP) with a 1:9 ratio. These polyalcohols were chosen because of their low costs and relatively small environmental impact, as glycerol is a secondary product from biodiesel production and ethylene glycol can be obtained from bio-ethanol. Liquefaction yield was determined in accordance to Eq. 1:

$$\text{Liquefaction Yield}(\%) = \frac{\text{Initial dry mass (g)} - \text{Solid dry residue (g)}}{\text{Initial dry mass (g)}} \times 100 \quad (1)$$

#### *Determination of the acid number and OH index*

The acid number and OH index were determined for the GP polyol obtained from the liquefaction of *E. globulus* branches. The acid number represents the amount of base required to neutralize 1 g of polyol. This number was determined in accordance with ASTM D466-08 (2008) using standardized NaOH (0.0971 mol/L). Approximately 2 g ( $\pm$  0.0001 g) of polyol were dispersed in 50 mL of ethanol and titrated with a pH meter. A

mixture of the solvents used in the liquefaction process was used as a blank. The acid number ( $A_n$ ) was calculated with Eq. 2,

$$A_n \text{ (mg KOH/g)} = \frac{[(B - A) \times C \times 56.1]}{W} \quad (2)$$

where  $A$  is the volume of NaOH solution required for titration of the sample (mL),  $B$  is the volume of NaOH solution required for titration of the blank (mL),  $C$  is the NaOH solution concentration (mol/L),  $W$  is the mass of the polyol (g), and 56.1 is the molar mass of KOH (g/mol).

The OH index, expressed in milligrams of potassium hydroxide per gram of sample (mg KOH/g), corresponds to the amount of hydroxyl groups available to react with isocyanates in the synthesis of PU foams. The most accepted method for experimentally determining the OH index is reacting the hydroxyl groups with an organic anhydride polyol, *e.g.*, acetic anhydride or phthalic anhydride. The principle when determining the OH index is that the hydroxyl groups of the polyol esterify the phthalic anhydride in the presence of pyridine and the catalyst imidazole. The excess carbon is subjected to hydrolysis with water and the phthalic acid that is formed is titrated with a sodium hydroxide solution standard to the final point determined using a digital pH meter.

The OH index was determined according to ASTM D4274-05 (2005). Twenty-five milliliters of the esterification mixture, composed of approximately 79 g of phthalic anhydride, 500 mL of dry pyridine, and 11 g of imidazole, was mixed with 1 g of polyol. This mixture was placed in an oven at  $98 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$  for 15 min and then removed and cooled down to room temperature. Afterwards, 50 mL of dry pyridine were added and 10 mL of distilled water were titrated with standardized NaOH (0.4836 mol/L) and a pH meter. The OH index ( $I_{OH}$ ) was calculated and corrected with Eq. 3,

$$I_{OH} \text{ (mg KOH/g)} = \frac{[(B - A) \times C \times 56.1]}{W} + A_n \quad (3)$$

where  $A$  is the volume of NaOH solution required for titration of the sample (mL),  $B$  is the volume of NaOH solution required for titration of the blank (mL),  $C$  is the NaOH solution concentration (mol/L),  $W$  is the mass of the polyol (g), 56.1 is the molar mass of KOH (g/mol), and  $A_n$  is the acid number (mg KOH/g) from Eq. 1.

### *Preparation of the foams*

For the production of the PU foams, the produced polyols were neutralized with an aqueous solution of 0.5 M NaOH until a pH around 7 measured in a pH meter, evaporated in a rotary evaporator (Heidolph Hei-Vap Precision, Heidolph Instruments GMBH & CO KG, Schwabach, Germany) to remove the methanol, and finally placed in an oven at  $105 \text{ }^\circ\text{C}$  to eliminate the remaining water.

Approximately 3 g of each polyol was mixed in a polypropylene glass with the catalyst (Polycat 34) with amounts ranging from 0.15 to 0.60 g, blowing agent (water) 0.1 to 0.4 g, and surfactant (Tegostab B8404) 0.075 to 0.300 g. This mixture was stirred for approximately 30 s at 750 rpm in an IKA Ost Basic mixer (Staufen, Germany) and then the polymeric isocyanate (MDI Voranate M229) was added (6 to 14 g). After the addition of the isocyanate, the mixture was agitated again for a few seconds at 750 rpm until the chemical reaction started. This procedure was repeated for all of the PU foams.

