Preparation of Polyols and Polyurethane Foams from Olein By-Product of Tanning Industry

by

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Abstract

Olein produced from the solid residues of the tanning industry is already employed as raw material to obtain greasing oil for leather. However, new applications for this product may be advantageous regarding environmental impact and sustainability of this industry. In this work, flexible polyurethane foams (FPUFs) were prepared from polyols obtained from olein. A polyol from olein was prepared through alkaline glycerolysis. The glycerolysis conditions of temperature, glycerol/olein molar ratio, amount of catalyst and reaction time were optimized using a 2^4 factorial design, resulting in an olein polyol containing around 75% of monoacylglycerols, hydroxyl value (388.68±0.40 mg $KOH.g^{-1}$), and hydroxyl functionality of 2.89. FPUFs were prepared at NCO/OH ratios of 1.2:1 and 1.3:1, using an aliphatic hexamethylene diisocyanate trimer and water as foaming agent. The foams were characterized through FTIR, thermogravimetry, morphology, extractable materials, and mechanical properties. Characteristics urethane/urea groups formation were verified by FTIR as well as typical mass loss steps in the thermal decomposition curves. The foams morphology showed a structure composed mainly for polygon-type closed-cells. The obtained FPUFs presented a content of extractable materials lower than 3%. The mechanical properties of the foams were dependent on the NCO/OH ratio, and the foam prepared at the ratio of 1.2:1 stood out as a potential material to be used in the production of mattresses. This study demonstrated the feasibility of transforming olein, a solid residue of the tanning industry, as a precursor to prepare PU foams, which may be a promising material for mattress applications, considering the observed features.

Introduction

The tanning industry is a global manufacturing sector that processes skins and hides of animals (tanning) to produce leather, a finished material used for the fabrication of a variety of articles, such as footwear, clothing, bags, automotive upholstery, fashion accessories, and furniture. The leather manufacturing process occurs basically in three steps: preparation, tanning and finishing. The preparation step begins with the ordering and salting (to prevent putrefaction) of the hide/skin and is followed of the beamhouse operations, which include soaking, liming, removal of extraneous tissues (unhairing and fleshing), deliming, bating, and pickling. The beamhouse process is particularly important when considering environmental aspects because it generates large amounts of solid waste, composed of hairs, epidermis, subcutaneous layer, non-collagenous proteins, salt, fats, blood, and dirt.

Considering specifically the pre-fleshing operation, the solid residues removed from the subcutaneous region of the skin contain about 32% (wt.) of fat content and 20% (wt.) of hide. This residue can be processed through digestion/extraction and winterization techniques in order to produce olein, a lipid matter, yellow and liquid at room temperature. Olein is composed of a mixture of saturated and unsaturated triglycerides (TAG), with oleic acid as the major component, corresponding to about 72%.[1] The olein obtained from pre-fleshing solid residue is used as raw material to produce greasing oil for leather.[2] Nevertheless, the search for new applications for this product is relevant in terms of the environmental impact and sustainability issues related to the tanning industry.

The use of this olein as raw material for the synthesis of polyols to produce polyurethanes appears as an interesting possibility. Polyurethanes (PUs) represent a broad class of polymers usually obtained by a step-growth reaction between a di/polyisocyanate and a di/polyol. A wide variety of products (such as rigid or flexible foams, rubbers, elastomers, coatings, and adhesives) can be produced by varying the proportions and type of isocyanate, polyol, blowing agent, catalyst, and other additives.[3]

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Manuscript received April 28, 2022, accepted for publication June 15, 2022

Polyols are hydroxylated compounds used to produce PUs. These polyols add specific characteristics to the final polymer, including mechanical properties such as flexibility, softness, tensile strength, and low-temperature elongation. Conventional polyols are obtained from petroleum derivatives; however, due to growing concerns over environmental pollution, the research on the production of polyols from renewable sources has increased significantly recently.[4] Among the renewable sources considered in the literature to produce polyols, vegetable oils stand out due to the availability, variety and relatively low cost. Castor[5], soybean[6] and andiroba[7] oils are examples of vegetable oils that have already been used in the synthesis of polyols for PUs. Due to its low cost and structural chemical similarity to the vegetable oils, olein has the potential to be used as raw material for polyol synthesis.

