Linseed Oil-Based Polyurethane Rigid Foams: Synthesis and Characterization

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ABSTRACT: Rigid polyurethane foams were synthesized by using a vegetable oil-based polyol and 4,4-diphenylmethane diisocyanate prepolymer as the majority of reactives,. The polyol was produced by hydroxylation of crude linseed oil with performic acid generated *in situ* by the reaction of hydrogen peroxide and formic acid. The characterization by FTIR, H[1]NMR, iodine and hydroxyl values of the polyol and its comparison with the original linseed oil supports the success of the reaction. The reference foam was subsequently modified by substituting part of the linseed oil polyol with glycerol, diethylene glycol, and a polyethylene glycol (all of them of lower molecular weight than the natural polyol). As was expected, glycerol acts as a crosslinker, increasing density and compression properties of the foams. The analysis of the compression results highlighted the importance of the concentration of the polymeric isocyanate (pMDI) in the initial formulation. The pMDI concentration also played a role in the char formation of the foams according to thermogravimetric analysis. The higher crosslinking density of the glycerol-modified foam resulted in better thermal stability among the different foams.

KEYWORDS: Bio-based polyol, linseed oil, rigid foams, mechanical characterization

1 INTRODUCTION

Rigid polyurethane foams are highly appreciated materials because they can be appropriate for diverse applications like thermal insulation, building materials, chemical pipelines, space filling, along with others [1,2]. Among the most interesting characteristics, they present high versatility in the obtained final properties, which can be easily adjusted, such as low density, good mechanical strength, low thermal conductivity and low humidity permeability [2,3].

As is well known, the main components of a polyurethane formulation are polyols and isocyanates that, as most of the raw materials for the plastics industry, come from petroleum feedstock [1,2].

In an effort to replace synthetic polymeric precursors by others that are more environmentally friendly, several scientific studies have been carried out. The

modification of vegetable oils in order to create polyols is an interesting alternative for including low-cost renewable natural resources in the preparation of polyurethanes [4–11].

Vegetable oils are triglycerides, in which different proportions and types of fatty acids are linked to a glycerol molecule through ester groups. Specifically, linseed oil is obtained from the ripened seeds of the flax plant. It is composed mainly of linolenic acid with three unsaturations per fatty acid, and because of that, it is known as a drying oil, meaning it can evolve to a tough, solid film after a period of exposure to air. This is the reason for its being widely required in the paint and varnish industry [12].

The introduction of hydroxyl groups (hydroxylation) of carbon-carbon double bonds in the vegetable oils can be chemically possible by reaction of triglycerides with peroxy acids [4,5,11]. Although the reaction proceeds through an epoxidation step, the oxirane ring is unstable in acid media and its opening takes place to finally obtain hydroxyl groups [11].

Bio-polyols derived from different vegetable oils have been used in the production of polyurethane foams such as rapeseed oil-based polyurethane foams

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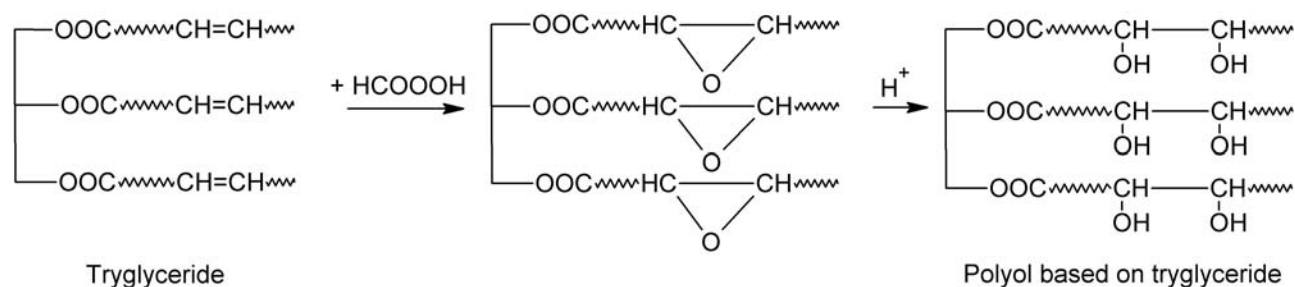
Scheme 1 General scheme of hydroxylation of unsaturated oil.

[6,11,13], and much more frequently, soy bean oil-based foams [14,15,16]

Although the bio-polyols from vegetable oils can be successfully used in the polyurethane formulations, the addition of other polyols like glycerol and glycols can be used to modify the polymer structure (e.g., crosslinking density), directly affecting some of the properties in the final foam.

In particular, the incorporation of glycerol as cross-link agent is also associated with technologies based on sustainable resources, since it is an important byproduct of biodiesel production. Glycerol can be used directly as a polyol or as an excipient in the production of other polyols based on different plant oils [17].

In addition, the manufacture of polyurethane foams also requires the use of a number of additives like catalyst, blowing agent and surfactant. Although the amounts used are considerably lower than the hydroxyl and isocyanate components, they are not always environmentally innocuous. In this way, the use of water as reactive blowing agent eliminates the need to add volatile organic compounds and also offers the additional advantage of accelerating the reaction, decreasing the amount of catalyst [6].

The aim of this work is the preparation of rigid polyurethane foams based on the use of a hydroxylated linseed oil. The reference foam was modified by the addition of different reactive modifiers: bifunctional ones such as diethylene glycol and polyethylene glycol, and trifunctional glycerol that acts as a crosslinker. The physical, chemical and mechanical characterizations of the foams were also analyzed.