After the initial screening, the 1:1 mixture of glycerol to ethylene glycol was considered to be the best and was therefore used for production of the foams and determining the effect of different isocyanate, catalyst, surfactant, and blowing agent

quantities on the foam properties. The range tested for each chemical was 200% to 467% isocyanate, 5% to 20% catalyst, 1% to 14% blowing agent, and 3% to 10% surfactant. All of the values were based on the polyol percentage (php).

#### *Determination of the physical and mechanical properties of the foams*

The density of the PU foams was determined with the ratio of the mass and volume of a cylindrical sample. The mass was measured on an ABT 100-5 M Kern digital scale (Nuremberg, Germany) with an uncertainty of 0.0001 g. The linear dimensions of the sample were assessed using a digital caliper (Absolute CD – 15DCX, Mitutoyo, Kanagawa, Japan) with an uncertainty of 0.01 mm.

The samples were left in a conditioning room (20°C and 65% relative humidity) for one week prior mechanical testing. The determination of the mechanical properties was done in triplicate on a Servosis I – 405/5 universal test machine (Servosis S. L., Madrid, Spain), according to ISO 844 (2014) with some modifications. Each PU foam slice (cylindrical shape) was placed on the machine and subjected to growing tension. The tests were done in triplicate.

Because it is impossible to find a maximum compressive strength for most foams, the compressive stress at 10% deformation ( $\sigma_{10\%}$ ) was determined. It was calculated with Eq. 4,

$$\sigma_{10\%} \text{ (kPa)} = \frac{F_{10}}{A_0} \times 1000 \quad (4)$$

where  $F_{10}$  is the applied force for 10% deformation of the sample (N) and  $A_0$  is the area of the base of the cylindrical specimen ( $\text{mm}^2$ ).

Eq. 5 was used to calculate the Young's modulus,

$$\text{Young's modulus (kPa)} = \frac{\Delta F / \Delta x \times h_0}{A_0} \times 1000 \quad (5)$$

where  $\Delta F / \Delta x$  is the slope of the linear zone of the stress vs. deformation curve ( $\text{N}/\text{mm}^2$ ),  $h_0$  is the average height of the cylindrical specimen (mm), and  $A_0$  is the area of the base of the cylindrical sample ( $\text{mm}^2$ ).

## RESULTS AND DISCUSSION

The possibility of using glycerol as the main polyalcohol in the liquefaction of eucalyptus branches increases the competitiveness of PU foams made with this liquefied material. Therefore, two different mixtures of polyalcohols were tested for liquefaction of eucalyptus branches. The liquefaction yields of the mixtures, one of which was GR and the other was GP, were 61% and 72%, respectively.

Table 1 presents the average values obtained for the density, compressive stress, and Young's modulus for the produced foams. The average density of the GR foams was  $41.1 \text{ kg}/\text{m}^3$ . Similarly, the average density of the GP foams was  $40.9 \text{ kg}/\text{m}^3$ . Although they had similar densities, the GP foams presented better mechanical properties than those produced with the GR polyol. The average compressive stress was 10.2 kPa and 27.2 kPa, while the Young's modulus was 150.9 kPa and 353.3 kPa for the GR and GP foams, respectively. These results showed that greater amounts of glycerol in the liquefaction

process led to decreases in the mechanical properties of the foams. For that reason, the optimization of the PU foams was done using the GP polyols.

**Table 1.** Mechanical Properties of the Foams Made with GR and GP Polyols

Sample	Density (kg/m <sup>3</sup> )	Compressive Stress 10% (kPa)	Young's Modulus (kPa)
GR	41.1±5.3	10.2±7.5	150.9±47.6
GP	40.9±4.9	27.2±12.1	353.3±98.4

The OH index obtained for the GP polyol from the *E. globulus* branches was 960 mg KOH/g (Table 2), which was higher than the values obtained for liquefied *E. globulus* bark (Mateus *et al.* 2017b). Mateus *et al.* (2017b) determined the variation in the OH index during liquefaction and found values between 300 mg KOH/g and 440 mg KOH/g. The main reason for this discrepancy was that diethylene glycol and 2-ethylhexanol were used in the presence of p-toluene sulfonic acid with a material to solvents ratio of 1:3, which is lower than the 1:10 ratio used in this work. Because both ethylene glycol ( $I_{OH} = 1808$ ) and glycerol ( $I_{OH} = 1827$ ) (Chajęcka 2011) have higher OH indices, this difference was expected. Similarly, Vale (2015) reported an OH index of 280 mg KOH/g for liquefied *E. globulus* bark, while dos Santos *et al.* (2018) reported 477 mg KOH/g for liquefied pinewood shreds and shaves. The value obtained for the OH content in this work was similar to that reported by Kunaver *et al.* (2010) for liquefied fir wood (1043 mg KOH/g) and by Zheng *et al.* (2011) for liquefied pine wood (700 mg KOH/g).