The chemical transformation of vegetable oils in polyols can be accomplished by functionalization of the double-bonds or by transesterification in order to obtain a product rich in hydroxyl groups. Glycerolysis, a well know transesterification reaction between glycerol and TAG, is one of the main routes for this process, classically used for the preparation of alkyd resins.[4,8] This reaction is carried out under an inert atmosphere and high temperature (200 to 250 ºC) to increase the solubility of glycerol in the oil phase, which is about 4% at room temperature. Besides, glycerol excess is added to shift the reaction equilibrium toward monoglycerides (MAG) and diglycerides (DAG) formation, and alkalis such as NaOH, KOH, and $Ca(OH)_2$ are used as catalysts.[9] The product of this reaction is a polyol that can be used in polymer manufacture.[4]

Therefore, considering the technical viability of the PU production from triglyceride (TAG) from vegetable oils and the great amount olein generated as residue in the tanning industry, this work aims to investigate: (i) the production of polyol by glycerolysis of olein obtained as residue of the pre-fleshing step; and (ii) the preparation of flexible polyurethane foams (FPUF) with the olein polyol (OP) obtained in this way.

Experimental

Materials

Olein produced from pre-fleshing residues was supplied by a tannery (Picada Café City – Brazil) and characterized through acid index (ABNT-NBR-11115:2014), kinematic viscosity (ABNT-NBR-10441:2014), water content (ABNT-NBR-10445:2013), high-performance liquid chromatography (HPLC), and nuclear magnetic resonance (NMR).

Aliphatic hexamethylene diisocyanate trimer (Tolonate® HDT 90) with a content of free isocyanate groups of 16.1±0.1 % (as determined by the ASTM D 2572 – 97 method) was supplied by VencoreX Chemicals © (Guarulhos – Brazil). Silicone-polyether copolymer surfactant (DABCO® DC5986) was supplied by Evonik Industries AG (Essen - Germany) and used as foam structure stabilizer. Deionized water was used as a blowing agent. Dibutyl-tin dilaurate – DBTDL (LIOCAT® 119, Miracema-Nuodex Chemical Industry Ltda., Campinas – Brazil) was used as catalyst. Chromatographic standards of monoolein, 1,3-diolein and triolein were acquired from Accustandard Company (New Haven - USA). Other reagents and solvents were of analytical or HPLC grade.

Synthesis of the olein polyols (OP)

The olein polyol was prepared by glycerolysis of the olein according to a method described by Barrios.[10] A 2^4 full factorial design experiment with four central points was carried out using a fixed amount of olein (10 g) and KOH as catalyst. Catalyst quantity (0.5, 1.0 and 1.5 $\%w_{olein}$), glycerol/olein molar ratio (2.5:1, 3.0:1 and 3.5:1), temperature (180, 200 and 220 °C) and reaction time (2, 4 and 6 h) were used as factors. All experiments were performed under inert atmosphere and magnetic stirring (~800 rpm). After the reaction, OP was neutralized with a 0.01 M HCl solution, at 60°C and under stirring. The water was then removed under reduced pressure (-0.08 MPa) at 80°C in a rotary evaporator.

Preparation of the flexible polyurethane foams (FPUF)

FPUFs were prepared via one-step method, according to the formulations in Table I. The olein polyol was previously heated at 60°C until liquid, then the surfactant, deionized water, catalyst, and HDT were added. The mixture was mechanically stirred at 2,500 rpm for 70 seconds and then transferred to a mold of 150×150×150 mm, previously lined with kraft paper. The FPUFs curing was performed in an oven at 60°C for 24 h and the post-curing by storage at 30°C for 72 h.

Table I

FPUFs formulations

		Parts by weight				
Formulation	NCO/OH*2 Molar ratio	Olein polyol*1	HDT	Deionized water	Surfactant	Catalyst
FPUF1	1.2:1	100	192	6	6	1
FPUF2	1.3:1	100	210	6	6	1

*1Olein Polyol 2 (OP2 - Experiment 2, Table II) was chosen to prepare FPUFs due to its higher MAG and lower DAG, TAG, and FFA contents. For more details, please refer to Section 3.1.

*2Isocyanates (NCO)/Hydroxyl (OH)

Physical and mechanical properties and extractable material of FPUFs

Physical properties (density, tear strength, tensile strength, compression force and resilience) were determined according to standard test methods for flexible cellular materials (ASTM D3574 – 17), with five replicates for each sample. The comfort factor was determined based on Brazilian Standard NBR 9176:2016 method.

Extractable materials in the FPUFs samples were evaluated in hexane, using samples of 20×20×20 mm, according to the following steps: i) the sample was placed in a beaker of 100 mL; ii) 50 mL of hexane was added; iii) static extraction at room temperature for 15 min; and iv) removal of the solvent containing the extracted material to an amber flask. These steps were performed five times for each sample for complete extraction. This experiment was conducted in triplicate. Afterwards, the amber flasks were kept in an oven at 70°C for 24 h to remove the solvent. The percentage of extractable materials was determined through the difference of the weight before and after the extractions. ^{1}H-NMR spectra were performed to identify the composition of the extracted materials.

