Synthesis and Characterization of Polyurethane Rigid Foams from Soybean Oil-Based Polyol and Glycerol

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ABSTRACT: Mixtures of biomass-derived polyols were used to synthesize rigid polyurethane (PU) foams. A commercial polymerized methylene diphenyl diisocyanate (pMDI) was used as crosslinker, and distilled water served as foaming agent. The morphology and mechanical properties of foams with different glycerol and water contents were compared in order to evaluate the most suitable formulations. The rigid foams with higher water contents had larger and more anisotropic cells, explaining their lower density. Compressive moduli ranged from about 2.5 MPa to above 20 MPa and collapse stresses from 55 kPa to more than 1 MPa for densities between 54 and 143 kg/m^3. Densification strain did not depend on the density or on the composition of the polymeric matrix. Moreover, results shown herein demonstrate that an increase in the glycerol content leads to an increase in the required pMDI for the synthesis of the PU, but with a negligible change in the mechanical properties of the prepared foams.

KEYWORDS: Polyurethane foams, hydroxylated soybean oil, glycerol, mechanical properties, morphology

1 INTRODUCTION

Polyurethanes (PU) constitute a very important class of polymeric materials with diverse industrial and domestic uses as adhesives, coatings, structural flexible foams and solid parts obtained by reaction injection molding (RIM), among many others [1]. This great versatility is the result of the wide variety of chemical structures available for their main precursors: polyols and isocyanates [2].

Nevertheless, PU precursors are generally derived from fossil oil, which is considered a weakness in view of the increasing concern for environmental issues and the depletion of nonrenewable resources. The reduction of petrochemical dependence of rigid PU (RPU) formulations could reduce the CO$_2$ fingerprint related to harsh petrochemical refinery processes. As a response to these concerns, much scientific effort has been devoted in the last decades to find suitable biogenic substitutes for the synthetic traditional polymer precursors in order to obtain materials with competitive properties compared with their petrochemical-based counterparts [3–5].

Usually RPU foams are prepared by combining a highly reactive diisocyanate, such as toluene diisocyanate (TDI), methylene diphenyl diisocyanate (MDI) or partially polymerized MDI (pMDI), with a mixture of multifunctional polyols and glycerol, which provide enough macromolecular crosslinking density as to provide mechanical rigidity and strength [6]. Approaches to incorporate biomass-derived raw materials to RPU formulations and replace synthetic reagents include the use of solid fillers such as lignins [7, 8], cellulose [9] and wood fibers [10, 11], or cocoa pod husk [12] and rice husk [13], but the most usual method is to replace the synthetic polyols derived from the petrochemical industry with natural oil-derived polyols. This path has led to the use of polyols based

on cocoa-shell oil [14], sugar cane molasses [15, 16], castor oil [17, 18], palm oil [19], tung oil [13, 20, 21] or soybean oil [22–25]. Because of its high crop yields and wide availability, together with stable prices of its oil, soybean is gaining growing attention as a replacement for petroleum-based polyols in the production of RPU.

In this context, Campanella *et al.* studied the influence of several variables (polyol reactivity, water content, curing temperature, type of catalyst, isocyanate, and surfactant) on the structure and properties of flexible foams and found that the foam structure was affected by the water and catalyst content, which controlled the density and the cure rate of the foam [24]. Gu *et al.* studied RPU systems consisting of soy-based polyol reinforced with wood-pulp fiber and analyzed their morphology and mechanical properties [26]. They showed that pulp fiber incorporation disrupted cell structure, and observed an increased cell size with water content, analogous to studies by Li *et al.* in which a petrochemical polyol was used [27]. Tu *et al.* replaced a synthetic high hydroxyl number polyol (Voranol 490) with a hydroxylated and oxidized-epoxydized soybean oil up to 50 wt%, and showed that some low density systems exhibited a better combination of density and compressive strength values than foams made with pure Voranol 490 [20].

The use of hydroxylated modifiers to tune the properties of foams is also a common practice. Calvo-Correas *et al.* [28] used 5–20 wt% of diethylene glycol, polyethylene glycol and glycerol to partially replace a linseed oil-based polyol, and they found that formulations containing glycerol displayed better compressive properties and a higher glass transition temperature. From the large number of available modifiers, glycerol is especially attractive, combining its high –OH number with a renewable origin. Moreover, it is generated in large volumes as a byproduct of biodiesel production (about 10% in weight of the biodiesel production), which makes it an abundant and low price raw material [29].

The objective of this article is to analyze the morphology and mechanical properties, and the relationship between them, for RPU foams synthesized using mixtures of a soybean oil-based polyol and glycerol as substitutes for the synthetic polyol. The effect of the glycerol and water contents on the behavior of foams was also analyzed.

2 EXPERIMENTAL

2.1 Materials

Hydroxylated soybean oil-based polyol (Agrol 3.6, BioBased Technologies) with an average hydroxyl number of 113.8 mg KOH/g (492.7 g/OH eq) was used as biobased polyol. Glycerol (Gly, Fluka) was incorporated as reactive modifier. The selected isocyanate was a 4,4-diphenylmethane diisocyanate prepolymer (pMDI; Desmodur 44V20L, Bayer) with an equivalent weight of 133.2 g/NCO eq. The surfactant agent was a commercial silicone oil (Tergostab B8404, Evonik Industries). Catalysts dibutyl tin dilaurate (DBTDL) and benzyldimethylamine (BDMA) were purchased from Sigma-Aldrich. Distilled water was used as foaming agent.