Additionally, the acid number obtained here (22.6 mg KOH/g ± 0.1 mg KOH/g) was quite similar to the value obtained from *E. camaldulensis* wood (25.23 mg KOH/g) by Ertaş *et al.* (2014). This value was also in the range of 20.1 mg KOH/g to 26.5 mg KOH/g reported by Kurimoto *et al.* (2001) for liquefied wood from six different species (three hardwoods and three softwoods).

A polyol viscosity from the liquefied *E. globulus* branches of 2.03 Pa·s (Table 2) was obtained. This value was within the range of 1.37 Pa·s to 2.31 Pa·s that was determined by Kurimoto *et al.* (2001) for liquefied wood.

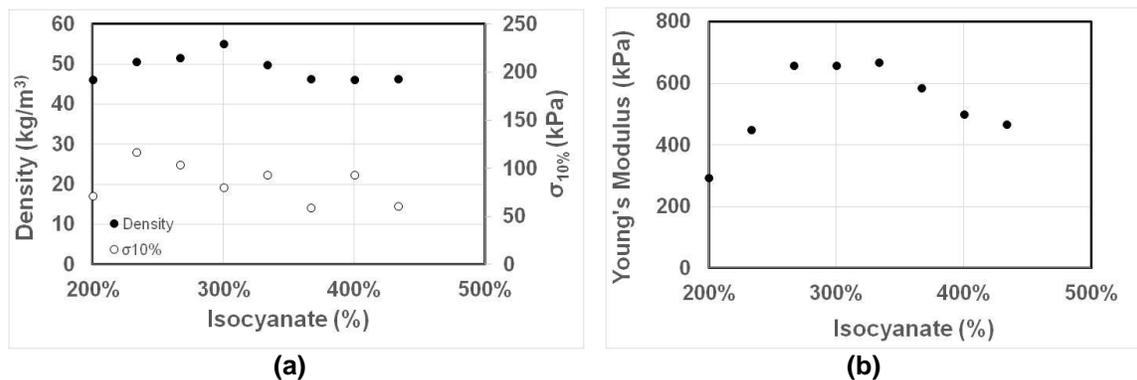
**Table 2.** Properties of the GP Polyol

OH Content (mg KOH/g)	Acid Number (mg KOH/g)	Viscosity (Pa·s)
960 ± 200	22.6 ± 0.1	2.03

During PU foam production, isocyanate reacts with hydroxyl groups from the polyol and forms urethane groups. The ratio between the quantities of isocyanate and polyol determines the properties of the PU foams. In general, the isocyanate group imparts rigidity to the foam, while the diol group imparts plasticity (Thomson 2005). Figure 1 presents the results concerning the influence of the isocyanate to polyol ratio on the properties of the foams obtained from the GP polyol. Analysis of Fig. 1 led to the conclusion that as the isocyanate content increased, the foam density increased from approximately 45 kg/m<sup>3</sup> to 55 kg/m<sup>3</sup>, and then it decreased to approximately 45 kg/m<sup>3</sup>. Similar results have been reported before. Hakim *et al.* (2011) reported an increase in the density up to a 1.2 nitrogen/carbon/oxygen (NCO) index (from 50 kg/m<sup>3</sup> to 55 kg/m<sup>3</sup>), after which there was a decrease (to 45 kg/m<sup>3</sup>). This trend was explained by the fact that

isocyanate reacts with urethane and urea groups when in excess to form allophanate and biuret, which builds new three-dimensional networks and hydrogen bonds in the foam and consequently decreases the density. Yan *et al.* (2008) reported a small increase in the density (from approximately 38 kg/m<sup>3</sup> to 40 kg/m<sup>3</sup>) for NCO indices ranging from 0.95 to 1.25, while Ertaş *et al.* (2014) reported a decrease in the density of PU foams made from liquefied eucalyptus and pine, although these authors only tested three different polymeric isocyanate contents. A similar decrease in the foam density has been described before for PU foams made with liquefied wheat straw (Chen and Lu 2009).