Analytical methods

The quantification of the glycerolysis products was carried out by high-performance liquid chromatography (HPLC) Agilent© 1260 Infinity (Agilent Technologies, USA), equipped with a column Agilent Zorbax Eclipse Plus C18 (250 × 4.6 mm, 5 µm particle size), according to the methodology proposed by Dupont.[11] Calibration curves of monoolein (R^2 = 0.9957), 1,3-diolein (R^2 = 0.9990) and triolein (R^2 = 0.9976) standards were used to quantify the reaction components. The samples eluted as a group of 3 to 5 peaks in the regions previously identified with these standards: 5–10 min to MAG; 20–28 min to DAG; and 30–37 min to TAG.

The hydroxyl value of the obtained polyols was determined by the ASTM D E222-17 method. Number-average functionality (f) was calculated by Eq. 1.

$$f = \frac{MM_{OP2} \times OH_{val}}{56110} \quad \text{(Eq. 1)}$$

where MM_{OP2} is the average molecular weight determined by HPLC and OH_{val} the hydroxyl value.

Fourier transform infrared (FTIR) spectroscopy measurements were performed on a MIR-FTIR Frontier Perkin Elmer spectrometer in attenuated total reflectance. Spectra were recorded with a resolution of 4 cm^{-1} from 4000 to 650 cm^{-1} with an average of 16 scans.

Thermogravimetric analysis (TGA) of the samples was performed using an SDT Q600 (TA Instruments-Waters, USA) from 0 to 900 °C at 10°C·min^{-1} and nitrogen flow rate of 100 mL·min^{-1}. The morphology of the obtained FPUFs was determined by scanning electron microscopy (SEM) in a JSM 6060 microscope (JEOL, Eching b. München-Germany). Cell area was analyzed using ImageJ software, averaging 100 measured cells of one image per formulation.

The statistical analysis of the data was performed with Statistica® 12.5 (Dell Inc - USA), using t-test (for data of mechanical properties and extractable materials) and analysis of variance – ANOVA (for yield of OP production), considering a significance level of 95% ($p<5\%$).

Results and Discussion

Glycerolysis of olein

The results of MAG, DAG, TAG and FFA yields in the experiments performed with catalyst quantity, glycerol/olein molar ratio, temperature and time as factors are presented in Table II, while Table III shows the significant factors ($p<0.05$) from the ANOVA on these data. Catalyst and temperature had positive effects ($p<0.05$) on MAG yield and negative effects on TAG yield. These effects reflect the fact that higher amount of catalyst and higher temperature (above 200°C) favor the conversion of TAG to MAG, as observed by Echeverri et al.,[12] in the study of biodiesel production through glycerolysis of methyl esters with crude glycerol. Besides, the temperature increase reduces the viscosity of the mixture, enhances the solubility of reactants, and improves their diffusion, reducing mass transfer resistances. Temperature and time had positive effects on DAG yield, which may be related to the reversible nature of the glycerolysis reaction that occurs in three stepwise consecutive reactions.[13] Besides, longer reaction times and higher temperatures can shift the reaction equilibrium toward DAG formation.[14] It is important to note that the factor time was not significant for MAG and TAG, probably because of the relatively long reaction times under consideration.[15,16]

The conditions used to produce the OP2 sample (Table I) were chosen to produce the olein polyol for the FPUFs preparation because this formulation led to the highest MAG yield and the lowest of DAG, TAG, and FFA final contents.

Characterization of olein and Olein Polyol 2 (OP2)

The main characteristics of the crude olein and OP2 are summarized in Table IV. OP2 showed a high content of MAG, as indicated by the hydroxyl value of 348.59±3.40 mg KOH/g. Additionally, OP2 presents functionality greater than two, being adequate to produce thermosetting polyurethane networks. The kinematic viscosity at 40°C increased approximately ten times from olein to OP2 sample, which may be attributed to the higher content of OH groups in the glycerolysis product and, consequently, the expected higher density of hydrogen bonding in OP2. At 60°C, the kinematic viscosity of the OP2 reduces 2.65 times. Since high viscosities can lead to inadequate mixing of the ingredients and imperfections in the cell structure of foams,[17] the use of heated OP2 (60°C) was the selected condition for the FPUFs preparation.

The low acid value of olein (1.18±0.12 mg KOH.g^{-1}, Table IV) can be attributed to its low content of free fatty acids (FFA). The higher value of this parameter for OP2 may be ascribed to FFA formation

Table II

Experiments performed according to a 2^4 factorial design and the respective results of yield.