2.2 Synthesis of Polyurethane Foams

The index (R = moles of NCO groups/moles of OH groups) was adjusted for the system in order to obtain stable, non-collapsing foams according to previous experimental work. The contributions of biobased polyol, glycerol and water were taken into consideration in the index calculation and it was maintained at 1.1. Biobased polyol and glycerol were dehydrated under vacuum before use. The formulations used to prepare the foams are shown in Table 1. The contents of DBTDL and BDMA were fixed at 0.25 and 0.20 wt% (based on the pMDI mass), and 0.50 wt% of surfactant

Table 1 Formulations used to prepare the biobased PU foams. Basis: 100 g of polyols (Agrol 3.6 + Gly).

Gly %	H_2O %	Agrol 3.6 mass (g)	Glycerol mass (g)	H_2O mass (g)	pMDI mass (g)
0	2.0	100.0	0.0	2.00	62.3
20	1.0	80.0	20.0	1.00	135.6
	1.5	80.0	20.0	1.50	143.8
	2.0	80.0	20.0	2.00	151.9
	2.5	80.0	20.0	2.50	160.1
30	1.0	70.0	30.0	1.00	180.4
	1.5	70.0	30.0	1.50	188.6
	2.0	70.0	30.0	2.00	196.7
	2.5	70.0	30.0	2.50	204.9

(based on the Agrol 3.6 + Gly + pMDI mass) was used for all the formulations. The biobased polyol, glycerol, surfactant, catalysts and foaming agent were mixed together for 120 s in a container and then the pMDI was added. The system was further mechanically mixed for 15 s and casted in rectangular cross-section molds. Foams were obtained by the free rise method at room temperature. During the reaction, the cream time (t_{CR}, taken as the time at which bubbles begin to form) and gelation time (t_{GEL}, taken as the time at which the foam reaches its maximum height) were recorded. After that, all foams were postcured for 6 h at 100 °C in a convection oven.

2.3   Characterization of Foams

Densities of foams were calculated by weighing and measuring the volume of compression test samples (25×25 mm^2 square cross section and 15 mm height). The weight was registered with an Ohaus Adventure AR2140 analytical balance with a precision of 0.1 mg and dimensions were measured with a Mitutoyo caliper (Kawasaki, Japan) with a precision of 0.01 mm. Reported results were the average of at least five measurements.

Porosity (e) was calculated according to Equation 1:

$$e = 1 - (\rho^*/\rho_s) \qquad (1)$$

where ρ^* is the foam apparent density and ρ_s is the polymeric matrix density. Solid density was estimated from density of the pure components using a mixture law [30]. The values used in this work were 1140 and 1170 kg/m^3 for the formulations with 20 and 30% Gly respectively.

Scanning electron microscopy (SEM) was used to study the foams' microstructure. Small specimens were cut (both parallel and perpendicular to the growing direction) from a middle height of the foam samples using a thin blade. Samples were sputter-coated with gold prior to SEM observation. A Jeol JSM-6460LV (Tokyo, Japan) scanning electron microscope operated at 10 kV was used. Cell diameters for every formulation were determined from the digitalized images.

Compressive tests were conducted, according to the ASTM D-1621 standard, at room temperature using an Instron MTS universal testing machine (Buckinghamshire, United Kingdom) and at a crosshead speed of 40 mm/min. Specimens of 25×25 mm^2 square cross section and 15 mm height were cut from the foams. The compressive modulus (E) was determined from the initial slope of the compressive stress-strain curve. Compressive strength (σ_C) was taken as the stress reached at the compressive yield or collapse point, since it occurs for all samples before 10% deformation. Densification strain (ε_D) was assessed by two

different methods, and a comparison between them was discussed. The first method directly estimates the ε_D from the apparent density using a lineal correlation derived by Gibson and Ashby from data obtained from flexible PU and polyethylene foams and polymethylacrylamide rigid foams [31, 32]. The second one was proposed by Tan *et al.* [33] for Al foams, and was also successfully applied to thermosetting epoxy foams [34], and defines ε_D as the strain value at which the energy absorption efficiency reaches its maximum.

One-way analysis of variance (ANOVA), together with the Tukey test for pair comparison, were employed to examine differences between groups, with a significance of the difference set at $a < 0.05$.

3   RESULT AND DISCUSSION

3.1   Foaming Behavior

The possibility of obtaining foams by using only Agrol 3.6 (i.e., with 0% glycerol) as hydroxylated precursor was initially evaluated. These formulations produced a stable foaming but did not show dimensional stability, and a significant contraction was produced within 24 h after the foam was synthesized, as a result of the collapse of the cells. With the aim of obtaining foams with dimensional stability and increasing the stiffness of the polymeric matrix, glycerol, a high functionality and low equivalent weight crosslinker, was added to the formulations. Preliminary tests showed that a minimum of 20% of glycerol in the formulations was necessary to obtain dimensionally stable foams. The photographs in Figure 1 show PU foams obtained from pure Agrol 3.6 (0% Gly and 2.0% H$_2$O in Table 1) immediately after the foaming process and after 24 h, and from an Agrol 3.6:Gly (80:20) mixture (also with 2.0% H$_2$O) 24 h after foaming. It can be clearly seen that the foam from pure Agrol 3.6 suffered a large contraction. Hence, the characterization techniques described in Section 2.3 were applied only to PU foams with 20% and 30% Gly, and formulations without glycerol were disregarded.