2 EXPERIMENTAL

2.1 Materials

Linseed oil (LO) supplied by Grainer S.A. (Entre Rios, Argentine) (iodine value = 132.19 g I/100 g oil) was used to obtain a natural polyol by means of a hydroxylation reaction carried out with hydrogen peroxide (30 wt%) and formic acid (85 wt%) from Ciccarelli and Biopack, Argentina, respectively.

For the preparation of the polyurethane foams, 4,4-diphenylmethane diisocyanate prepolymer, p-MDI (Rubinate 5005, Huntsman Polyurethanes, USA, 131 g/eq as measured in our laboratory, with average functionality of 2.7 and viscosity 170–250 cp from the supplier data sheet) was selected as the isocyanate component. Diethylene glycol, DEG (53.1 g/eq and viscosity 38 cp) polyethylene glycol, PEG200 (200 g/mol, functionality = 2, and viscosity 50 cp), and glycerol, GLY, (30.7 g/eq and viscosity 1.26 cp), all of them from Fluka, were incorporated as reactive modifiers. Besides, different additives were incorporated to the formulations: surfactant agent (Tergostab B8404 Hunstman Polyurethanes), catalysts (tertiary amine, N,N-dimethyl benzylamine, DMBA (Aldrich) and dibutyltin dilaureate, DBTDL (Aldrich) and water as blowing agent.

2.2 Hydroxylation of Linseed Oil

Linseed oil-based polyol (LOP) was obtained by hydroxylation reaction as illustrated in Scheme 1. The hydrogen peroxide and formic acid were added in a reactor with mechanical stirrer at 40°C for 5 min in order to obtain performic acid, then LO was added dropwise. After LO had been added, the reactor temperature was raised to 50°C and the reaction was continued for 3.5 h. The used $C=C/H_2O_2$ and $H_2O_2/HCOOH$ molar ratios were 1/1 and 1/1.4, respectively. The product was allowed to lie overnight at room temperature and became separated in two layers. Distillate water was added to the product and mixed slowly. Once two layers reappeared, the bottom layer was removed. This process was repeated three times in order to eliminate, as much as possible, the acids from the upper layer. Finally, the upper layer was recovered and distilled under vacuum (70–80°C at 100 mbar) to eliminate the remaining water and acids, to obtain the hydroxylated LO.

The resulting LOP is a polyol with functionality higher than two (as is discussed in further sections),

Table 1 Designation, formulation and apparent densities for polyurethane rigid foams.

Designation [a]	GLY (wt%)	DEG (wt%)	PEG (wt%)	pMDI (wt%)	ρ (kg/m³)
PU	-	-	-	44.82	41.01 ± 0.70
PU-5GLY	5	-	-	49.46	45.54 ± 0.97
PU-10GLY	10	-	-	53.26	45.38 ± 1.34
PU-15GLY	15	-	-	56.08	51.56 ± 1.08
PU-20GLY	20	-	-	58.50	55.47 ± 0.76
PU-5DEG	-	5	-	47.11	43.75± 0.63
PU-10DEG	-	10	-	49.14	39.05 ± 0.62
PU-15DEG	-	15	-	50.87	40.18 ± 0.22
PU-20DEG	-	20	-	52.35	40.76 ± 0.92
PU-20PEG	-	-	20	47.66	43.86 ± 0.82

[a] The polyurethane foams were designed as PU – (weight percentage of reactive modifier with respect to the polyol weight)

and thus it also contributes to the crosslinking and formation of the final network.

2.3 Preparation of Polyurethane Rigid Foams

The index (moles of NCO groups/moles of OH groups) was adjusted at 1.1 for all the systems. The contributions of bio-polyol, reactive modifiers and water were taken into consideration in the index calculation. LOP and glycerol were dehydrated at 80°C under vacuum before their use.

The foams were obtained by the free-rise method at room temperature and the formulations and designation of the polyurethane rigid foams are summarized in Table 1. The bio-polyol, modifiers, blowing agent (2 wt%), surfactant agent (1.5 wt%) and catalysts (3 wt% of each one) were mechanically mixed together for 20 s in a container and then the pMDI was added. The system was further mixed for 20 s and then the foam was allowed to freely rise. During the reaction, the cream, end of rise and tack-free times were recorded. All the mentioned percentages are calculated with respect to the weight of the bio-polyol.

3 CHARACTERIZATION OF LO, LOP AND POLYURETHANE RIGID FOAMS

3.1 Iodine Value

The iodine value of LO and LOP was determined according to ASTM D 5554.

3.2 Hydroxyl Value

The hydroxyl value of LO and LOP was determined by an acetylation method with acetic anhydride in pyridine solution according to ASTM D4274.

3.3 Proton Nuclear Magnetic Resonance Spectroscopy (H¹NMR)

H¹NMR spectra of LO and LOP were recorded on a Bruker AM500 spectrometer (500 MHz) using deuterated acetone and deuterated dimethylsulfoxide as solvents, respectively.

3.4 Fourier Transform Infrared Spectroscopy (FTIR)

Measurements were performed with a Thermo Scientific Nicolet 6700 FT-IR spectrometer used in ATR (attenuated total reflectance) mode. The spectra of the samples were obtained after 32 scans in a range from 4000 to 500 cm⁻¹ with a resolution of 2 cm⁻¹.

3.5 Density Measurements

The density of the foam was obtained as the ratio between the weight and volume of a cylindrical specimen (28 mm diameter x 30 mm height). The density values were averaged for five specimens.

3.6 Scanning Electron Microscopy (SEM)

Small specimens were cut from the foam samples and a scanning electron microscope Philips model SEM 505 was used to obtain photographs of the surfaces.

Specimens were coated with gold previously to the microscopy observation.