Polyol sample designation*1	Factor				Yield (%)			
	Glycerol/olein (mol mol^{-1})	Catalyst (%w_{olein})	Temperature (°C)	Time (h)	MAG	DAG	TAG	FFA*3
OP1	3.5:1	1.5	220	6	68.41	29.57	0.21	1.81
OP2	3.5:1	1.5	220	2	72.49	25.39	0.51	1.61
OP3	3.5:1	1.5	180	6	68.82	29.12	0.21	1.85
OP4	3.5:1	1.5	180	2	60.85	25.45	11.52	2.18
OP5	3.5:1	0.5	220	6	68.98	28.59	0.78	1.65
OP6	3.5:1	0.5	220	2	10.57	7.95	79.65	1.83
OP7	3.5:1	0.5	180	6	23.56	24.44	50.36	1.64
OP8	3.5:1	0.5	180	2	3.34	1.2	94.58	0.89
OP9	2.5:1	1.5	220	6	62.18	33.32	2.46	2.04
OP10	2.5:1	1.5	220	2	69.8	26.01	0.51	3.68
OP11	2.5:1	1.5	180	6	65.61	30.81	0.86	2.72
OP12	2.5:1	1.5	180	2	12.99	2.50	82.66	1.85
OP13	2.5:1	0.5	220	6	65.24	31.64	1.09	2.03
OP14	2.5:1	0.5	220	2	62.13	35.07	0.84	1.96
OP15	2.5:1	0.5	180	6	16.52	9.95	70.90	2.62
OP16	2.5:1	0.5	180	2	21.6	16.25	60.59	1.56
OP17*2	3.0:1	1.0	200	4	64.36	26.51	6.03	3.09
OP18*2	3.0:1	1.0	200	4	62.61	34.22	1.34	1.83
OP19*2	3.0:1	1.0	200	4	63.57	30.37	3.38	2.68
OP20*2	3.0:1	1.0	200	4	63.59	27.78	3.28	5.35
Yield at the central point [%]					63.53±0.72	29.72±3.40	3.51±1.93	3.24±1.50

*1Sample designation scheme: i) OP stands for olein polyol; ii) the number indicates the specific treatment in the factorial design, according to the standard order.
*2Central point replicates.
*3Free fatty acid

Table III

MAG, DAG, and TAG yields: effects of the significant factors ($p<0.05$) from the ANOVA on data of Table I

Components	Factor*1	Effects	Std.Err.	t(5)	p	-95.%	+95.%	R^2
MAG	Mean/Interc.	50.361	2.983	16.884	0.00001	42.694	58.028	0.9213
	(2)Catalyst (%w_{olein})	13.076	3.335	3.921	0.011	4.503	21.648	
	(3)Temperature (°C)	12.907	3.335	3.870	0.012	4.335	21.479	
DAG	Mean/Interc.	23.807	1.597	14.907	0.00002	19.702	27.912	0.8764
	(3)Temperature (°C)	4.864	1.786	2.724	0.042	0.274	9.454	
	(4)Time (h)	4.851	1.786	2.717	0.042	0.261	9.441	
TAG	Mean/Interc.	23.588	4.661	5.061	0.004	11.607	35.569	0.9032
	(2)Catalyst (%w_{olein})	-16.241	5.211	-3.117	0.026	-29.635	-2.846	
	(3)Temperature (°C)	-17.852	5.211	-3.426	0.019	-31.247	-4.457	

*1Factors are coded by numbers: (1) glycerol/olein (mol.mol^{-1}), (2) catalyst (%w_{olein}), (3) temperature (°C) and (4) time (h)

Table IV
Properties of olein and OP2

Properties	Olein	OP2
MAG (%)	1.08±0.10[b]	74.68±0.14[a]
DAG (%)	2.18±0.11[b]	22.10±0.08[a]
TAG (%)	96.14±0.16[a]	0.75±0.11[b]
FFA (%)	0.59±0.05[b]	2.47±0.02[a]
Hydroxyl value (mg KOH.g^{-1})	-	348.59±3.40
MM (g.mol^{-1})[*1]	-	417.15
Relative functionality	-	2.6
Kinematic viscosity at 40 °C (cSt)	58.11±0.15[b]	548.56±2.81[a]
Kinematic viscosity at 60 °C (cSt)	-	206.85±0.59
Acid value (mg KOH.g^{-1})	1.18±0.12[b]	4.90±0.03[a]
Water content (%)	0.41±0.15[b]	7.39±0.20[a]

[*1]Molecular weight determined using HPLC analysis (supplementary information);

(a-b) Different letters within the same line indicate significant difference between the respective mean values ($p < 0.05$).