It should be noted, however, that the addition of glycerol also has a negative aspect, since due to its low equivalent weight, even the addition of small amounts of glycerol also needs the addition of a significantly larger amount of pMDI in order to keep R = 1.1, and hence the percentage of biogenic component decreases considerably. Taking this into consideration, the percentage of glycerol used as a substitute for biobased polyol was limited to 30 wt% (i.e., an Agrol 3.6:Gly weight relation of 70:30). Table 2 shows cream and gelation times recorded during the foaming process for the different formulations analyzed. It was observed that the addition of glycerol accelerated the polymerization
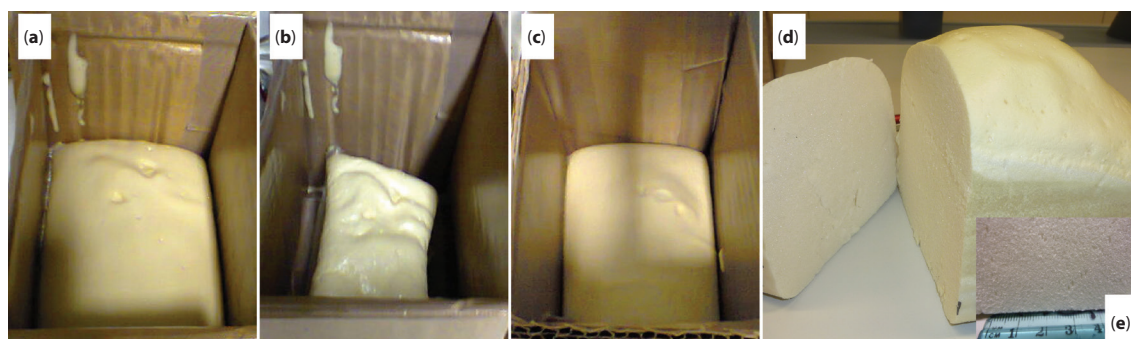
Figure 1 Photographs of the PU foams: (**a**) 0% Gly, immediately after foaming; (**b**) 0% Gly, 24 h after foaming; (**c**) 20% Gly, 24 h after foaming; (**d**) cut of the PU foam with 20% Gly, and (**e**) a close-up of the same PU foam.

Table 2 Cream and gelation time (t_{CR} and t_{GEL}, respectively) of formulations.

% Gly	% H_2O	t_{CR} (s)	t_{GEL} (s)
20	1.0	52	103
	1.5	53	106
	2.0	56	105
	2.5	54	101
30	1.0	52	77
	1.5	50	77
	2.0	52	79
	2.5	53	75

Table 3 Apparent densities and porosities for polyurethane rigid foams.

Gly %	H_2O %	ρ (kg/m³)[a]	e (%)[a]
20	1.0	133.3 ± 10.0 a	88.3 ± 0.9 a
	1.5	87.7 ± 3.3 b	92.3 ± 0.3 b
	2.0	73.7 ± 3.2 c	93.5 ± 0.3 c
	2.5	56.8 ± 2.9 d	95.0 ± 0.2 d
30	1.0	125.5 ± 3.8 a	89.3 ± 0.3 a
	1.5	95.9 ± 8.3 b	91.8 ± 0.7 b
	2.0	66.0 ± 2.0 c,d	94.4 ± 0.2 c,d
	2.5	60.2 ± 2.8 d	94.9 ± 0.2 d

[a]Same letters in each individual column indicate that there is no significant difference between mean values when comparing them by pairs (Tukey test with significance level $a = 0.05$).

reaction (lower t_{GEL}) but t_{CR} was not affected. This was probably a consequence of the higher reactivity of the glycerol primary hydroxyl groups, compared to the secondary ones in Agrol 3.6, more sterically hindered, and led to an important reduction of the gelation times [28, 35]. In contrast, the cream and gelation times were not markedly affected by water content for formulations with the same glycerol content.

3.2 Foam Density

Foam density and porosity can be controlled using different amounts of water as foaming agent (1 to 2.5%). Table 3 presents average density and porosity data for foams prepared with different contents of Gly and water. As expected, an increase of water content in the formulation led to a lower foam density and higher porosity. The results obtained revealed that average density and porosity differed significantly ($p < 0.05$) for formulations with different water content (except for the samples with 30% Gly with 2 and 2.5% water, which did not present significant differences). However, no significant difference ($p < 0.05$)

in average density and porosity was detected with increasing glycerol content for the formulations analyzed herein.

3.3 Morphology

Figure 2 shows a representative SEM image of a cross section perpendicular to the rising direction of the foam (30% glycerol and 1.5% water). The cells reach their final shape when the bubbles touch each other during the growing step, before gelation [36–38]. All foams exhibit polygon-cell structures with pentagonal and hexagonal faces and the round window on the cell wall typically observed in low density foams [36]. The intersection of several cells results in the formation of a cell strut, the main structural member of the foam. Several cell struts are depicted in Figure 2, and some of them are circled to enhance visualization. The image also reveals that the cell walls are very thin (typically only a few microns in thickness), indicating that the majority of polymer resides in the struts.

Figure 3 shows SEM images of the foams obtained with different water contents for 20% of glycerol. This figure also presents statistical data of cell size at cross sections perpendicular and parallel to the rising direction of foams (width and height, respectively). It is
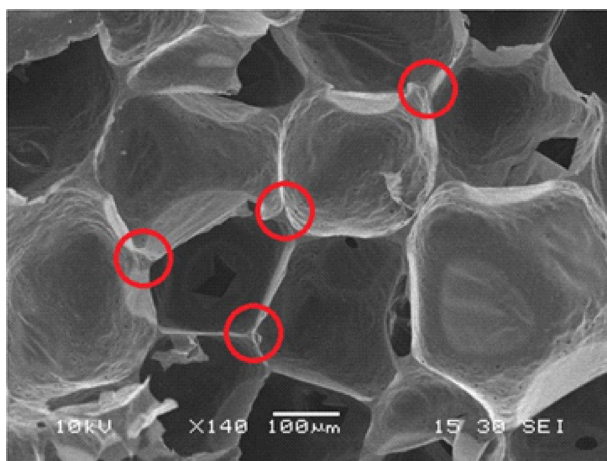