The Young's modulus and compressive stress seemed to have a similar trend to that of the density, although with a higher range of values. The GP foam presented compressive stress and Young's modulus values that ranged from 71.2 kPa to 121.8 kPa and from 295 kPa to 670 kPa, respectively. Yan *et al.* (2008) reported that there were increases with the NCO index until it reached a value of 1.15, after which the properties decreased. The compressive stress values ranged from 90 kPa to 130 kPa for Yan *et al.* (2008), which were similar to those obtained in this study. The same trend was reported by Hakim *et al.* (2011), with compressive stress values that ranged from 80 kPa to 90 kPa, and by Ertaş *et al.* (2014), who reported higher values that reached 150 kPa for pine and 250 kPa for eucalyptus-based polyols. Additionally, Chen and Lu (2009) reported similar behavior for PU foams made from liquefied wheat straw, which had compressive stresses of 169 kPa to 212 kPa.



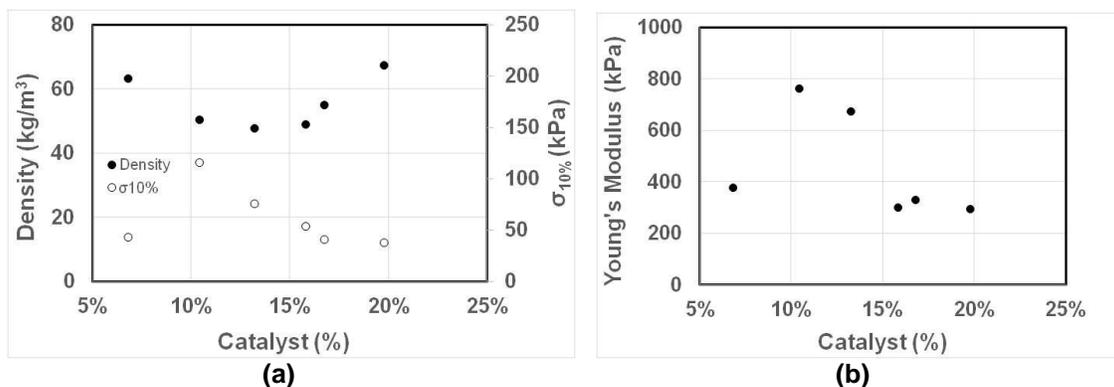
**Fig. 1.** Change in the density and compressive stress (a), and Young's modulus (b) with the isocyanate content

The choice of catalyst is essential for the synthesis of PU foams and foam formation because there are two reactions that compete with each other, namely the gelling reaction (reaction of isocyanate with polyol) and expansion reaction (reaction of isocyanate with water in the polyol). Thus, a balance between the speeds of these reactions must be achieved. If the gelling reaction is notably faster than the expansion reaction, then the foam shrinks, and if the expansion reaction is notably faster, the foam expands and bursts (Choe *et al.* 2004; Gama *et al.* 2015b). There are studies that simultaneously use both types of catalysts. One acts on the gelling reaction and the other acts on the expansion reaction (Choe *et al.* 2004; Yan *et al.* 2008). The catalyst tested in this study was Polycat 34® which, according to the manufacturer, is a balanced catalyst with a tertiary amine that primarily promotes the urethane reaction in rigid foam formulations. The amounts tested ranged from 5% to 25% based on the polyol amount (php), but it was only possible to form a foam with amounts over 7%. In contrast, catalyst amounts of over 20% resulted in a

reaction that was too fast and did not leave enough time to properly mix the compounds. Figure 2 shows that increases in the amount of catalyst initially caused the density to decrease from  $63 \text{ kg/m}^3$  (7% catalyst) to  $50 \text{ kg/m}^3$  (13% catalyst). However, with further increases in the catalyst amount, the density increased and reached a maximum of  $67 \text{ kg/m}^3$  (17% catalyst). Somewhat comparable results were obtained by Yan *et al.* (2008), who concluded that the increase in the percentage of expansion or gelling catalysts led to a decrease in the density. However, according to Choe *et al.* (2004), increases in the expansion catalyst or gelling catalyst contents had no remarkable influence on the density. Likewise, Seo *et al.* (2004) reported that higher amounts of blowing or gelling catalyst had no remarkable effects on the foam density, but did on the cream, gel, and tack-free times. The blowing catalyst led to faster cream times, and the gelling catalyst led to faster gel and tack-free times.

