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Article

Polyurethane Foams for Thermal Insulation Uses Produced from Castor Oil and Crude Glycerol Biopolyols

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Abstract: Rigid polyurethane foams were synthesized using a renewable polyol from the simple physical mixture of castor oil and crude glycerol. The effect of the catalyst and blowing agent in the foams properties was evaluated. The use of physical blowing agent (cyclopentane and n-pentane) allowed obtaining foams with smaller cells in comparison with the foams produced with a chemical blowing agent (water). The increase of water content caused a decrease of density, thermal conductivity, compressive strength and Young's modulus, which indicates that the increment of CO_2 production contributes to the formation of larger cells. Higher amount of catalyst in the foam formulations caused a slight density decrease and an increase small significance of thermal conductivity, compressive strength and Young's modulus values. These green foams presented properties that indicate a great potential to be used as thermal insulation, as density (23 - 41 kg m^{-3}), thermal conductivity (0.0128 – 0.0207 W m^{-1} K^{-1}), compressive strength (45 - 188 kPa) and Young's modulus (3 - 28 kPa). These biofoams are also environmental friendly alternatives and can aggregate revenue to biodiesel industry, contributing for reduction of this fuel prices.

Key words: polyurethane foams; castor oil; crude glycerol; biopolyols

1. Introduction

Rigid polyurethane foams are usually applied in thermal insulation of buildings, automobile and aerospace industry. The global rigid polyurethane foams market expectative is to reach USD 20.40 billion by 2020 in construction applications, as in residential and commercial roofs, walls, panels and doors, and in appliance applications [1]. For insulation purposes, thermal conductivity is one of the most important properties. Typical thermal conductivity values for polyurethane foams are between 0.02 and 0.03 W m^{-1} K^{-1} and the very efficient thermal insulation of these materials is due to the extremely low thermal conductivity of the blowing agent gas trapped in the closed porous structures [2,3]. Additives, as blowing agents, catalysts and surfactants, are very important to adjust the final properties of the foams synthesis from the main reaction of an isocyanate with a polyol. However, most of these reagents are derived from petrochemicals, increasing the petroleum dependence and, as consequence, environmental problems. These aspects have encourage the production of rigid foams from renewable materials [4].

In the last years, the uses of bio based polyols have being investigated to produce sustainable and eco-friendly rigid polyurethane foams, like lignin [5,6], biopitch [7,8], glycerol [9–11], and vegetable oils as castor [3,12–19], palm [20,21], soybean [22,23], starch [24,25], etc. Castor oil (CO) is a mixture of triglycerides, mainly ricinoleic acid, which is produced from the seed of *Ricinus communis* plant. This low cost renewable raw material has been usually used as polyol for flexible materials production, as polyurethane foams and elastomers. However, most of these materials are produced after chemical modifications of castor oil, as transesterification, oxypropilation, hydroformilation and ozonolysis, in order to introduce reactive hydroxyl groups, which involve oil pre-treatment with multiples steps and high costs.

Castor oil has high molecular weight, low hydroxyl number and poor reactivity and also a slow cure time, low flame retardancy and low miscibility with other components. These properties limited the use of castor oil as a raw material polyol, especially to prepare rigid polyurethane foams, and the pre-treatment reaction seems to be efficient to minimize these disadvantages. Transesterification [16,18,19,26], thio-ene [27] and amidization [28] reactions have been employed to introduce reactive OH groups in castor oil in order to produce suitable polyols to synthesize rigid polyurethane foams. . Recently, a work was published presenting a polyol production from the polymerization of glycerol followed by condensation of this polymerized material with castor oil. After this, rigid polyurethane foams were synthesized by partial substitution of a petrochemical polyol with the polyol produced [29]. These reactions are usually performed in the presence of an alcohol and the use glycerol, a co-product from biodiesel production, have been also extensively studied. The foams produced from these two types of industrial crops' processing products presented good mechanical properties, as densities (35 - 50 kg m^{-3}), compressive strength (127 - 475 kPa), and also great thermal stabilities, as limit oxygen index (20 - 30%) and thermal conductivity (0,021 - 0,029 W mK^{-1}). However, the reactions to modify the oil and enhance its reactivity are conducted between 160 to 240°C, during 2 - 6 hours, multiple steps and some reactants, increasing the foam costs.

In the present study, similar foams were prepared using a simple mixture of crude glycerol and pure castor oil to increase the functionality of this bio polyols without extra costs. It occurs because the crude glycerol has three hydroxyl groups and short chain, besides good miscibility in the castor oil. The polyol was produced from the physical mixing of raw materials without any type of chemical or physical pre-treatment and for direct use in polyurethane synthesis. This simple and innovative approach allowed the production of renewable rigid polyurethane foams for thermal insulation uses. The effect of the catalyst and blowing agent in the mechanical and thermal conductivity properties of the foams were evaluated. This process is inexpensive, simple, and sustainable, suitable to produce environmental friendly materials with good properties.