Figure 2 SEM picture of a PU foam with 30% Gly and 1.5% H_2O. Circles show some of the cell struts.

known that foaming of PU systems is due to the CO_2 released through isocyanate decarboxylation after reaction with water. Hence, an increase of the water content leads to a more expanded material, resulting in larger foam cells and producing changes in the foam density and their morphology. Analysis of the SEM images of the vertical planes revealed deformed cells in the growth direction. This effect is usually observed when the foam grows freely in one preferential direction, but it is constrained in the others by the mold [6, 39]. When these restrictions are present, anisotropic stresses are generated in the whole volume and cells tend to grow preferentially in one direction, giving place to anisotropic cells [39]. In the SEM images it can be appreciated that the average cell volume increases with the H_2O%. This trend can also be observed in the statistical analysis shown at the right in Figure 3. Besides the slight increase in the cell size with the amount of water, it is also noteworthy that there is a much stronger increase in the cells anisotropy (relationship between parallel and perpendicular size to growing direction). Several groups have studied the influence of water content in the foaming process and
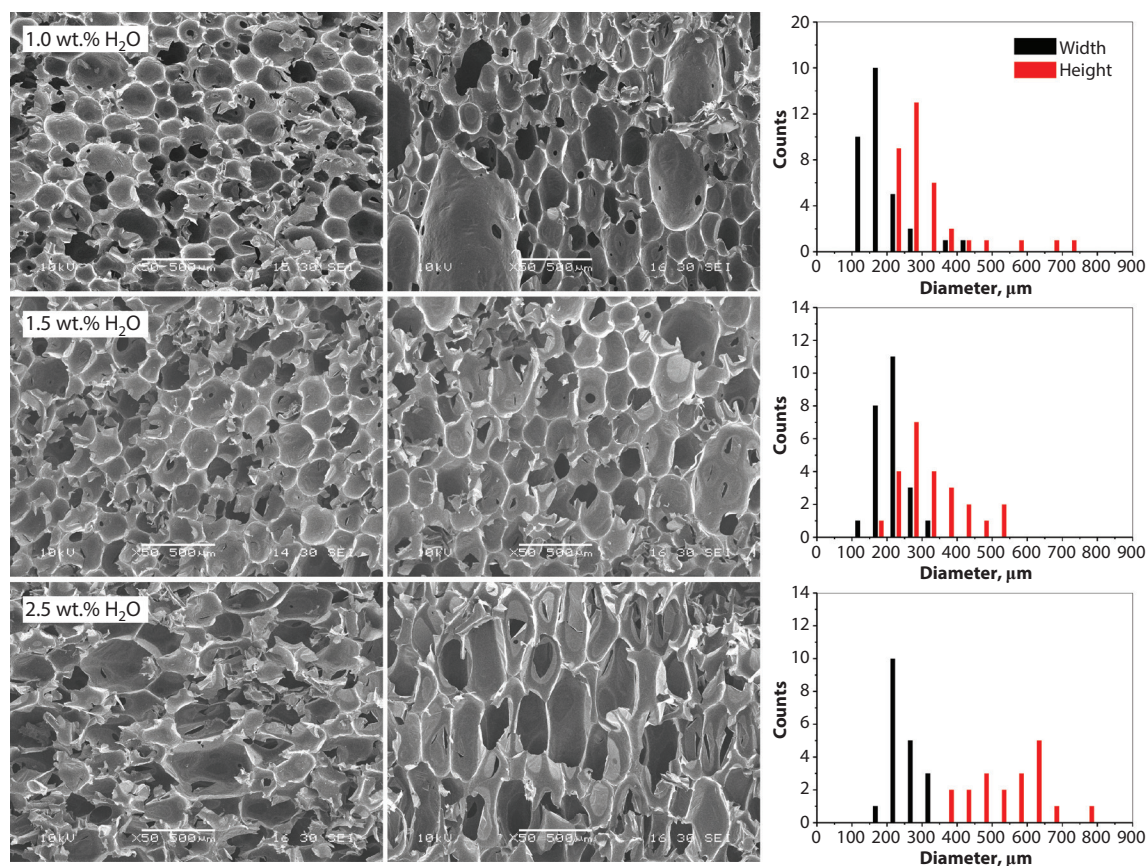

Figure 3 SEM images of horizontal (left) and vertical (center) planes, and cell size distribution (right) of the foams with 20 wt% Gly, and different water contents.
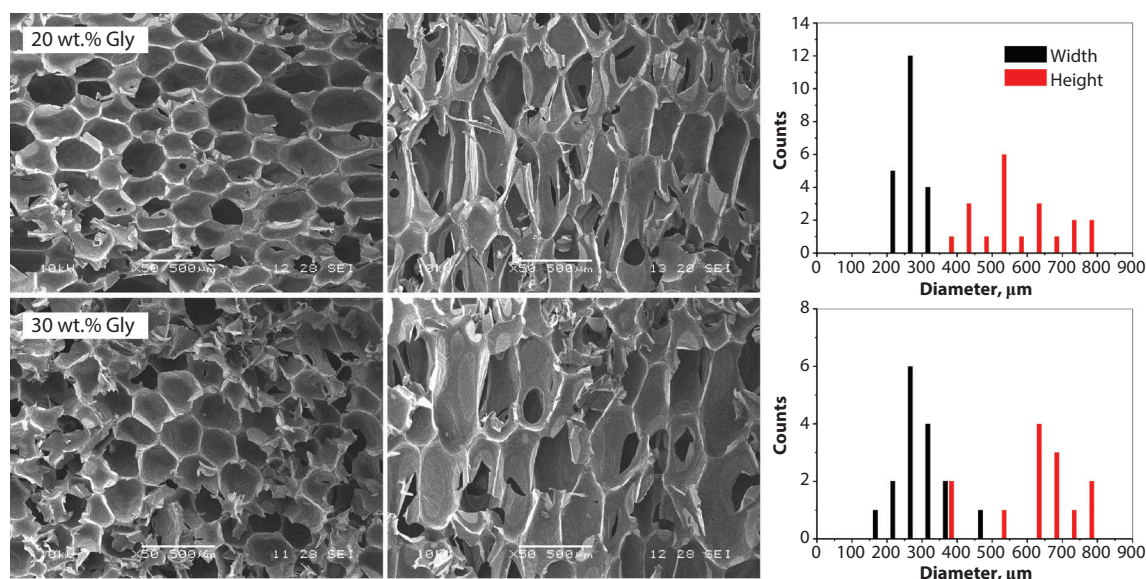
Figure 4 SEM images of horizontal (left) and vertical (center) planes, and cell size distribution (right) of the foams with 2.0 wt% water, and different Gly contents.