The effect of increasing the catalyst amount on the foam mechanical properties was more irregular. The compressive stress increased from 43 kPa with 7% catalyst to 116 kPa with 10% catalyst, after which it began decreasing. Similar results have been presented before; Seo *et al.* (2004) reported that an increase in the gelling catalyst led to a small increase and then a decrease in the compressive stress. For the blowing catalyst content, there were no notable differences. The differences may have occurred because of the amount of the other compounds, as an increase in the blowing catalyst increased the density and compressive stress, but only for the hydrofluorocarbon/water blowing agent (Choe *et al.* 2004). Choe *et al.* (2004) also reported that an increase in the gelling catalyst had no influence on the foam density or compressive stress.

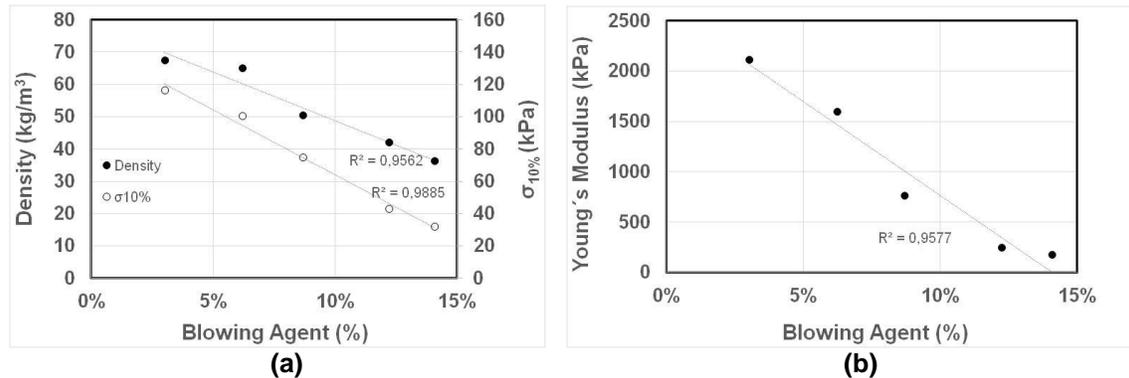
The Young's modulus followed a similar pattern to that of the compressive stress.



**Fig. 2.** Change in the density and compressive stress (a), and Young's modulus (b) with the catalyst content

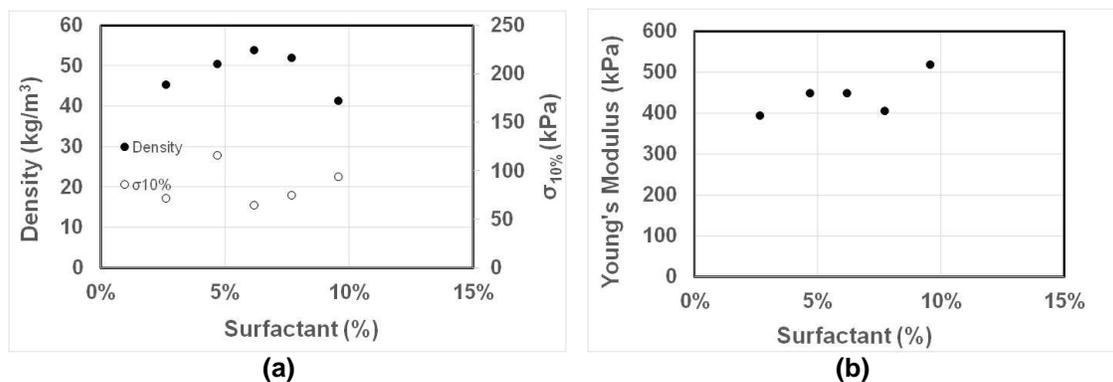
The changes in the density, compressive stress, and Young's modulus with changes in the water content are presented in Fig. 3. The density ranged from  $36.3 \text{ kg/m}^3$  to  $67.6 \text{ kg/m}^3$  and decreased with an increasing water content. The linear regression showed that the decreasing trend was almost linear with a  $R^2$  of 0.96. This was expected, as increasing the blowing agent leads to an increase in the reaction of the isocyanate with water. This reaction results in the release of more carbon dioxide and therefore increases foam growth. The compressive stress had a similar trend to that of the density and ranged from 116 kPa to 32 kPa. Likewise, the Young's modulus ranged from 2115 kPa to 183 kPa. The linear regressions for the compressive stress and Young's modulus values had  $R^2$  values of 0.96 and 0.99, respectively. Similar results have been reported before in the literature (Seo *et al.*

2003; Yan *et al.* 2008; Hakim *et al.* 2011). However, these authors reported more asymptotic decreases.