2. Materials and methods

2.1. Materials

Castor oil used was provided by PolyUrethane Company (Betim, Minas Gerais - Brazil). Crude glycerol, a co-product of biodiesel production, was kindly provided by Petrobrás (Usina Darcy Ribeiro - Montes Claros - MG). Pure glycerol (99.5%) was supplied by Synth. The isocyanate source (Desmodur 44 V 20), a mixture of 4,4'-diphenylmethane-diisocyanate, was supplied by Bayer Company. The surfactant was Tegostab 8460 (Evonik), a polyether-modified polysiloxane. The catalyst used in polyurethane foams synthesis was DBTDL (DiButil Tin DiLaurate), an organometalic catalyst, manufactured by Evonik. The blowing agents used were cyclopentane (Sigma Aldrich), n-pentane (Sigma Aldrich) and distilled water.

2.2. Foams synthesis

Rigid polyurethane foams were synthesized using the batch process method. Initially, the polyols were produced by mixturing of castor oil (CO) and crude glycerol (G) in a mechanical stirrer (Fisatom model 713 D) until the system became homogenized. Foams with different amounts of castor oil/ crude glycerol were synthesized. The NCO/OH molar ratio was kept equal to 2.0. 2% (w/w) of surfactant and different contents of catalyst and blowing agent were added to the polyol, and this mixture was kept under vigorous stirring for 1 minute at 500 rpm. At least, the isocyanate was added to the pre mixture and stirred until the complete homogenization. The formulation was poured into a wooden mold with dimensions 7.0 x 7.0 x 20.0 cm for the growth of the polymer foam to cure for 24 hours, at room temperature. After the curing time, the foam was demolded and the

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characterizations were performed. The catalyst and blowing agent amount was evaluated in the foams synthesis in order to produce cells with high content of closed cells and more rigid.

2.4. Characterization

Fourier transform infrared (FTIR) was recorded on a ABB Bomer spectrometer using 0.1% KBr pellets and ATR accessory with resolution of 4 cm^{-1}, in the range of 4000 – 400 cm^{-1}. The thermal behavior of the foams was evaluated by thermogravimetric analysis (TGA), which was carried out on a TA equipment model TA-50 Q at temperatures ranging from 30 °C to 800°C with heating rate of 10°C min^{-1} under nitrogen flow of 40 mL min^{-1}. The images obtained by optical microscopy were collected on an Olympus Optical Microscope Model BX41M coupled to a TecVoz camera model DNS 480. The morphology of polymers structure was characterized to observe the foam cellular structure by scanning electron microscope (SEM) images, which were obtained with a JSM - 6360LV, a scanning microscope JEOL. Polyurethane foam densities were calculated according to the ASTM D-1622 standard by measuring three specimens of each sample with dimensions of 50 × 50 × 25 mm^3. Mechanical testing (10% compressive strength) of PU foams was performed on a testing machine Autograph Precision Universal Testing Machine AG-Xplus Series (Shimadzu), according to ASTM D1621 standard method, and at least five samples were analyzed to obtain the average value, the specimens size was 50 × 50 × 25 mm^3. Thermal conductivity tests were performed by an instrument developed by professor Vagner Carvalho in the Surface Laboratory at the Physics Department at Universidade Federal de Minas Gerais- Brazil [30]. This equipment has a unit that contains a tip, which is electronically controlled and a temperature sensor. The measures are based on the thermal comparison method by copper-constantan differential thermocouples that measure the contact temperature gradient and the changes in the sample temperature. The samples were tested six times a simple average was taken as the comparator output. A calibration curve was constructed using various ranges of samples with a wide thermal conductivity and the data were plotted in order to get the relation between the thermal conductivity and the comparator output.

3. Results and Discussion

The polyol production was preliminary studied by the physical mixture of pure glycerol and castor oil, varying the glycerol content. Some foams did not present good dimensional stability (Figure 1a), but increasing the content of pure glycerol it was observed that the foams became denser and softer. The formulations with 20% and 40% (w/w) of pure glycerol content did not grow as typical foam, yielding a very rigid solid material. The foams produced with the polyol containing 50% (w/w) of pure glycerol presented a high homogeneity, but increasing this content up 50%, the foams became very friable.

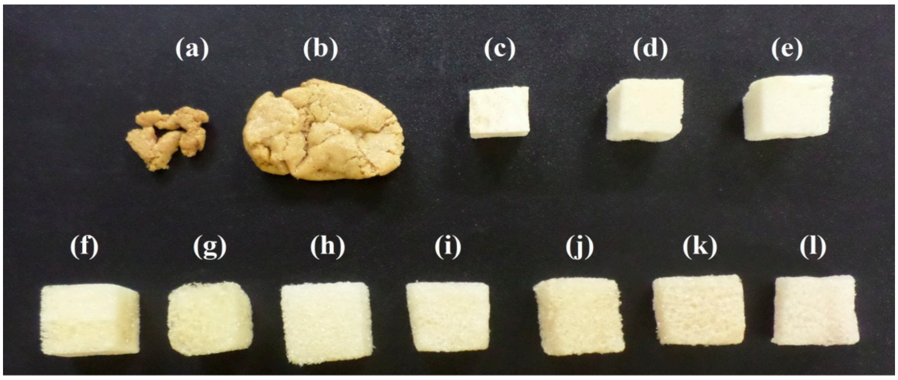

Figure 1. Foams produced varying the pure glycerol content: (a) 20%; (b) 40%; (c) 50%; (d) 60% e (e) 80% and crude glycerol content (f) 10%; (g) 20%; (h) 30%; (i) 40%; (j) 50%; (k) 60% e (l) 70% in the polyols.