foam structure of RPU systems with different compositions, obtaining similar results [11, 17, 24].

The influence of glycerol content on the foaming and gelation kinetics was already commented in a previous section. The replacement of secondary hydroxyl groups from Agrol 3.6 by primary hydroxyl groups from glycerol also has an effect on the foaming process and on the foam structure, which was studied accordingly. Figure 4 shows SEM images of foams synthesized with 2 wt% H_2O and different Agrol 3.6:Gly ratios. The statistical analysis of the cell size parallel and perpendicular to rising direction indicates that as glycerol content increased, a slight increase was measured in both cell size and eccentricity. The slight increase in anisotropy can be associated with a higher expansion rate of the foam along the mold opening (vertical direction) during the foaming process, and a plausible explanation for this could be the higher reaction rate achieved when the glycerol content was increased (this can be deducted from the gelation times; Table 1). Another reason could be associated with the reduced viscosity of the glycerol. In other words, the slight change in morphology is a result of the effect that varying the content of glycerol has on the rheology and reaction kinetics of the system. However, it should be considered that this trend was not followed by all water contents, maybe because the lower t_{GEL} of the formulations with 30% Gly could prevent the foam from achieving a higher expansion level. As a consequence of these two opposed effects, it was found that, statistically, density and porosity show no significant changes with the glycerol content.
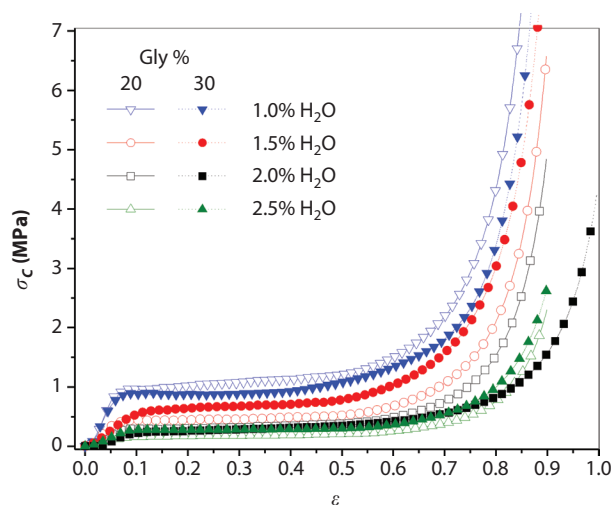

Figure 5 Strain-stress curves for rigid PU foams with different glycerol and water contents.

3.4 Mechanical Properties

Figure 5 illustrates representative stress-strain curves obtained in the foam growth direction, representing the typical behavior of obtained polyurethane foams with different water and glycerol content. For low strain values ($\varepsilon < 0.05$) the foams exhibited linear-elastic deformation. This initial region defines the modulus of the foams. After that, the foam specimens show a relatively abrupt yielding, followed by a sustained plateau region over which there is little increase in stress with increasing strain. The plateau region results from collapse or cell wall buckling, and the

characteristic stress value for this stage is referred to as the collapse stress. In the final region (from $\varepsilon \approx 0.5$–0.6), the densification of the foams, which is characterized by a steep increase of the stress, controls the material behavior.

Compressive performance of rigid foams depends mainly on their density, which is in turn related to the foaming agent content in each formulation. The compressive strength and compressive modulus of foams in the foam growth direction are summarized in Table 4. Compressive modulus and compressive strength decrease with increasing content of blowing agent, which is consistent with the reduction in the apparent density. In this regard, in the same way as the density, the apparent modulus and the yield strength showed no significant differences ($p < 0.05$) with the glycerol content (for the same water content). Both morphology and glycerol content play an important role in the compression behavior. As explained above, the cells' size and also the anisotropy increased with the glycerol content. Hence, lower mechanical properties could be

expected for higher glycerol contents due to a lower concentration of cell struts. Nevertheless, an increase in the glycerol content also leads to an increase in both crosslinking density and aromatic group concentration (since a higher pMDI amount is required in the synthesis reaction) [28], thus obtaining stiffer cell walls for higher glycerol contents. As a result of these two counteracting effects, the analyzed formulations showed no significant change in the compression behavior with glycerol content. Notably, mechanical properties were close to those reported by Stefani *et al.* for commercial polyurethane foams [40].

Figure 6 shows the dependence of the apparent modulus and yield strength with the apparent density. Experimental data was fitted to Equations 2 and 3 [32]:

$$E = A.(\rho*)^n \tag{2}$$

$$\sigma_C = B.(\rho*)^m \tag{3}$$

where E and σ_C are expressed in MPa and $\rho*$ in kg/m³, A and B are constants related to the polymeric matrix

Table 4 Mechanical properties of polyurethane rigid foams in the growth direction.