**Fig. 3.** Change in the density and compressive stress (a), and Young's modulus (b) with the blowing agent (water) content

The analysis results of the influence of the surfactant on the properties of the foams are presented in Fig. 4. The density showed small variations and ranged from 41 kg/m<sup>3</sup> to 51 kg/m<sup>3</sup>; however, there was a slight increase and then decrease as the surfactant amount increased. The compressive stress seemed to increase with larger surfactant amounts, although the maximum was achieved at 4.7% php. This property ranged from approximately 65 kPa to 116 kPa. The same trend was observed for the Young's modulus, although the increase was smaller and ranged between 406 kPa and 519 kPa.



**Fig. 4.** Change in the density and compressive stress (a), and Young's modulus (b) with the surfactant content

Somewhat similar results were presented by Yan *et al.* (2008) and Hakim *et al.* (2011), who studied the effect of the surfactant amount on the compressive stress of PU foams and concluded that the property displayed nonlinear behavior in relation to the surfactant content. According to these authors, the compressive stress initially increased, decreased, and finally increased again. Other studies have presented different results. For instance, Lim *et al.* (2008) suggested that when the surfactant concentration increases, the foam density should decrease sharply until it reaches a minimum, after which an increase in the surfactant slightly increases the density. According to these authors, an increased surfactant content reduces the size of the cells and surface tension and increases the number of closed cells. Consequently, this causes a decrease in the thermal conductivity and

increases the resistance to compression. The greater mechanical resistance because of the smaller sizes of the cells remains until a certain surfactant content, after which the resistance begins to decrease, as the size of the cells cease to decrease, which is called the “plasticized” effect (Seo *et al.* 2003).

Comparing the properties of the foams from this study with those of similar studies and bearing in mind that the quantities of chemicals used are different from study to study, it can be said that the values obtained for the properties of the PU foams synthesized from liquefied *E. globulus* branches were in the same order of magnitude of those obtained in other studies. The density ranged from 36 kg/m<sup>3</sup> to 108 kg/m<sup>3</sup>, which was similar to values obtained by Hakim *et al.* (2011) with liquefied sugar bagasse (50 kg/m<sup>3</sup> to 80 kg/m<sup>3</sup>). The compressive stress ranged from 15 kPa to 149 kPa and the Young’s modulus ranged from 64 kPa to 2100 kPa. The comparison of these results with a commercial foam showed that both the density (40 kg/m<sup>3</sup>) and Young’s modulus (124 kPa to 152 kPa) values of the commercial foam were within these ranges. However, the compressive stress (200 kPa) was remarkably higher (Mahmood *et al.* 2016).

## CONCLUSIONS

1. The results showed that it was possible to convert forest residues like *E. globulus* branches into PU foams with properties somewhat similar to those of commercial foams, although with a lower compressive strength.
2. To produce foams from liquefied eucalyptus branches with good properties, liquefaction should not be done with glycerol alone because the compressive properties of these foams were worse than those of the foams made from materials liquefied with a mixture of glycerol and ethylene glycol.
3. Overall the amount of each chemical used in the production of PU foams had a notable effect on the density and compressive properties. However, the clearest effects were caused by the water (blowing agent) content, which decreased both the density and compressive properties because of higher foam expansion.
4. Increasing the isocyanate amount increased and then decreased the density. To some extent, similar behavior was observed for the compressive properties. Initially, increasing the catalyst amount decreased the density. However, with further increases in the catalyst, the density also increased until it reached a maximum of 67 kg/m<sup>3</sup>.
5. The density of the produced foams ranged from 36 kg/m<sup>3</sup> to 108 kg/m<sup>3</sup>, the compressive strength ranged from 15 kPa to 149 kPa, and the Young’s modulus ranged from 64 kPa to 2100 kPa.

## REFERENCES CITED

ASTM D4274-05 (2005). “Standard test methods for testing polyurethane raw materials: Determination of hydroxyl numbers of polyols,” ASTM International, West Conshohocken, PA.