The pure glycerol was then replaced by crude glycerol, a co product from biodiesel production in order to synthesize new foams and the results were quite different. The foams with crude glycerol and castor oil (named GCo, Figure 1f - 1l) polyol were more homogeneous and with good dimensional stability in comparison to those synthesized with pure glycerol (Figure 1a - 1e). Based on these experimental behaviors, we believe that the crude glycerol impurities (alkaline catalyst, methanol, methyl esters of fatty acids - FAME) are responsible for the best properties of the foams. Further investigations can be made to understand this behavior. Similar behaviors have already related in literature, evaluating the effects of the replacement of pure glycerol by crude glycerol for producing polyols from biomass liquefaction. These studies also affirm that these impurities of crude glycerol can improve the polyols and polyurethanes properties [22,31,32].

It was observed that with increasing the amount of crude glycerol, there was a decrease in the rigidity and the dimensional stability of the foams. For this reason, the foam produced from the polyol containing 10% of crude glycerol and 90% of castor oil (w/w) was chosen to perform further studies. The hydroxyl number (240 mg KOH g^{-1}) and viscosity (436.5 mm^{2} s^{-1}) of this polyol were measured, indicating that these polyols are adequate to produce rigid foams. [4]. Similar results have already reported in literature for polyols from castor oil [27].

It is important to point out that the polyol used to produce our best foam, with 10% of glycerol and 90% of castor oil (w/w), have the molar ratio glycerol/castor oil approximately equal to 1 (considering the molar weight of glycerol and castor oil 92.09 and 895.33 g mol^{-1}, respectively). Observing the structure of this molecules (Figure 2), there are three hydroxyl groups in each glycerol molecule and three instaurations of ricinoleic acid in the triglyceride structure that are suitable to be transformed in OH groups by pre-treatment reactions. So, we can consider that 1 mol of glycerol has the same number of OH groups that 1 mol of pre-treated castor oil. In our proposal, we can obtain the same hydroxyl content using 10% of crude glycerol (w/w), instead perform the castor oil pre-treatment, besides to use a simple and inexpensive process.

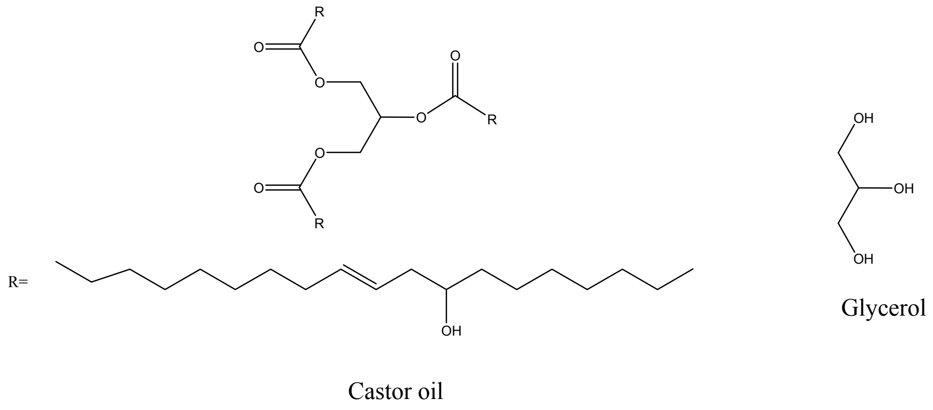

Figure 2. Structure of the castor oil and glycerol molecules.

The spectra of the renewable raw materials used to produce GCo polyols are shown in Figure 3. The band corresponding to hydroxyl group's vibration is observed at approximately 3700-3000 cm^{-1}. The characteristic stretches of double bonds in the castor oil groups C = C - H and C = C are observed in 3020 and 1740 cm^{-1}, respectively. The bands around 3018 and 2710 cm^{-1} are assigned to CH_2 and CH_3 stretches of aliphatic chains, which are quite pronounced in castor oil due to the 18 carbons chain. The characteristic band of carbonyl and carboxyl groups is observed centered at 1743 cm^{-1} in the castor oil spectrum. The alkenes deformation of CH_2 groups, present in castor oil structure, is observed in a strong band at 1458 cm^{-1}. The bands around 1112 - 1000 cm^{-1} indicate the presence of primary and secondary hydroxyl groups. These bands are very pronounced in crude glycerol spectrum, due to the three hydroxyl groups present in its structure [16,18].