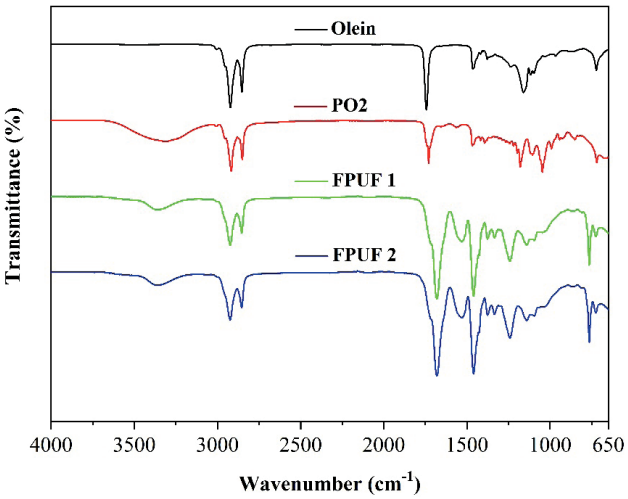

Figure 1. FTIR spectra of the FPUFs.

during the glycerolysis reaction due to the presence of water in glycerol and olein.[10] The water content of OP2 was higher than that of olein, indicating low efficiency of the drying process performed after the neutralization step; however, this residual water may act as a blowing agent during the FPUF preparation.

Characterization of the produced flexible polyurethane foams (FPUFs)

Structural characterization

Figure 1 shows the FTIR spectra of olein, OP2 and the two polyurethane foams prepared (FPUF1 and FPUF2). The OP2 spectrum presents a broad band at ~3600-3100 cm^{-1}, which is absent in the olein spectrum and is related to the stretching of OH groups that arose after the glycerolysis reaction. The peak appearing in the same region in FPUF1 and FPU2 spectra is attributed to the overlap of -NH from the urethane group and OH stretching of the unreacted polyol. The intensity of this peak is lower for FPUF1 than FPUF2 due to the consumption of OH groups in the polymerization reaction. The peaks at 1686 cm^{-1} and 1562 cm^{-1} are related to the stretching vibrations of carbonyl of urethane and urea groups, and urethane N-H bending vibrations associated with C-N stretching vibrations (amide II), respectively.[18,19] The peaks at 1464 cm^{-1} and 1249 cm^{-1} correspond to the C-N bond of the urethane groups and to –C-O-C ester stretching vibration,[20] respectively. So, these bands suggest the formation of a polyurethane matrix. Besides, the absence of bands in the range from 2274 to 2100 cm^{-1} indicates complete reaction of the isocyanate groups.

Figure 2 shows the weight loss (TGA, 2a) curves and their first derivate (DTG, Figure 2b) for the olein, glycerol (for reference), OP2 sample, FPUF 1 and FPUF 2. Olein exhibited only one step of weight loss in the range of ~290 – 500 °C, which corresponds to the ester linkages decomposition. OP2 presented two steps of weight loss, being the first one (~150 – 230 °C) attributed to the thermal decomposition of the residual glycerol, and the second one (~330 – 500 °C) related to the thermal degradation of the ester bonds.[21,22] The FPUFs present four steps of weight loss. The first one was attributed to non-reacted