3.7 Dynamic Mechanical Tests

Measurements were performed using an Anton Paar, Physica MCR 301 rheometer. Torsion geometry was used with solid rectangular samples with dimensions of 30 x 10 x 3 mm^3. Measurements were carried out as temperature sweeps in the range from −20°C to 230°C at a heating rate of 10°C/min. The frequency was kept in 1 Hz and the applied deformation was 0.5%. The thermal transition temperatures were arbitrarily selected as the temperature of the maximum in the loss modulus curve.

3.8 Compression Tests

Cylindrical specimens of 28 mm diameter x 30 mm height were cut from the upper side of foams, and tested at room temperature in an INSTRON 8501 Universal testing machine. The compression force was applied in the foam rise direction. Samples were compressed at a fixed length of 22 mm at a crosshead speed of 10 mm/min. The average values of compression modulus (calculated as the slope of the stress-strain curve at low deformations), compressive strength (in accordance with ASTM D1621; taken as the stress reached the compressive yield point that occurred below 10% deformation for all samples) and densification strain (taken as the strain at the intersection point between the stress plateau and a line extrapolated from the densification line) were calculated from these tests. Compression values were averaged for five specimens.

After compression, the samples were unloaded and allowed to recover for 1 min and 24 h. The length reached after the recovery time (l_r) was compared to the initial specimen height (l_i) and used to calculate the recovery ratio (R_r), as indicated in Equation 1.

$$R_r = (l_r / l_i) \times 100 \qquad (1)$$

3.9 Thermogravimetric Analysis (TGA)

The thermal properties of foams were analysed in a Mettler Toledo TGA/SDTA851 thermogravimetric analyzer. The samples were scanned from room temperature to 600°C at a heating rate of 10°C/min under nitrogen atmosphere.

4 RESULTS AND DISCUSSION

4.1 Characterization of the Oil and Derived Polyol

The iodine values of LO and LOP were determined, being 132.2 and 56.5 g I/100 g, respectively. As can be observed, the iodine value was lower for the LOP, since C=C bonds in the vegetal oil were replaced by hydroxyl groups in LOP. However, not all C=C bonds were reacted in the hydroxylation reaction, since the final iodine value is not null. The OH value of the LOP is 216.4 mg KOH/g; this value is high enough for the preparation of rigid and semirigid foams.

Figure 1a shows the H^{1}NMR spectra of LO and LOP. The peaks have been assigned according to the following [18–20]:

- 0.9 ppm, methyl protons at the end of the fatty acid chains;
- 1.3–1.4 and 1.6 ppm, olefinic protons separated by at least one carbon from the ester groups and at least one carbon from the unsaturations;
- 2.3 ppm, protons in the methylene groups close to the carbon-carbon insaturations;
- 2.3–2.4 ppm (multiplets), methylene neighbor to the carboxylic groups in the triglycerides;
- 2.8–2.9 ppm, CH$_2$ protons between two C=C;
- 4.2–4.3 ppm, protons in the methylene groups of the glycerol fragment;
- 5.2–5.5 ppm, vinylic protons.

The comparison of both spectra shows clear differences between LO and LOP structures. The LOP spectrum suggests the presence of a very low amount of carbon-carbon double bonds as the resonance peaks are much reduced after the hydroxylation reaction (5.35 ppm). Additionally, there is a new peak centered at 1.5 ppm which is due to H's that are neighboring -COH groups in the LOP [19] and that originally belonged to the methylene group neighbors to double bonds (2.3 and 2.8–2.9 ppm). Furthermore, changes can be observed in the region of 3.5–4.0 ppm that are also reported as chemical shifts for protons in carbons linked to hydroxyl groups [21,22].

These last two observations are relevant to indicate the disappearance of the double bonds and the appearance of OH-containing groups.

Figure 1b shows the FTIR spectra of LO and LOP. The spectrum of the LO shows a broad but shallow band at 2500-3500 cm^{-1} related to the stretching vibration of the hydroxyl group (O-H) of the carboxylic acids, which was probably formed by the hydrolysis of the triglyceride during storage [18]. In addition, the stretching vibration of the carbonyl group of the carboxylic acids, at 1710 cm^{-1}, is also observed. Moreover, in the carbonyl stretching region, at 1741 cm^{-1}, the band related to the carbonyl of the ester groups from the triglycerides can be observed. The band at 3010 and the small peak at 1650 cm^{-1} can be attributed to the stretching vibration of =C-H and C=C groups, respectively, and are related to the
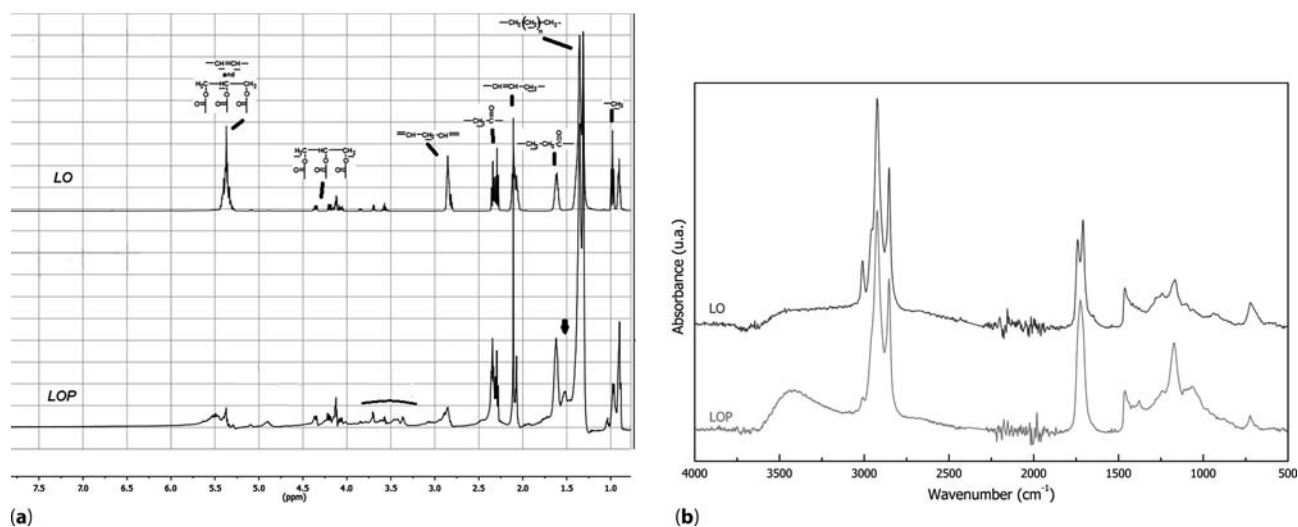
Figure 1 (a) H1 NMR and (b) FTIR spectra of LO and LOP.