%Gly	%H$_2$O	E (MPa)[a]	σ_C (kPa)[a]	ε_D (Tan *et al.*, 2005)[a]	ε_D (Gibson and Ashby, 1989)[a]
20	1.0	18.6 ± 2.3 a	880.8 ± 141.9 a	0.54 ± 0.02 a	0.836 ± 0.012 a
20	1.5	8.7 ± 1.3 b	428.4 ± 23.9 b	0.53 ± 0.02 a	0.892 ± 0.004 b
20	2.0	5.3 ± 0.7 c	280.9 ± 21.8 c	0.56 ± 0.02 a	0.907 ± 0.005 c
20	2.5	3.1 ± 0.3 c	179.0 ± 14.9 c	0.53 ± 0.02 a	0.930 ± 0.004 d
30	1.0	17.0 ± 1.9 a	858.0 ± 50.9 a	0.57 ± 0.01 a	0.849 ± 0.005 a
30	1.5	8.4 ± 1.8 b	486.3 ± 103.7 b	0.52 ± 0.03 a	0.885 ± 0.010 b
30	2.0	4.8 ± 0.7 c	249.2 ± 23.5 c	0.57 ± 0.04 a	0.921 ± 0.002 c,d
30	2.5	3.0 ± 0.7 c	181.3 ± 11.6 c	0.56 ± 0.01 a	0.928 ± 0.003 d

[a]Same letters in each individual column indicate that there is no significant difference between mean values when comparing them by pairs (Tukey test with significance level $a = 0.05$).
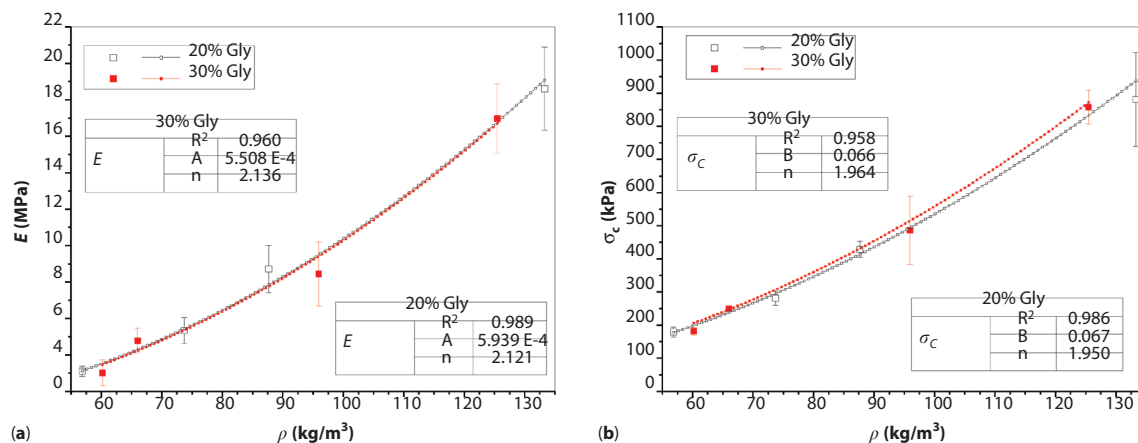

Figure 6 (**a**) Compressive modulus (E) and (**b**) compressive strength (σ_C) dependence with the apparent density ($\rho*$).

properties, and the exponents n and m depend on the foam structure and deformation mechanisms [32, 41]. Exponents n and m, for both 20% and 30% Gly foams, are very close to 2, which indicates that most of the polymeric material resides in the cell struts and edges rather than in the cell faces [32], in agreement with the open-cell structure observed by SEM images.

The value of strain at which densification starts (ε_D) is an important parameter, especially for foams used in shock absorption applications. Gibson and Ashby [31, 32] gave a simple formula to estimate the ε_D for polymeric foams with relative densities between 0.02 and 0.4:

$$\varepsilon_D = 1 - 1.4 \cdot (\rho^*/\rho_s) \tag{4}$$

Tan *et al.* [33] developed a different method for aluminum foams, taking into consideration that ε_D is directly related to the energy absorbed during the deformation process. According to this method, densification starts when the maximum energy absorption efficiency (i.e., the energy absorbed at any given moment during the compressive test, divided by the instantaneous stress applied at that moment) is reached. The values determined by both methods are summarized in Table 4.

Since both methods yield very different results, normalized stress-strain curves were plotted to compare them in a straightforward way. Normalized tension (σ/σ_C)-deformation (ε) curves are depicted in Figure 7. A good overlapping of the curves is obtained, indicating that the densification, characterized by a straight increase in normalized stress, begins at similar strain
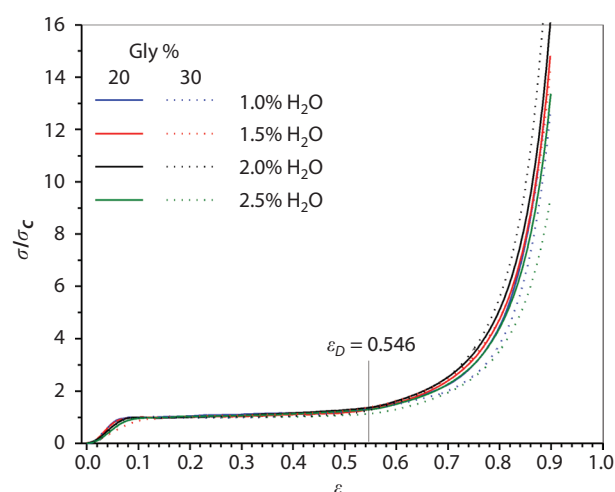
values regardless of the foam's apparent density. Based on this evidence, it can be assured that the best measure of the ε_D value is that proposed by Tan *et al.* [33]. Moreover, a value of 0.53–0.57 for ε_D (as given in Table 4) seems to be in agreement with the shape of the curves displayed in Figure 7.