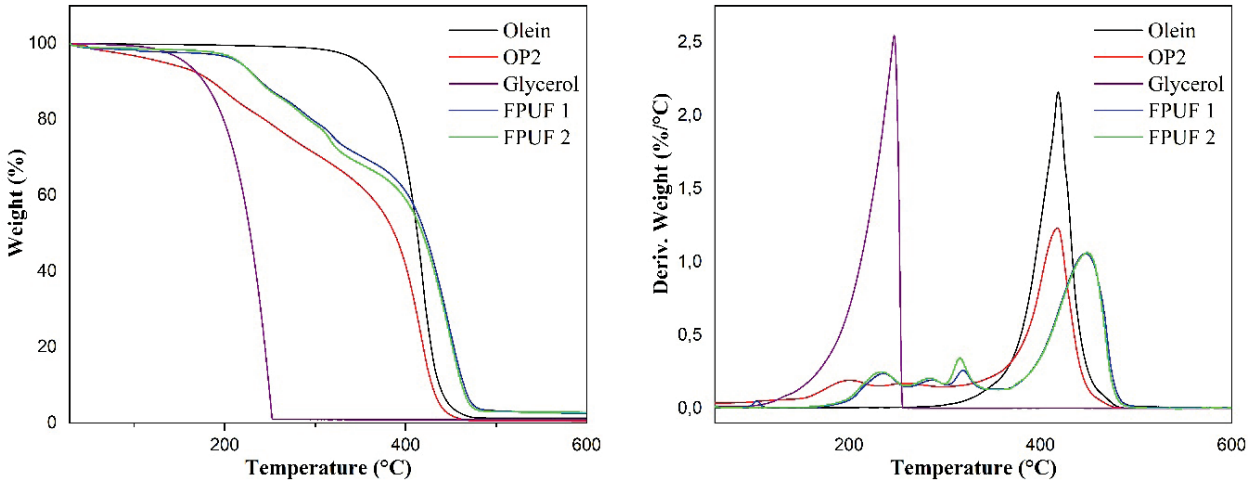

Figure 2. TGA **(a)** and DTG **(b)** curves for O, OP2, FPUF1, and FPUF2.

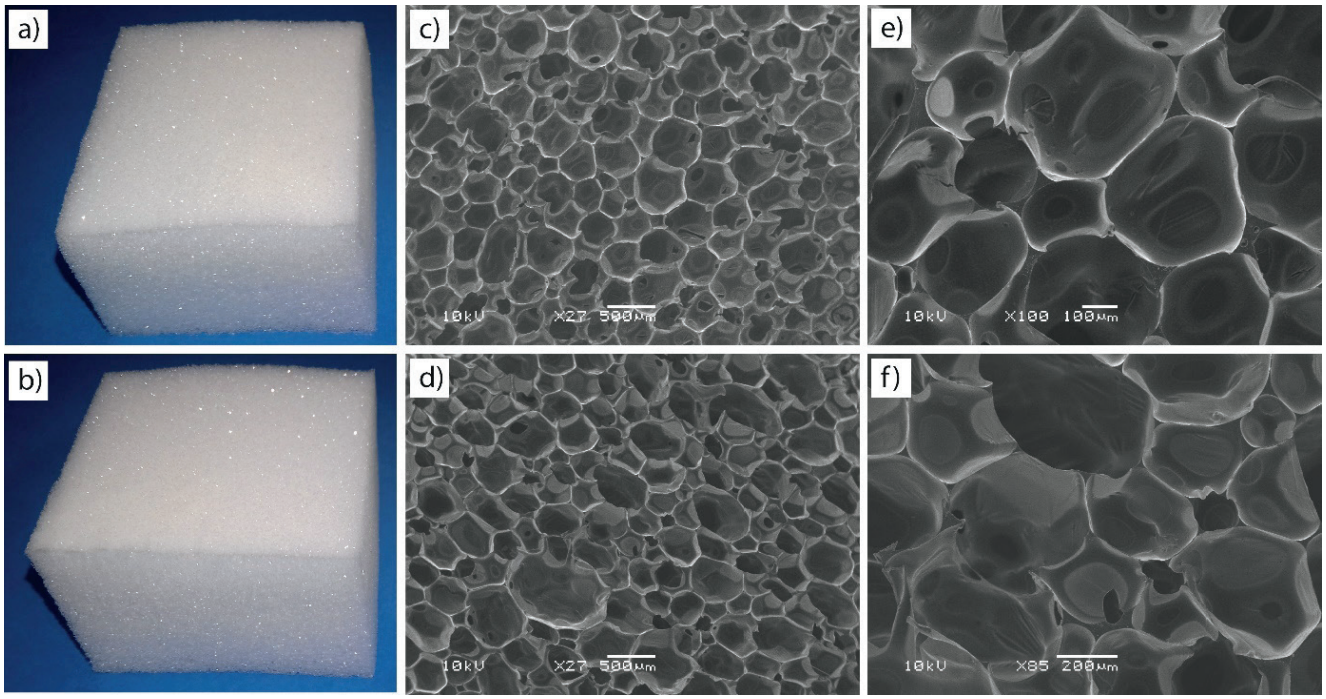

Figure 3. The visual aspect of FPUF1 **(a)**, FPUF2 **(b)** and SEM morphologies of FPUF1 **(c, e)**, FPUF2 **(d, f)**.

glycerol, the second and third ones (~250 – 350 °C) to the degradation of urethane/urea bonds and hydrocarbon chains,[21,22] and the last one (~350-490°C) to the degradation of the polyol ester bonds.[21,22] The third stage of weight loss was higher for FPUF 2, which is in agreement with the higher amount of isocyanate in its production.

Figure 3 shows the visual aspect (Figure 3a, b) and the SEM morphologies (Figures 3c-f) of the produced FPUFs. Both FPUF1 and FPUF2 were glossy white and dimensionally stable in the absence of applied stress (Figure 3a, b). Polygon shaped closed cells were predominant, but structures with openings (probably caused by the passage of CO_2) and many wrinkled walls were also observed, mainly in FPUF2 (3d, f).