triglyceride unsaturations. The main differences observed in the LOP spectrum after hydroxylation are the broad and more intense band of hydroxyl group at 3500 cm^{-1} and the decrease of the stretching bands at 3010 and 1650 cm^{-1} due to the attachment of hydroxyl groups to C=C bonds by means of nucleophilic addition reaction. These results agree with the reduction of the iodine value and, correspondingly, increased hydroxyl value. In the carbonyl stretching region, only the band attributed to the carbonyl ester group was observed.

4.2 Characterization of the Foams

4.2.1 *Density*

Density measurement results are shown in Table 1. Higher density values were observed when a part of linseed oil-derived polyol was replaced by trifunctional GLY. The density increases as GLY content increases due to the decrease of chain length between crosslinking points. For systems containing DEG, the density also increases with DEG content. However, if compared with the GLY analogous foams, the DEG series have lower density, which is probably related to the DEG being bifunctional while GLY is a triol. This is also true for the PU-20PEG that shows lower density than the GLY-modified foam.

4.2.2 *Morphology*

Figure 2 shows scanning electron microscopy images of the foams analyzed on a plane parallel to the foam rise direction. Microscopic examination reveals the formation of non-uniform cell structures with large

and small polygonal-shaped cells. The irregular distribution of cell sizes observed in reference foam can be related to different structural factors. It must be taken into account that linseed oil is a heterogeneous triglyceride containing different fatty acid chains. Moreover, after the hydroxylation of linseed oil double bonds, OH groups could be in different positions along the chain [23]. Comparing the cell size distribution of reference foam and PU-20PEG, more uniform cell sizes can be distinguished in PU-20PEG foam, probably because the addition of an oligomer with a molecular weight similar to the equivalent weight of LOP contributes to reduce the overall chain size polydispersity in the polyol mixture. Foams with different concentrations of GLY and DEG show that cell structure becomes more uniform as the modifiers' content increases. The PU-DEG series showed larger cell sizes than the PU-GLY series, because in the latter case the trifunctional glycerol allows higher crosslinking density to be reached and lower expansion of the cell's volume. The result of the increased crosslinking density and reduced overall cell size, agrees with the higher density values measured for this foam series. As can be observed in the micrographs, cell sizes decrease as GLY content increases, in agreement with the observed density increase. This observed effect is in agreement with the results of other authors whose work with soy bean-based polyols of different hydroxyl values found that cell size was smaller in the foams prepared with the polyol of higher OH value [17]. Moreover, as GLY content increases, higher anisotropy can be observed in the foam, since the rigidity of the formed network restricts the expansion of the cells during foaming.
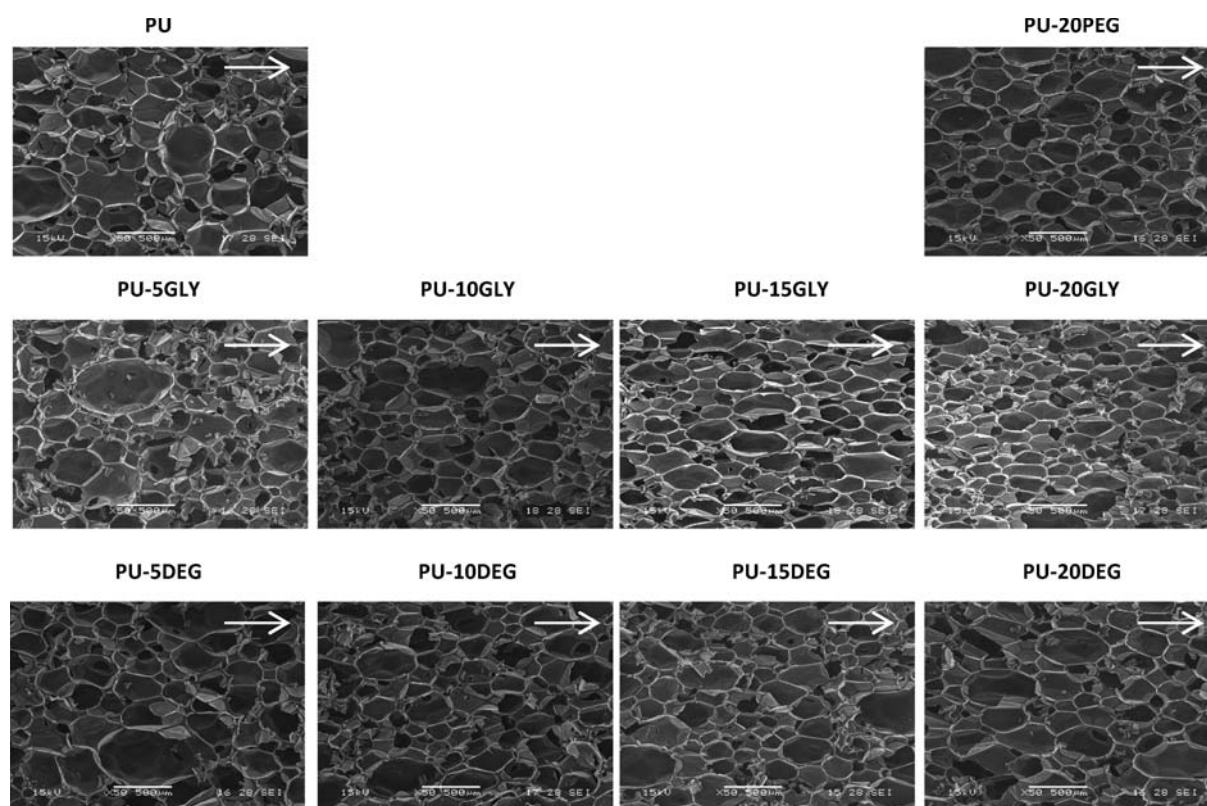
Figure 2 SEM micrographs of synthesized foams. Arrows denote the rise direction of the foams.