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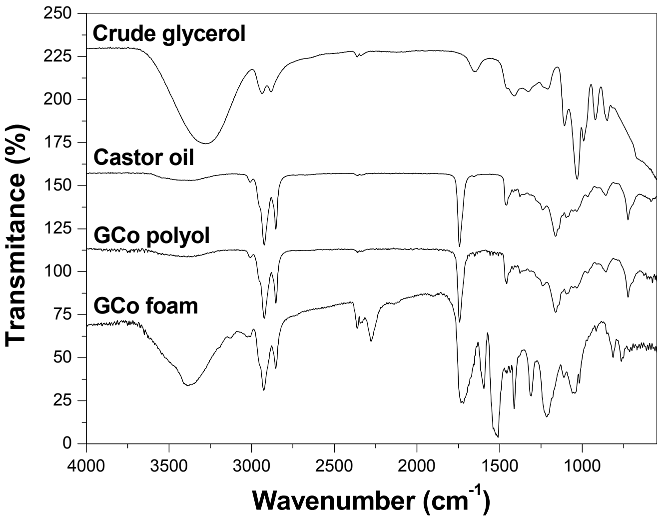
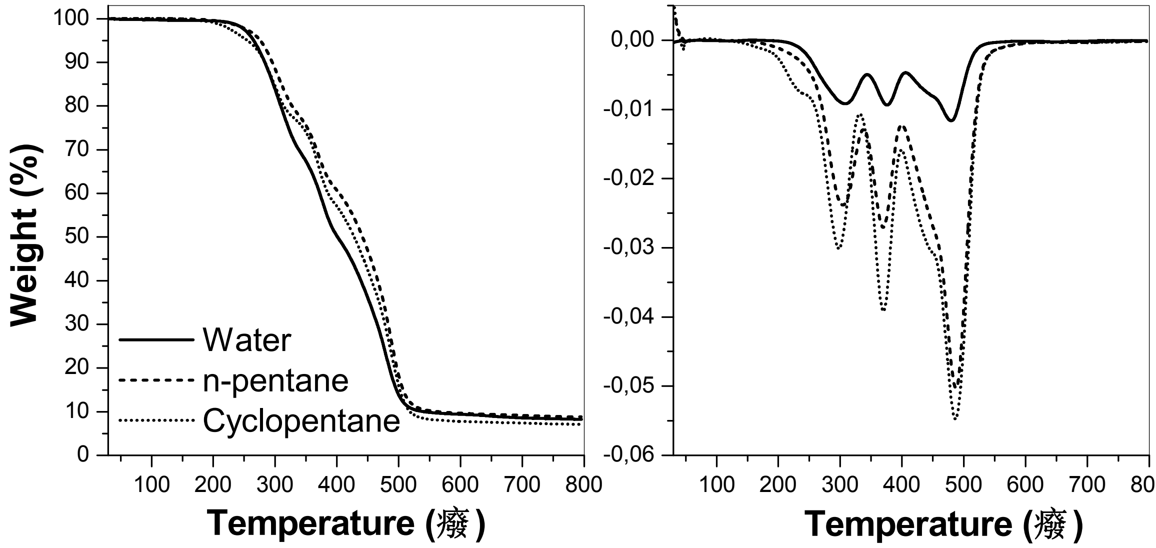


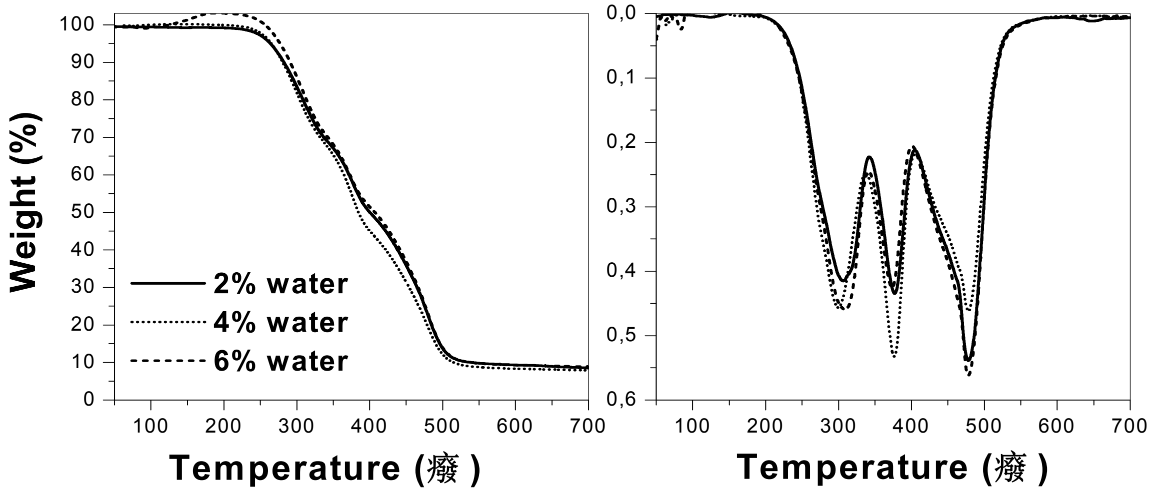
Figure 3. Spectra of raw materials, GCo polyol and foam