4 CONCLUSIONS

Polyurethane foams with a high biobased content were successfully synthesized and mechanically characterized. According to the results displayed in this paper, hydroxylated soybean oils in combination with glycerol constitute a suitable replacement for traditional polyols for the preparation of rigid polymeric foams, allowing replacement of a significant amount of fossil fuel-derived raw materials.

The incorporation of glycerol provided the foams with the necessary dimensional stability by increasing the crosslinking density of the polymeric matrix. This was a critical aspect, preventing shrinking after the foam was synthesized. A minimum amount of 20% glycerol was used as a substitute of Agrol 3.6 in order to obtain dimensionally stable foams and with competitive properties to PU foams based on commercial polyols. A further increase in the glycerol content did not generate a significant change in the mechanical properties of the foam. Furthermore, higher glycerol contents bring along the disadvantage of abruptly raising the isocyanate content in the formulation, hence decreasing the biobased content in the formulation (i.e., when glycerol content is increased from 20% to 30%, the total biobased content drops from 38–42%, depending on the water content, to about 32–35% in mass).

Figure 7 Normalized strain-stress curves for rigid PU foams with different glycerol and water contents. The samples shown here are the same as those shown in Figure 5. The vertical line indicates the value obtained by the method developed by Tan *et al.* [33].

REFERENCES

1. A. Noreen, K. M. Zia, M. Zuber, S. Tabasum, and A. F. Zahoor, Bio-based polyurethane: An efficient and environment friendly coating systems: A review. *Prog. Org. Coat.* **91**, 25–32 (2016).

2. J.-P. Pascault, H. Sautereau, J. Verdu, and R. J. J. Williams, *Thermosetting Polymers*, 1st ed., Marcel Dekker, New York, NY (2002).

3. A. Corma, S. Iborra, and A. Velty, Chemical routes for the transformation of biomass into chemicals. *Chem. Rev.* **107**, 2411–2502 (2007).

4. L. Shen, E. Worrell, and M. Patel, Present and future development in plastics from biomass. *Biofuel. Bioprod. Bior.* **4**, 25–40 (2010).

5. C. Panoutsou and K. Maniatis, Biomass futures: Estimating the role of sustainable biomass for meeting the 2020 targets and beyond. *Biofuel. Bioprod. Bior.* **7**, 97–98 (2013).

6. D. Eaves, *Handbook of Polymer Foams*, Rapra Technology, Shawbury (2004).

7. X. Luo, A. Mohanty, and M. Misra, Lignin as a reactive reinforcing filler for water-blown rigid biofoam composites from soy oil-based polyurethane. *Ind. Crops Prod.* **47**, 13–19 (2013).

8. M. E. Porras Cárdenas, C. P. Muñoz Vásquez, A. M. Gil Pilonieta, and G. C. Quintana Marín, Obtención de espumas de poliuretano con materiales lignocelulósicos. *Rev. Investig. Apl.* **6**, 93–102 (2012).

9. S. Li, C. Li, C. Li, M. Yan, Y. Wu, J. Cao, and S. He, Fabrication of nano-crystalline cellulose with phosphoric acid and its full application in a modified polyurethane foam. *Polym. Degrad. Stab.* **98**, 1940–1944 (2013).

10. A. K. Bledzki, W. Zhang, and A. Chate, Natural-fibre-reinforced polyurethane microfoams. *Compos. Sci. Technol.* **61**, 2405–2411 (2001).

11. R. Gu, M. Khazabi, and M. Sain, Fiber reinforced soy-based polyurethane spray foam insulation. Part 2: Thermal and mechanical properties. *BioResources* **6**, 3775–3790 (2011).

12. G. Padrón-Gamboa, E. M. Arias-Marín, J. Romero-García, A. Benavides-Mendoza, J. Zamora-Rodríguez, and S. P. García Rodríguez, Efecto de la cáscara de cacao en la obtención de espumas de poliuretano para uso hortícola. Propiedades físicas y de biodegradabilidad. *J. Mex. Chem. Soc.* **48**, 156–164 (2004).

13. V. Ribeiro da Silva, M. A. Mosiewicki, M. I. Yoshida, M. Coelho da Silva, P. M. Stefani, and N. E. Marcovich, Polyurethane foams based on modified tung oil and reinforced with rice husk ash I: Synthesis and physical chemical characterization. *Polym. Test.* **32**, 438–445 (2013).

14. S. Arango Osorio, J. García Henao, Y. Velez Salazar, L. Rendón Castrillón, and M. Ramírez Carmona, Síntesis de Poliuretano Rígido Empleando Cáscara de Cacao como Fuente de Polioles. *Ingeniar UPB* **1**, 1052–1064 (2013).

15. J. Vega-Baudrit, K. Delgado-Montero, M. Sibaja-Ballestero, and P. Alvarado-Aguilar, Uso alternativo de la melaza de la caña de azúcar residual para la sintesis de espuma rígidas de poliuretano (ERP) de uso industrial. *Tecnol. Cienc. Educ.* **22**, 101–107 (2007).

16. J. Vega-Baudrit, K. Delgado-Montero, M. Sibaja-Ballestero, and P. Alvarado-Aguilar, Materiales poliméricos compuestos obtenidos a partir de los residuos generados por la agroindustria de la caña de azúcar. Una alternativa adicional. II. *Rev. Iberoam. Polímeros Univ. País Vasco* **9**, 389–406 (2008).