4.2.3 Cream, End of Rise and Tack-Free Times

Foams were prepared adding different contents of three different modifiers to the high-functional polyol derived from linseed oil. The reference foam was the one prepared with linseed oil-derived polyol as the only source of hydroxyls. Table 2 shows the cream, end of rise and tack-free times recorded during the synthesis of foams with 20 wt% of DEG, GLY and PEG and the reference foam.

Clearer differences can be established between the end of rise and tack-free times of the unmodified PU foam and those of the modified ones. The last ones show shorter characteristic times, which correlate with a higher reactivity of the OH of the smaller molecules and with the higher viscosity of the bio-polyol that conspire against a rapid expansion of the foam. It is reasonable that the reactivity of the OH groups of the bio-polyol should be lower because of the internal location of the OH (in the middle of the LOP chain) than those present in the lower molecular weight glycerol or the primary OH in the short diols.

Additionally, the addition of 20 wt% of DEG leads to the foam with the lowest characteristic times of the study, which could be related to the combined effects

Table 2 Foaming characteristic times of foams.

	Cream time (s)	End of rise time (s)	Tack free time (s)
PU	40	160	215
PU-20GLY	42	88	92
PU-20DEG	31	84	90
PU-20PEG	45	117	122

of increased concentration of primary hydroxyl groups in the mixture and viscosity reduction contributed by the low molecular weight DEG.

4.2.4 FTIR Spectroscopy

The spectra for the synthesized foams containing 0 and 20 wt% of GLY, DEG and PEG together with the spectra of polymeric diisocyanate are shown in Figure 3. The spectra of polyurethane foams were similar and the stretching vibrations of the isocyanate group (N=C=O) of pMDI at 2270 cm^{-1} were not observed, which confirmed that the reaction proceeded successfully. Moreover, a broad band at 3200-3400 cm^{-1}, characteristic of the stretching vibration of the urea and
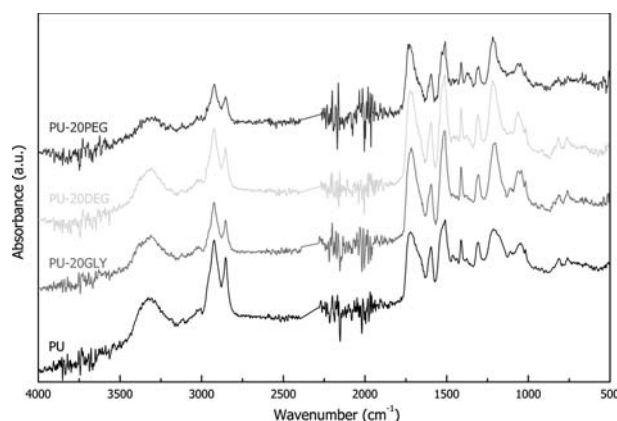
Figure 3 FTIR spectra of PU, PU-20GLY, PU-20DEG and PU-20PEG foams.

urethane N-H bonds, can be observed in the spectra of all the polyurethane foams.

On the other hand, in the carbonyl stretching region (1630-1730 cm^{-1}), in addition to the carbonyl stretching at 1740 cm^{-1}, corresponding to the LOP ester group, a shoulder at lower wavenumber related to the carbonyl stretching of urethane and urea groups (amide-I band) can be observed. At 1535 cm^{-1} the amide-II band related to stretching vibration of C-N combined with bending vibration of N-H can be also observed.

4.2.5 Dynamic Mechanical Analysis

Figure 4a and b shows the dynamic mechanical behavior of the foams prepared with different concentrations of glycerol. The first thing to notice is that the glass transition temperature of these materials is above room temperature, T_{room}, so that they are rigid foams at that temperature.

The storage modulus at T_{room} of the samples shows a trend of modulus increasing with the concentration of glycerol in the formulation. This feature is a result of different contributing effects: (a) increasing glycerol increases the crosslinking density of the foam because glycerol is a trifunctional small molecule; (b) because of the low equivalent weight of the glycerol, the higher the glycerol concentration, the higher the pMDI percentage in the formulation (in order to maintain constant the NCO:OH molar ratio). The higher crosslinking density improves the cohesive density of the material and the incorporation of increasing amounts of the aromatic and polyfunctional isocyanate also contributes to an increase in the rigidity of the polymer. These effects are also observed in the rubbery region of these materials, although in some cases the

expected rubbery plateau would be fully developed at temperatures above those used in the tests.