All the foams spectra produced from GCo polyols are very similar and one of these foams spectra is showed in Figure 3, which presented the typical polyurethane bands. The stretching and vibrations of NH groups were observed between 3808- 3308 and 1512 and 1510 cm^{-1}, respectively. The deformation of CH_2 bonds was observed by the two thin bands at 2900 and 2890 cm^{-1}. The vibration of N=C=N and N=C=O groups are attributed to bands between 2390 and 2150 cm^{-1}. Other vibration modes of CH bond were also observed at 1464, 1418, 1364 and 1294 cm^{-1}. The band between 1730 and 1720 cm^{-1} corresponds to the stretch of CO free urethane bond, and around 1700 cm^{-1}, the hydrogen bond between the carbonyl and hydrogen atoms (from NH groups) from urethane is also observed. A band related to stretching asymmetric links OCONH was revealed in 1380 cm^{-1}. The bands between 1100 and 1000 cm^{-1} were attributed to primary and secondary hydroxyl groups [16,17].

The thermal behavior of the GCo foams containing different types and amounts of catalyst, showed in Figure 4, were evaluated by thermogravimetric analysis (TGA and DTG). The different foams presented similar thermal stability and DTG curves showed three regions of weight loss. The first event (around 300°C) correspond to urethane thermal degradation, free isocyanate and alcohols; the second event was related with the degradation of rigid segments, at 370°C; and the third event, approximately at 480°C, is associated to the thermal degradation of flexible segments and others segments of the remaining structure [33,34].



(a) (b)



(c)

(d)

Figure 4. TGA (a and c) and DTG (b and d) curves of foams with GCo polyol with different types and amount of blowing agents.

The effect of different blowing agents in thermal stability of the GCo foams was evaluated as showed in Figures 4a and 4b. The results indicate that the blowing agent type did not modify significantly the thermal behavior of the foams, which is suggested by the similar curves of foams synthesized with water, cyclopentane and n-pentane.

It was also investigated the effect of the amount of blowing agent (water) in the formulations (Figure 4c and 4d). The results show that the amount of water as blowing agent did not significantly affect the thermal stability of the foams produced with polyol GCo, taking into account that all the curves presented the same profile, indicating a similar thermal stability.

Apparent density is an important parameter of cellular polymers. The effect of the blowing agent type in apparent density of the foams produced from GCo polyols (Table 1) showed that formulations with physical blowing agents (cyclopentane and n-pentane) produced foams with higher densities than those synthesized with the chemical blowing agent (water). Similar results have been reported in the literature [34–36] and this behaviour indicates that smaller cells are formed due to the rapid volatilization of physical blowing agents, which have low boiling point, during the highly exothermic foam growth step in comparison with the CO$_2$, produced by the reaction of water with isocyanate [37].

Table 1. Density values of foams with different blowing agents.

Blowing agent	Apparent density (kg m^{-3})
Water	37.4
n-pentane	61.3
Cyclopentane	99.3

The effect of blowing agent (water) content in the foams apparent density was also evaluated, as showed in Figure 5a. Increasing the water amount is observed an decrease of density, which suggests that higher cells are formed with the increasing of CO$_2$ production from the water and isocyanate reaction [38]. Figure 5a also shows the influence of the catalyst content in the foams density. A decrease of apparent density was observed increasing the catalyst amount in the formulations. This behavior can be explained by the increment in the polymerization rate with the enhancement of the organometallic catalyst content in the formulation, avoiding the CO$_2$ releasing during the foams cell formation [4]. As the reaction occurs with higher speed, the blowing agent is trapped in the structure and the cells presented higher diameter and lower densities (Figures 5b and 5a, respectively) [39]. This effect is more prominent in foams with higher water contents. These