- ASTM D4662-08 (2008). "Standard test methods for polyurethane raw materials: Determination of acid and alkalinity numbers of polyols," ASTM International, West Conshohocken, PA.
- Chajęcka, J. M. (2011). *Synthesis of Biodegradable and Biocompostable Polyesters*, Ph.D. Thesis, Universidade Técnica de Lisboa, Lisboa, Portugal.
- Chen, F., and Lu, Z. (2009). "Liquefaction of wheat straw and preparation of rigid polyurethane foam from the liquefaction products," *J. Appl. Polym. Sci.* 111(1), 508-516. DOI: 10.1002/app.29107
- Choe, K. H., Lee, D. S., Seo, W. J., and Kim, W. N. (2004). "Properties of rigid polyurethane foams with blowing agents and catalysts," *Polym. J.* 36(5), 368-373. DOI: 10.1295/polymj.36.368
- Cinelli, P., Anguillesi, I., and Lazzeri, A. (2013). "Green synthesis of flexible polyurethane foams from liquefied lignin," *Eur. Polym. J.* 49(6), 1174-1184. DOI: 10.1016/j.eurpolymj.2013.04.005
- Cruz-Lopes, L. P., e Silva, H. C., Domingos, I., Ferreira, J., de Lemos, L. T., and Esteves, B. (2016). "Optimization of *Quercus cerris* bark liquefaction," *Int. J. Chem. Biomol. Eng.* 10(8), 1073-1076. DOI: 10.1999/1307-6892/10005169
- da Silva, V. R., Mosiewicki, M. A., Yoshida, M. I., da Silva, M. C., Stefani, P. M., and Marcovich, N. E. (2013). "Polyurethane foams based on modified tung oil and reinforced with rice husk ash. I: Synthesis and physical chemical characterization," *Polym. Test.* 32(2), 438-445. DOI: 10.1016/j.polymertesting.2013.01.002
- dos Santos, R. G., Acero, N. F., Matos, S., Carvalho, R., Vale, M., Marques, A. C., Bordado, J. C., and Mateus, M. M. (2018). "One-component spray polyurethane foam from liquefied pinewood polyols: Pursuing eco-friendly materials," *J. Polym. Environ.* 26(1), 91-100. DOI: 10.1007/s10924-016-0931-z
- Ertuş, M., Fidan, M. S., and Alma, M. H. (2014). "Preparation and characterization of biodegradable rigid polyurethane foams from the liquefied eucalyptus and pine woods," *Wood Res.-Slovakia* 59(1), 97-108.
- Esteves, B., Cruz-Lopes, L., Ferreira, J., Domingos, I., Nunes, L., and Pereira, H. (2017a). "Optimizing Douglas-fir bark liquefaction in mixtures of glycerol and polyethylene glycol and KOH," *Holzforschung* 72(1), 25-30. DOI: 10.1515/hf-2017-0018
- Esteves, B., Dulyanska, Y., Costa, C., Ferreira, J. V., Domingos, I., Pereira, H., de Lemos, L. T., and Cruz-Lopes, L. V. (2017b). "Cork liquefaction for polyurethane foam production," *BioResources* 12(2), 2339-2353. DOI: 10.15376/biores.12.2.2339-2353
- Gama, N. V., Soares, B., Freire, C. S. R., Silva, R., Brandão, I., Neto, C. P., Barros-Timmons, A., and Ferreira, A. (2015a). "Rigid polyurethane foams derived from cork liquefied at atmospheric pressure," *Polym. Int.* 64(2), 250-257. DOI: 10.1002/pi.4783
- Gama, N. V., Soares, B., Freire, C. S. R., Silva, R., Neto, C. P., Barros-Timmons, A., and Ferreira, A. (2015b). "Bio-based polyurethane foams toward applications beyond thermal insulation," *Mater. Design* 76, 77-85. DOI: 10.1016/j.matdes.2015.03.032
- Hakim, A. A. A., Nassar, M., Emam, A., and Sultan, M. (2011). "Preparation and characterization of rigid polyurethane foam prepared from sugar-cane bagasse polyol," *Mater. Chem. Phys.* 129(1-2), 301-307. DOI: 10.1016/j.matchemphys.2011.04.008
- Hu, S., Luo, X., and Li, Y. (2014). "Polyols and polyurethanes from the liquefaction of lignocellulosic biomass," *ChemSusChem* 7(1), 66-72. DOI: 10.1002/cssc.201300760