The glass-rubber transition is wide for all the foams, and shifts towards higher temperatures as the concentration of glycerol is increased in the initial formulation, in perfect agreement with the effects already discussed for the storage modulus.

The loss modulus shows that the transition of glass to rubber is wide and it is the sum of two overlapping events. There is a low temperature transition occurring around 50°C that does not suffer shift, although the composition of the material changes. It is proposed that this transition corresponds to the relaxation of the dangling chains that are formed when the hydroxylated oil reacts. On the other hand, the higher temperature relaxation, which is related to the glass transition temperature of the polyurethane network, varies with the glycerol concentration (shown with dashed lines in the figure). As already discussed, there is a good agreement with the increased crosslinking density of the material.

Similar effects can be detected in the loss modulus curves of the DEG-containing samples (Figure 4c). On the other hand, variations on the storage modulus are much more moderate than observed in the glycerol-containing samples (not shown).

Comparison of the loss modulus of materials prepared with 20 wt% of the three different modifiers and the unmodified linseed oil is presented in Figure 4d. As anticipated, glycerol-containing samples show a broader and higher temperature transition than the other formulations. Instead, the incorporation of the diols led to narrower transitions than those measured for glycerol-containing samples, or even the linseed oil foams. PEG-containing foams showed the lowest Tg, because the diol does not contribute to crosslinking and the longer chains of PEG contribute with added mobility to the network. It must also be noticed that the pMDI wt% is also lowest in this sample, which also contributes to higher chain mobility.

4.2.6 Compression Properties

The samples showed the typical compression behavior observed in foams as illustrated in Figure 5 for the glycerol set of samples. There is an initial linear elastic response of stress vs strain, followed by an extended plateau (in certain cases preceded by a local maximum at the yield point) and a final region of increasing stress. Initial bending and buckling occurs on the cell walls as compression is applied, but some cracking initiates at the yield point and the plateau is the result of the progressive brittle crushing of the cells under the compressive loads. In the final region, densification of the foam is controlling the material behavior that becomes closer to that of a non-foamed one.
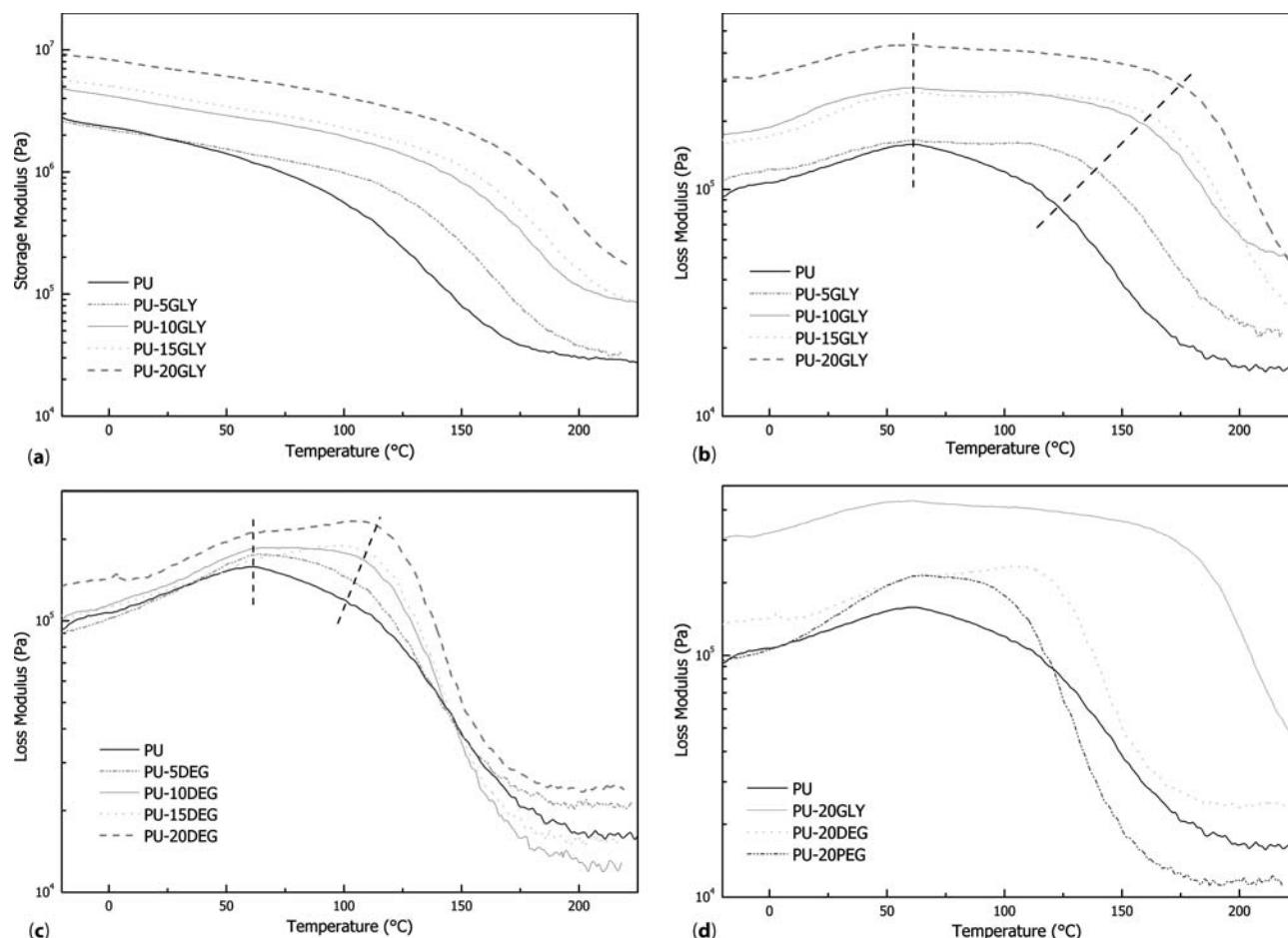
Figure 4 (a) Storage modulus of the series of foams prepared with added glycerol, (b) loss modulus of the series of foams prepared with added glycerol, (c) loss modulus of the series of foams prepared with added diethylene glycol and (d) loss modulus of foams prepared with 20% replacement of LO by other reactive modifiers. In all the sets of curves, the one corresponding to the PU is added for comparison.