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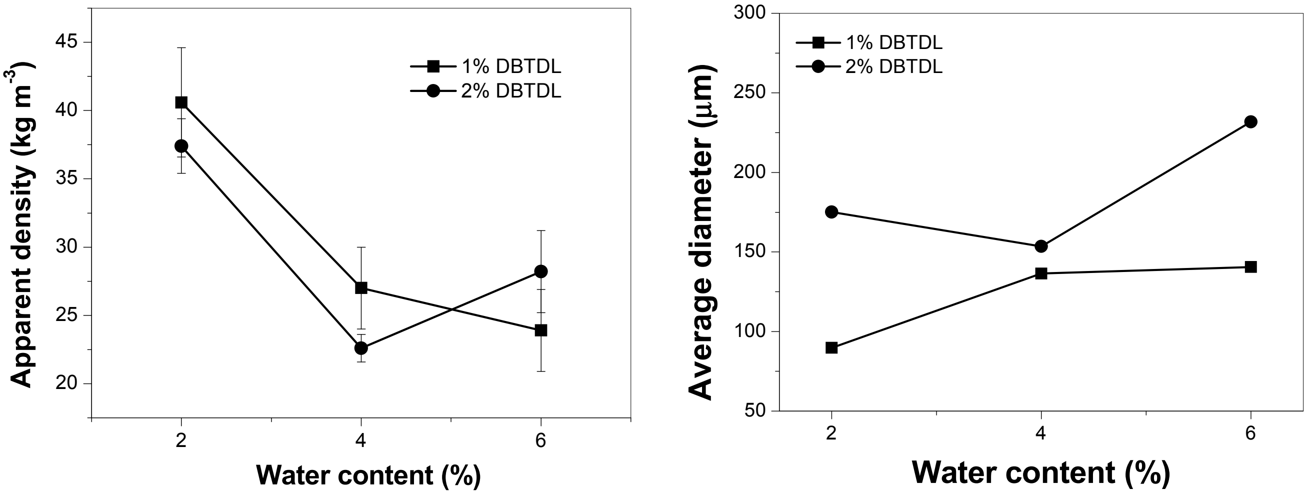
apparent density results are according o the values measured for same rigid polyurethane foams synthesized using castor oil polyols [19,27].



(a) (b)

Figure 5. (a) Apparent density and (b) average diameter of foams with different contents of blowing agent (water) and catalyst.

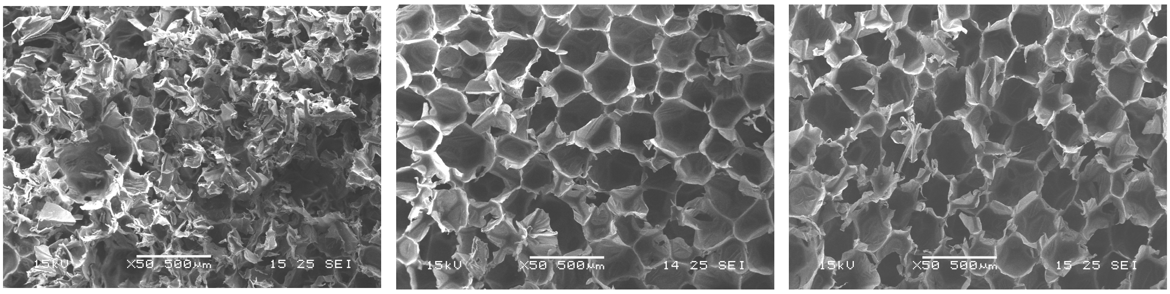
The effect of different blowing agents in the foams cellular structure can also be observed in Figure 6, which showed SEM images of the foams synthesized with water and cyclopentane. The foams synthesized with water as blowing agent showed largest cell size, confirming the densities data (Figure 5a). This pentane has a low boiling temperature (around 50°C) and volatizes very quickly, as explained before, in density discussion. The foam with 6% of cyclopentane presented a low dimensional stability and, for this reason, its SEM micrograph was not showed here.

The foams produced formulated with water as blowing agent presented the best dimensional stability, the lowest apparent density and the higher cells homogeneity, and based on these results, we chosen this formulation for the evaluation of the catalyst amount in mechanical and conductivity properties. Other important aspect is that the use of water as blowing agent is considered a green and inexpensive alternative.

The effect of the water content as blowing agent was also evaluated by SEM images in Figure 6. It was observed that the water concentration is directly proportional to the cell size, a showed in Figure 5b. These analyses are in concordance with densities data (Figure 5a). The foams produced with 4% of water presented higher cell homogeneity in comparison to those containing 2% of water. The foams formulated with 6% of water produced bigger and heterogeneous cells, indicating that 4% of water is the optimal quantity to be used in the foam formulations.

1% DBTDL

2% water 4% water 6% water



(a) (b) (c)

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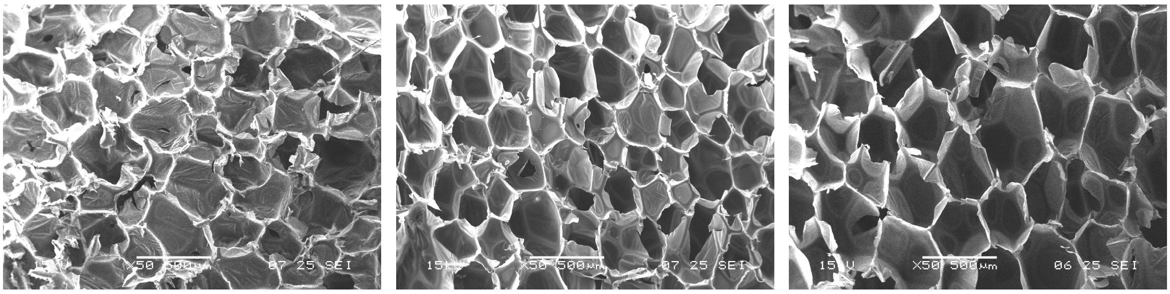
2% DBTDL