Figure 4 shows the histograms of cell area distribution obtained for FPUF1 and FPUF2 from the analysis of the images of Figures 4c, d. Both histograms are quite similar and the frequency of cells with the measured area between 25 and $174\times10^3\mu m^2$ represents about 60% for both FPUFs. This indicates the efficacy of the type and amount of surfactant used in the formulation in promoting cell size uniformity. This is attributed to fact that the surfactant acts controlling the process of foaming and regulates the ratio of open/closed cells, producing fewer cells with smaller size.[23,24]

Extractable material

Both samples presented low contents of extractable materials, 2.83±0.69% for FPUF1, and 0.93±0.33% for FPUF2, indicating that both samples presented a crosslinked structure. Nevertheless, the

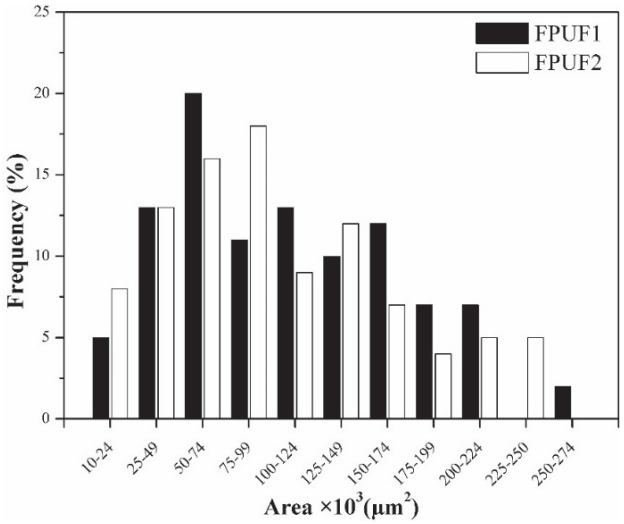

Figure 4. Distribution of the measured cell area of FPUF1 and FPUF2.

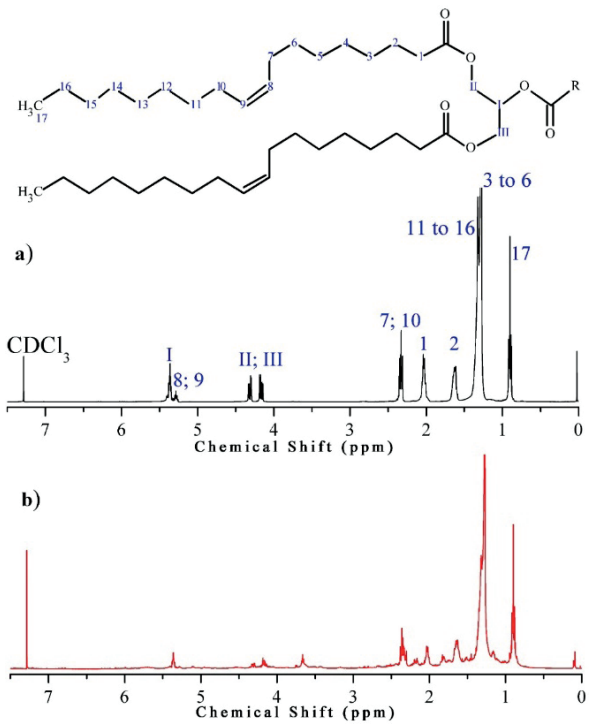

Figure 5. ^{1}H NMR spectra of olein **(a)** and extractable material of FPUFs **(b)**.

difference of extractable material content between the two samples was statistically significant ($p < 0.05$) and in qualitative agreement with their relative NCO/OH ratios. The extractable fraction of the produced FPUFs was composed mainly of TAG (about 0.75±0.11 %, Table V), since the signals of H_I, H_{II} and H_{III} were observed in the ^{1}H NMR spectrum of Figure 5b.[25] Additionally, the presence of unreacted components in the samples is confirmed by the signals in the 3.7 ppm region (Figure 5b). These signals are attributed to unreacted MAG, DAG or FFA, since the region from 3.3 to 4.2 ppm is characteristic of methylenic protons next to an oxygen atom ($-CH_2-O-$).[26]

Physical and mechanical properties

Table V presents the physical and mechanical properties of the FPUFs. Considering the evaluated properties, FPUF1 and FPUF2 were statistically different only in terms of density, comfort factor, rebound, compression force and elongation at break. Such differences can be explained based on the values NCO/OH ratios used in the formulations. The higher the NCO/OH ratio, the greater the number of rigid segments formed. Consequently, FPUF1 is expected to present higher concentration of rigid segments than FPUF1, which would explain its higher density and lower elongation at break. The fact that FPUF2 presented the higher rebound value and compression force is also in agreement with this analysis, since the capacity of recovering of the foam is expected to increase with the increase of rigid domains in the system.