Figure 5 shows that increasing the concentration of glycerol leads to the increase of the modulus (E) and the height of the stress plateau, while overall reducing the deformation at the yield point (reference foam, PU, does not follow the trend) and that of the deformation at which densification settles down. The increased fragility and higher rigidity of the cell walls due to increased crosslinking density and isocyanate concentration led to the observed trend on the two critical compression strains.

Table 3 summarizes the compression properties of all the prepared foams. The deformation at which densification appears is in the range of 62–69% strain for all the foams, with the lowest value occurring for the unmodified foam, closely followed by the PU-20PEG sample. This could be related to the similar equivalent weight of LOP and PEG as well as similar initial
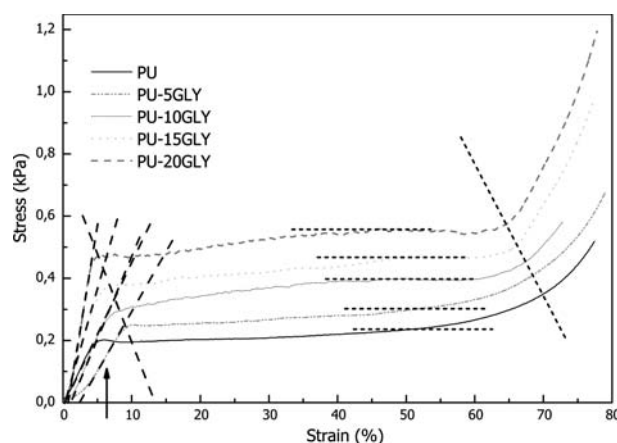

Figure 5 Comparative results of the glycerol-containing series of foams from compression tests.

Table 3 Compression properties of foams.

|	E (kPa)	yield stress (kPa)	yield deformation (%)	Densification strain (%)	$Rr_{1\,min}$ (%)	$Rr_{24\,h}$ (%)
PU	4.17 ± 0.58	0.197 ± 0.004	5.28 ± 0.75	62.72 ± 2.41	59.49 ± 2.60	81.82 ± 2.01
PU-5GLY	3.50 ± 0.55	0.241 ± 0.018	8.75 ± 1.41	64.07 ± 0.59	58.16 ± 1.84	75.48 ± 1.42
PU-10GLY	7.40 ± 2.44	0.301 ± 0.013	5.33 ± 1.20	65.74 ± 0.90	58.26 ± 2.68	74.70 ± 2.64
PU-15GLY	10.70 ± 2.21	0.395 ± 0.022	4.63 ± 0.95	66.29 ± 0.52	54.17 ± 2.70	70.81 ± 3.15
PU-20GLY	12.73 ± 3.01	0.470 ± 0.015	4.69 ± 0.93	66.38 ± 0.32	54.42 ± 0.59	71.10 ± 1.92
PU-5DEG	3.90 ± 0.23	0.223 ± 0.013	6.46 ± 0.89	68.54 ± 1.73	57.54 ± 2.38	74.56 ± 2.92
PU-10DEG	4.69 ± 0.45	0.212 ± 0.006	5.40 ± 0.18	67.21 ± 0.90	56.44 ± 1.89	71.21 ± 1.94
PU-15DEG	5.36 ±0.45	0.240 ± 0.006	5.03 ± 0.50	64.49 ± 0.36	54.60 ± 1.01	66.46 ± 0.20
PU-20DEG	6.04 ± 0.41	0.256 ± 0.016	5.00 ± 0.32	65.12 ± 1.58	55.01 ± 0.80	66.30 ± 0.18
PU-20PEG	5.69 ± 0.34	0.227 ± 0.009	4.72 ± 0.28	63.05 ± 1.76	55.21 ± 0.39	67.22 ± 0.48
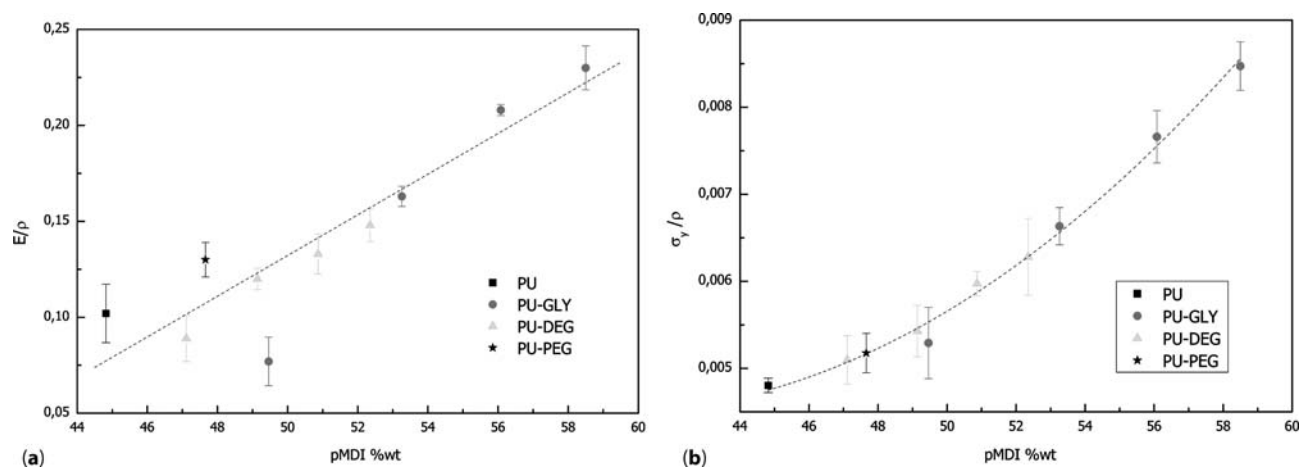
Figure 6 (a) Specific modulus and (b) specific yield stress as function of the percentage of pMDI in the initial formulation for all foams prepared.