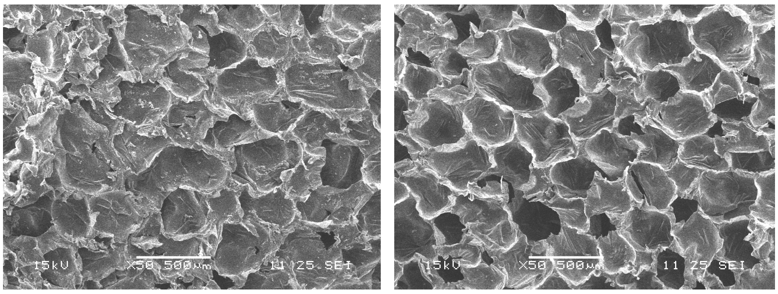
2% water 4% water 6% water



(d) (e) (f)

2% DBTDL

2% cyclopentane 4% cyclopentane



(g) (h)

Figure 6. SEM micrographs of GCo foams with different types and contents of blowing agent and catalyst.

The comparison of the catalyst amount in the foams cells (Figure 6) formulated with water showed that an increment of the catalyst content yielded cellular materials with higher cells average diameters, confirming the density values in Figure 5a. The foams synthesized with 2% of DBTDL showed the best cells homogeneity, despite higher diameter cells, as observed in Figure 5b. The cells average diameter of the foams produced in this present process is smaller than the data reported in the literature of foams synthesizes from pre-polymerized castor oil [29], which is an important result for our foam uses.

The main property for foams application as thermal insulation is the thermal conductivity. This parameter was measured for the rigid foams synthesized with water as blowing agent, and the results are presented in Figure 7. It was observed that increasing the water amount in these formulations there was a decrease of the thermal conductivity. This results can be explained by density decrease and the enhancement of cell average diameter of the foams [40].

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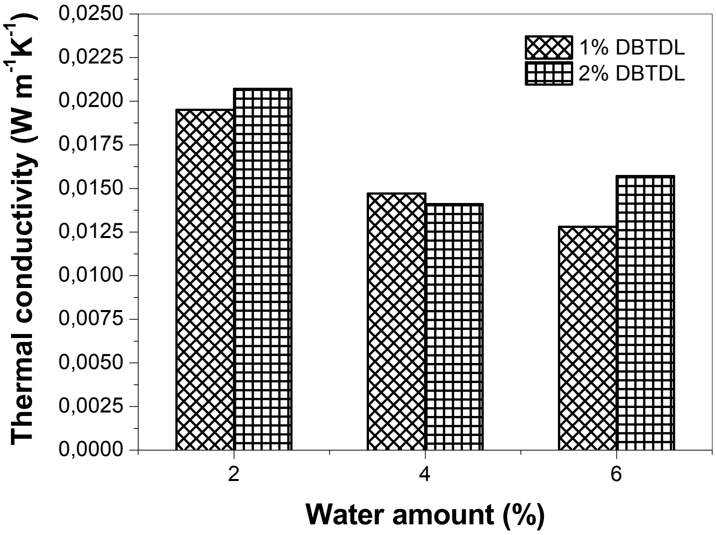
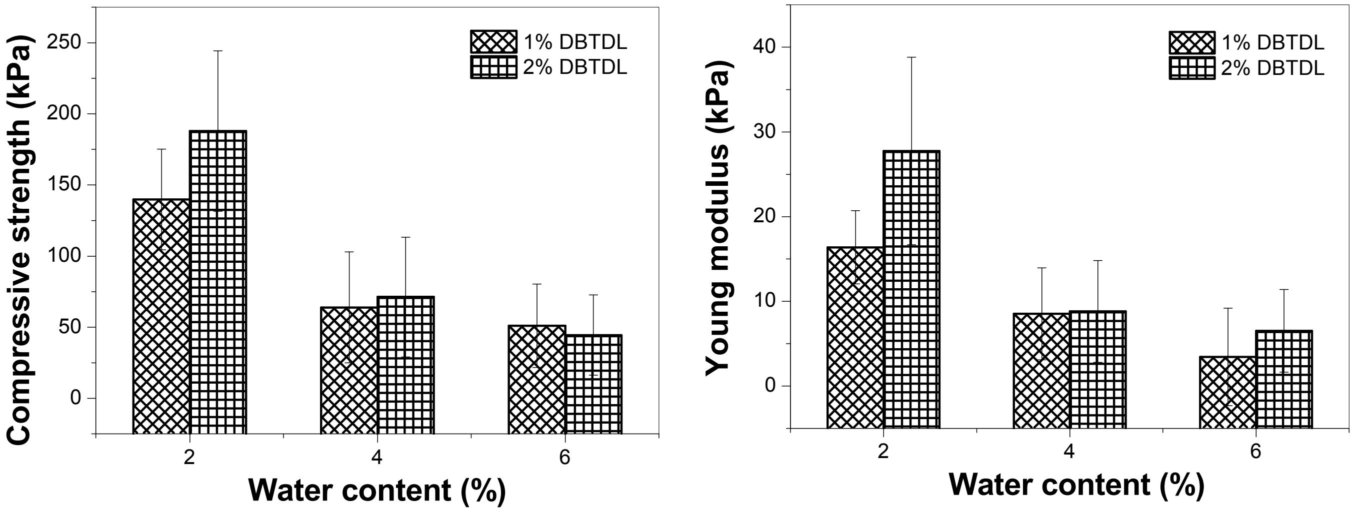


Figure 7. Thermal conductivity of foams with different contents of blowing agent (water) and catalyst.