- Hu, S., Wan, C., and Li, Y. (2012). "Production and characterization of biopolyols and polyurethane foams from crude glycerol based liquefaction of soybean straw," *Bioresour. Technol.* 103(1), 227-233. DOI: 10.1016/j.biortech.2011.09.125
- ISO 844 (2014). "Rigid cellular plastics—Determination of compression properties," International Organization for Standardization, Geneva, Switzerland.
- Kunaver, M., Jasiukaityte, E., Čuk, N., and Guthrie, J. T. (2010). "Liquefaction of wood, synthesis and characterization of liquefied wood polyester derivatives," *J. Appl. Polym. Sci.* 115(3), 1265-1271. DOI: 10.1002/app.31277
- Kurimoto, Y., Koizumi, A., Doi, S., Tamura, Y., and Ono, H. (2001). "Wood species effects on the characteristics of liquefied wood and the properties of polyurethane films prepared from the liquefied wood," *Biomass Bioenerg.* 21(5), 381-390. DOI: 10.1016/S0961-9534(01)00041-1
- Lim, H., Kim, S. H., and Kim, B. K. (2008). "Effects of silicon surfactant in rigid polyurethane foams," *eXPRESS Polym. Lett.* 2(3), 194-200. DOI: 10.3144/expresspolymlett.2008.24
- Mahmood, N., Yuan, Z., Schmidt, J., and Xu, C. C. (2016). "Depolymerization of lignins and their applications for the preparation of polyols and rigid polyurethane foams: A review," *Renew. Sust. Energ. Rev.* 60, 317-329. DOI: 10.1016/j.rser.2016.01.037
- Mateus, M. M., Acero, N. F., Bordado, J. C., and dos Santos, R. G. (2015). "Sonication as a foremost tool to improve cork liquefaction," *Ind. Crop. Prod.* 74, 9-13. DOI: 10.1016/j.indcrop.2015.04.063
- Mateus, M. M., Vale, M. d., Rodrigues, A., Bordado, J. C., and dos Santos, R. G. (2017a). "Is biomass liquefaction an option for the viability of poplar short rotation coppices? A preliminary experimental approach," *Energy* 124, 40-45. DOI: 10.1016/j.energy.2017.02.059
- Mateus, M. M., Guerreiro, D., Ferreira, O., Bordado, J. C., and dos Santos, R. G. (2017b). "Heuristic analysis of *Eucalyptus globulus* bark depolymerization via acid-liquefaction," *Cellulose* 24(2), 659-668. DOI: 10.1007/s10570-016-1175-8
- Seo, W. J., Jung, H. C., Hyun, J. C., Kim, W. N., Lee, Y.-B., Choe, K. H., and Kim, S.-B. (2003). "Mechanical, morphological, and thermal properties of rigid polyurethane foams blown by distilled water," *J. Appl. Polym. Sci.* 90(1), 12-21. DOI: 10.1002/app.12238
- Seo, W. J., Park, J. H., Sung, Y. T., Hwang, D. H., Kim, W. N., and Lee, H. S. (2004). "Properties of water-blown rigid polyurethane foams with reactivity of raw materials," *J. Appl. Polym. Sci.* 93(5), 2334-2342. DOI: 10.1002/app.20717
- Soares, B., Gama, N., Freire, C., Barros-Timmons, A., Brandão, I., Silva, R., Neto, C. P., and Ferreira, A. (2014). "Ecopolyol production from industrial cork powder via acid liquefaction using polyhydric alcohols," *ACS Sustain. Chem. Eng.* 2(4), 846-854. DOI: 10.1021/sc400488c
- Thomson, T. (2005). *Polyurethanes as Specialty Chemicals: Principles and Applications*, CRC Press, Boca Raton, FL.
- Vale, M. F. L. d. (2015). *Lignopolyol Based One-component Polyurethane Foams*, Master's Thesis, University of Lisbon, Lisbon, Portugal.
- Wang, T., Zhang, L., Li, D., Yin, J., Wu, S., and Mao, Z. (2008). "Mechanical properties of polyurethane foams prepared from liquefied corn stover with PAPI," *Bioresour. Technol.* 99(7), 2265-2268. DOI: 10.1016/j.biortech.2007.05.003

- Yan, Y., Pang, H., Yang, X., Zhang, R., and Liao, B. (2008). "Preparation and characterization of water-blown polyurethane foams from liquefied cornstalk polyol," *J. Appl. Polym. Sci.* 110(2), 1099-1111. DOI: 10.1002/app.28692
- Zheng, Z., Pan, H., Huang, Y., Chung, Y. H., Zhang, X., and Feng, H. (2011). "Rapid liquefaction of wood in polyhydric alcohols under microwave heating and its liquefied products for preparation of rigid polyurethane foam," *The Open Materials Science Journal* 5(1), 1-8. DOI: 10.2174/1874088X01105010001

Article submitted: July 18, 2018; Peer review completed: September 9, 2018; Revised version received and accepted: October 3, 2018; Published: November 5, 2018.  
DOI: 10.15376/biores.14.1.31-43