17. A. M. Gil Pilonieta, F. Jaramillo I., and L. J. Cruz Riaño, Poliuretanos degradables a partir de aceite de higuerilla. *Sci. Tech.* **XIII**, 1–6 (2007).

18. P. C. Mazo, O. Yarce, and L. A. Rios, Síntesis de espumas rígidas de poliuretano obtenidas a partir de aceite de castor y poliglicerol empleando calentamiento por microondas. *Polímeros* **21**, 59–66 (2011).

19. P. C. Mazo, A. Franco, L. A. Ríos, and G. Restrepo, Obtención de espumas flexibles de poliuretano apartir de aceites de palma y castor modificados. *Sci. Tech.* **XIII**, 607–612 (2007).

20. Y.-C. Tu, P. Kiatsimkul, G. Suppes, and F.-H. Hsieh, Physical properties of water-blown rigid polyurethane foams from vegetable oil-based polyols. *J. Appl. Polym. Sci.* **105**, 453–459 (2007).

21. M. A. Mosiewicki, U. Casado, N. E. Marcovich, and M. I. Aranguren, Polyurethanes from tung oil: Polymer characterization and composites. *Polym. Eng. Sci.* **49**, 685–692 (2009).

22. Y.-C. Tu, H. Fan, G. J. Suppes, and F.-H. Hsieh, Physical properties of water-blown rigid polyurethane foams containing epoxidized soybean oil in different isocyanate indices. *J. Appl. Polym. Sci.* **114**, 2577–2583 (2009).

23. H. Fan, A. Tekeei, G. J. Suppes, and F.-H. Hsieh, Rigid polyurethane foams made from high viscosity soy-polyols. *J. Appl. Polym. Sci.* **127**, 1623–1629 (2013).

24. A. Campanella, L. M. Bonnaillie, and R. P. Wool, Polyurethane foams from soyoil-based polyols. *J. Appl. Polym. Sci.* **112**, 2567–2578 (2009).

25. Z. S. Petrovic, T. W. Abraham, and R. Degenova, Polioles con alto contenido de renovables para el mercado de espumas rígidas de poliuretano. *Rev. Plásticos Mod. Cienc. Tecnol. Polímeros* **636**, 440–446 (2009).

26. R. Gu, M. Khazabi, and M. Sain, Fiber reinforced soy-based polyurethane spray foam insulation. Part 2: Thermal and mechanical properties. *BioResources* **6**, 3775–3790 (2011).

27. X. Li, H. Cao, and Y. Zhang, Structures and physical properties of rigid polyurethane foams with water as the sole blowing agent. *Sci. China Ser. B Chem.* **49**, 363–370 (2006).

28. T. Calvo-Correas, M. A. Mosiewicki, M. A. Corcuera, A. Eceiza, and M. I. Aranguren, Linseed oil-based polyurethane rigid foams: Synthesis and characterization. *J. Renew. Mater.* **3**, 3–13 (2015).

29. C. A. G. Quispe, C. J. R. Coronado, and J. A. Carvalho Jr., Glycerol: Production, consumption, prices, characterization and new trends in combustion. *Renew. Sustain. Energy Rev.* **27**, 475–493 (2013).

30. R.H. Perry, D.W. Green, and J.O. Maloney (Eds.), *Perry's Chemical Engineers' Handbook*, 7th ed., McGraw-Hill, New York, NY (1997).

31. S. K. Maiti, L. J. Gibson, and M. F. Ashby, Deformation and energy absorption diagrams for cellular solids. *Acta Metall.* **32**, 1963–1975 (1984).

32. L. J. Gibson and M. F. Ashby, *Cellular Solids: Structure and Properties,* Cambridge University Press, Cambridge, NY (1999).

33. P. J. Tan, S. R. Reid, J. J. Harrigan, Z. Zou, and S. Li, Dynamic compressive strength properties of aluminium foams. Part I—Experimental data and observations. *J. Mech. Phys. Solids* **53**, 2174–2205 (2005).

34. F. I. Altuna, R. A. Ruseckaite, and P. M. Stefani, Biobased thermosetting epoxy foams: Mechanical and thermal characterization. *ACS Sustain. Chem. Eng.* **3**, 1406–1411 (2015).

35. K. Ashida, *Polyurethane and Related Foams Chemistry and Technology,* CRC/Taylor & Francis, Boca Raton, FL (2007).

36. J. R. Dawson and J. B. Shortall, The microstructure of rigid polyurethane foams. *J. Mater. Sci.* **17**, 220–224 (1982).

37. J. H. Marciano, M. M. Reboredo, A. J. Rojas, and R. J. J. Williams, Integral-skin polyurethane foams. *Polym. Eng. Sci.* **26**, 717–724 (1986).

38. D. Niyogi, R. Kumar, and K. S. Gandhi, Water blown free rise polyurethane foams. *Polym. Eng. Sci.* **39**, 199–209 (1999).

39. D. Klempner, V. Sendijarevic, and R. M. Aseeva, *Handbook of Polymeric Foams and Foam Technology,* Hanser Publishers; Hanser Gardener Publications, Munich, Cincinnati (2004).

40. P. M. Stefani, R. Speroni, O. Faure, J. M. Kenny, and A. Vazquez, Rigid polyurethane foams modified with wood sawdust, in: *Polymer Analysis, Degradation, and Stabilization,* G. E. Zaikov and A. Jiménez (Eds.), pp. 141–151, Nova Science Publishers, New York, NY (2005).

41. S. H. Goods, C. L. Neuschwanger, L. L. Whinnery, and W. D. Nix, Mechanical properties of a particle-strengthened polyurethane foam. *J. Appl. Polym. Sci.* **74**, 2724–2736 (1999).