The effect of catalyst amount in this property is also presented in Figure 7. The use of higher catalyst content in the formulations causes a slight thermal conductivity values enhancement, despite of density decrease as consequence of cell size increase, as showed in Figure 5. The foams synthesized in this study presented better results in comparison to those reported in the literature for foams derived from renewable raw materials, whose values vary between 0.0233 - 0.0505 W m^{-1}K^{-1}, suggesting that these materials have a potential use on thermal insulation [23,41,42]. These thermal conductivity results are also better than those found for foams produced from pre-treatment reactions of castor oil, by using a very simple an inexpensive method of production [19,29].

The mechanical properties of the foams synthesize with different contents of blowing agent and catalyst were evaluated and the results are shown in Figure 8. These properties results presented similar values to those reported in the literature of foams produced from castor oil polyols [16,19,26,27]. A significant decrease in the compressive strength and Young modulus of the foams were observed with the addition of the higher blowing agent amounts, which can be related with the density decreases and the cell size increase. As the cell structure becomes higher, less force is necessary to cause deformation in this foams [38].



(a) (b)

Figure 8. (a) Compressive strength and (b) Young modulus of foams with different contents of blowing agent (water) and catalyst.

The results of compressive strength and Young modulus of foams with different amounts of catalyst in the formulations (Figure 8a and 8b) showed that there are no significantly changes of the values increasing the catalysts amount, especially for the formulations with 4 and 6% of water. The variations are within the experimental error.

Comparing all the formulations, it was observed that the foam with best thermal conductivity (0.0141 W m^{-1} K^{-1}) was formulated with 1% of DBTDL and 6% of water, which also showed a low apparent density value (23.9 kg m^{-3}). However, this sample showed a low compressive strength (51.01 kPa) and Young modulus (3.44 kPa), suggesting your application to insulation of places that not receive high loads. The foam containing 2% of DBTDL and 2% of water posses the higher compressive strength (187.93 kPa) and Young modulus (27.74 kPa), besides a low apparent density value (37.4 kg m^{-3}). On the other hand, the thermal conductivity was the higher value (0.0207 W m^{-1} K^{-1}) in comparison with the other formulations, indeed, the insulation property of this foam is in the range of typical insulation foam [2].

4. Conclusions

Rigid polyurethane foams were synthesized from a polyol produced by the physical mixture of castor oil and crude glycerol, a co product from biodiesel industry. The polyol preparation method is simple and do not required any pre treatment of the raw materials. The best formulation was obtained with 10% of crude glycerol and 90% of castor oil (w/w, molar ratio = 1:1) and water as blowing agent. The addition of 10% glycerol increased the OH content of the biopolyol to the same extent if the castor oil had been pre-treated in order to insert one hydroxyl group in each instauration (C=C) of ricinoleic acid.

The effect of the blowing agent in the foam synthesis was evaluated and the results showed that increasing water amount causes a decrease in density, thermal conductivity, compressive strength and Young's modulus. These behaviors are due to the cell size enhancement.

The evaluation about the effect of catalyst (DBTDL) amount showed that increasing the catalyst content, it is observed a decrease of density and increase of thermal conductivity, however just a slight influence of compressive strength and Young's modulus.

These innovative foams presented properties that indicate a great potential for their use as thermal insulation. These materials are inexpensive, environmental friendly and can contribute to reduce the biodiesel prices in a bio refinery approach. These biopolymers can be synthesized by a simple process, which can be easily used in large scale.

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Figure captions

Figure 1. Foams produced varying the pure glycerol content: (a) 20%; (b) 40%; (c) 50%; (d) 60% e (e) 80% and crude glycerol content (f) 10%; (g) 20%; (h) 30%; (i) 40%; (j) 50%; (k) 60% e (l) 70% in the polyols.

Figure 2. Structure of the castor oil and glycerol molecules.

Figure 3. Spectra of raw materials, GCo polyol and foam

Figure 4. TGA (a and c) and DTG (b and d) curves of foams with GCo polyol with different types and

Figure 5. (a) Apparent density and (b) average diameter of foams with different contents of blowing agent (water) and catalyst.

Figure 6. SEM micrographs of GCo foams with different types and contents of blowing agent and catalyst.

Figure 7. Thermal conductivity of foams with different contents of blowing agent (water) and catalyst.

Figure 8. (a) Compressive strength and (b) Young modulus of foams with different contents of blowing agent (water) and catalyst.