concentration of pMDI in the formulation. On the other hand, the smallest modifier, DEG, leads to the highest values for the deformation at the densification point. Table 3 also includes the recovery ratio of the foams once the compressive stress was removed. The large difference between the instantaneous recovery and that measured after 24 hours indicates that these foams are viscoelastic materials with long relaxation times. The highest recovery was reached for the reference foam due to the nature of the bio-polyol that presents alkyd chains and relatively long pendant chains that add mobility to the structure. Additionally, a functionality per molecule higher than 3 (it acts as a crosslinker) and a high relatively equivalent weight allows the achievement of a highly crosslinked structure with high capability for deformation recovery.

The analysis of the results presented in Table 3 highlights the effect of the foam density and the chemistry of the formulation. Changing the nature of the polyol mixture used, changes the amount of pMDI added to maintain constant (and equal to 1.1) the NCO:OH molar ratio, which in turn changes the crosslinking density and the rigidity of the polymer chains that form the network. For these reasons, the results were further analyzed by comparing the specific modulus (modulus/foam density) and specific stress at yield (yield stress/foam density) vs pMDI wt%. The lines are included to facilitate the analysis. From Figure 6a and 6b, it appears that density and isocyanate concentration in the initial formulation are the controlling factors that lead to the observed behavior of the samples. In particular, the specific yield stress shows the collapse of the results of all the samples in a single curve that also includes the sample made from LOP without additional OH components.
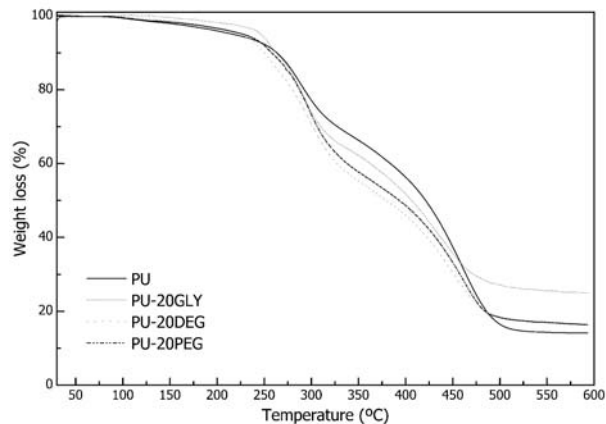
Figure 7 Thermogravimetric behavior of PU, PU-20GLY, PU-20DEG and PU-20PEG foams.

4.2.7 Thermal Stability

The thermal stability of PU foams with 20 wt% of GLY, DEG and PEG was analyzed by thermogravimetric analysis from room temperature to 600°C and their thermograms are shown in Figure 7, presenting qualitatively similar degradation profiles. The thermal stability of polyurethane foams depends on the crosslink density, cure conditions and the structure of the network.

As observed in Figure 7, PU-20GLY system is more stable than the rest of the foams (degradation beginning about 15°C above that of the unmodified foam). This can be due to the higher functionality of GLY (trifunctional) with respect to DEG and PEG (difunctional), resulting in a more crosslinked network. For all systems, two degradation steps can be distinguished. The first one, in the temperature range of 250–335°C, corresponds to urethane bond degradation. Since degradation starts at urethane groups, once they are broken the foams prepared with low molecular weight modifiers will release volatile compounds with higher probability. Thus, PU-20DEG shows the largest mass loss, followed by PU-20PEG, PU-20GLY and PU.

In the temperature range of 370–500°C, the residues formed during the first degradation step further degrade to form char residue. Moreover, it can be noted that the char residue of PU-20GLY, about 550°C, is higher than that of the rest of the systems (26%), which can be related to the high content of pMDI in the initial formulation of the PU-20GLY system (Table 1). On the other hand, the PU system presents the lowest char value (14%), probably also related to the lowest aromatic isocyanate content in the formulation.

5 CONCLUSIONS

Novel bio-based polyurethane foams were prepared using a polyol derived from linseed oil. The replacement of the linseed oil polyol by hydroxyl-containing modifiers of lower molecular weight in concentrations between 5 and 20 wt% changed the reactivity of the system and directly affected the final properties of the foams.

The modified foams showed shorter characteristic times than that of the reference foam, which was related to a higher reactivity of the OH groups of the modifiers and the lower viscosity of the initial modified systems.

The dynamic mechanical tests showed the increased glass transition of the glycerol-modified foam, which also showed the highest storage modulus among the different series. This modification also led to higher compression properties. The analysis of the compression results highlighted the importance of the concentration of the polymeric isocyanate in the initial formulation. The pMDI concentration also played a role in the char formation of the foams according to TG analysis. The higher density of crosslinking of the GLY-modified foam resulted in a better thermal stability among the different foams.

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