These results, more specifically for density and compression force, are supported for those found in the other works of the literature for similar systems. For example, Kattiyaboot and Thongpin[27] prepared FPUFs from blends of petroleum-based and vegetable-based polyols (NCO/OH fixed at 1) and blown by distilled water, observing a directly proportional correlation between the foam density and the compression force. Hoong Yeoh et al.,[28] studying FPUFs prepared with palm oil-based polyester polyol, have also attributed the variations in the mechanical properties to the content of hard segments, although they have not found a significant correlation between the compressive properties and density.

The fact that some parameters (maximum strength, tear strength, breaking load, and modulus of rupture) were not statistically different between the produced FPUFs, indicates that these properties are less sensitive to the NCO/OH ratio than those discussed in the last paragraph. Similar results were reported by Hoong Yeoh et al.,[28] who reported that FPUFs prepared at an NCO/OH ratio of 1.1:1 and 1.2:1 presented a small variation in the tensile strength (from 85.27±8.5

Table V

Extractable materials, physical and mechanical properties of the prepared FPUFs.

Tests	Parameters	FPUF1	FPUF2
Extractable materials	Weight of extractable materials (%w)	2.83±0.69[a]	0.93±0.33[b]
Density	Density (kg.m^{-3})	48.42±4.34[a]	36.42±2.15[b]
Tear strength	Maximum strength (N)	4.30±0.48[a]	4.47±0.42[a]
	Tear strength (N.mm^{-1})	172.03±18.72[a]	179.17±13.46[a]
Tensile strength	Breaking load (N)	11.42±3.20[a]	9.22±2.07[a]
	Modulus of Rupture (MPa)	0.07±0.01[a]	0.06±0.01[a]
	Elongation at break (%)	182.88±33.63[a]	157.61±14.36[b]
Compression Force	Compression Force (N)	10.69±2.22[a]	15.75±2.66[b]
Resilience	Rebound value (%)	10.77±1.32[b]	16.03±3.03[a]
Comfort Factor	C.F	4.38±0.88[a]	2.74±0.39[b]

(a-b) Means values within a same line are significantly different ($p < 0.05$).

to 70.85±13.4 kPa) compared to the elongation at break (from 45.86±3.6 to 32.12±1.6%) and compression stress (from 49.19±7.6 to 115.09±18.2kPa).

Regarding potential applications of the FPUFs produced from olein obtained as byproduct of the tanning industry, it is worthwhile to mention that, according to NBR 13579-1:2011, density greater than 30 $kg{\cdot}m^{-3}$, resilience up to 15% and comfort factor above 1.8 are some of the basic requirements for viscoelastic foams. Considering that FPUF1 exhibited those features, it may be a potential material to be used in mattresses. Besides, FPUF1 is favorable in an economic sense, since it uses nearly 10% less isocyanate, which has a significant impact on the production cost.

Conclusions

This work demonstrated the feasibility of using olein, a byproduct of the tanning industry, as a raw material for preparing polyols for flexible polyurethane foams. The olein polyol was prepared through glycerolysis of the olein. The content of monoglycerides in the final product was experimentally maximized by using a full factorial design with catalyst quantity, glycerol/olein molar ratio, temperature, and reaction time as factors. The highest MAG content was of 74.68±0.14%, obtained at the following conditions: molar ratio between glycerol and olein of 3.5:1, 1.5% of catalyst (KOH), 220°C, and reaction time of 2 h. The flexible PU foams prepared with olein polyol and HDT isocyanate had a low content of extractable materials (below 3%), indicating that the polymerization reaction was successful. Density, compression force, elongation at break and resilience of the produced FPUFs were dependent on the NCO/OH ratio. The obtained FPUFs showed a structure composed mainly of polygon closed cells, with some wrinkled walls. The mechanical properties observed are like that of viscoelastic foams, and it is suggested that that PU foams from olein are potential materials to be used in mattresses. In this way, the use of olein to prepare polyol and produce PU foams can add value to this byproduct and contribute to the productive chain of the tanning industry.

Acknowledgments

The authors gratefully acknowledge the CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico - National Council for Scientific and Technological Development) for the study grant and the financial support from the FINEP (Financiadora de Estudos e Projetos - Financier of Studies and Projects) in the Project Ref. 1097/13 approved the MCTI/FINEP CT-HIDRO 01/2013.

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