Rigid Polyurethane Foam Based on Modified Vegetable Oil

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ABSTRACT: Soybean oil and castor oil were modified and used to prepare rigid polyurethane foam with similar properties to a commercial foam used for thermal insulation applications. Soybean oil was firstly modified according to a peracid method, using formic acid and hydrogen peroxide to yield a formiated soy polyol. Furthermore, transesterification was performed with a polyfunctional alcohol to increase OH-functionality. Castor oil, which has hydroxyl groups in the molecular structure, was only transesterified. The vegetable polyols were characterized by OH-number, Brookfield viscosity, differential scanning calorimetry, and size exclusion chromatography. The foams were prepared at constant NCO/OH ratio (1.2 : 1) by the hand mix method and poured into a closed steel box. They were characterized using scanning electron microscopy, thermogravimetric analysis, and dynamic mechanical analysis. The apparent density and the compression strength of foams were determined, respectively, by the mass/volume relation and through the table tensile tester. After modification, the polyols reached an OH-number between 393 and 477 mg KOH/g oil, showing a low viscosity and molecular weight, allowing the preparation of a rigid vegetable foam with an apparent density of 50 ± 1 kg/m^3 and compression strength around 200 kPa. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 530–537, 2011

Key words: soybean oil; castor oil; mechanical properties; polyurethane foam; thermal properties

INTRODUCTION

One of the most important polyurethane applications is foam, which can be rigid or flexible and can be produced in blocks or molded in different forms and sizes.[1] Rigid polyurethane (PUR) foams are widely used as thermal insulation in refrigerator chambers and constructions, and for acoustic isolation, because of their combination of low density, low thermal conductivity, and good mechanical properties.[2–4]

The essential components of the PURs are polyols and diisocyanates, and efforts are currently being made to replace synthetic petrochemical polyols with vegetable polyols to obtain bio-based PURs with a lower process cost.[5–7]

Petrovic et al. synthesized two types of polyols based on soybean oil, the first resulting from the epoxidation of the double bonds followed by methanolysis, and the second from hydroformylation followed by hydrogenation, to measure the reactivity of polyols in the preparation of PUR foams.[8,9]

Zhang et al. also synthesized by epoxidation, soybean oil-derived polyol, followed by an oxirane ring-opening reaction using a mixture of water and methanol to prepare foams. They observed that the soybean oil-derived polyol is less reactive than conventional polyols because of its secondary hydroxyl groups; however, this polyol improved the foam compression properties in flexible foams.[10]

Narine et al. prepared rigid PUR foams based on canola oil modified by ozonolysis and hydrogenation reactions. The foam based on canola showed better compressive properties than commercially available soybean polyol, but not as good as castor oil foam. The differences in performance occurred because of the number and position of OH-groups in the molecular structure for each oil.[11]

Chian et al. developed a polyol derived from refined-bleached-deodorized palm oil with 300 mg KOH/g to produce PUR foams. The foams obtained exhibited high compression strength and showed useful and promising properties.[12]

Petzhold et al. synthesized a series of soy-formiated polyols through a one-step reaction using the *in situ* performic acid generation method, yielding an OH-number from 104 to 162 mg KOH/g. Further polymerization with diisocyanates at NCO/OH molar ratio of 0.8 yielded elastomeric PURs with glass transition temperature from −13 to 47°C.[13,14]

Recently, water-blown rigid PUR foams have been prepared by reacting isocyanates with polyols

containing a mixture of vegetable oil-based polyols and petroleum-based polyols.[15,16] Most of them showed properties inferior to the foams made from 100% petrochemical polyol.

In this work, we synthesized rigid PUR foams based on 100% modified soybean or castor oil polyols and diphenylmethane diisocyanate using a nonharmful foaming agent (pentane). PUR foams with apparent density (50 ± 1 kg/m^3) were prepared and characterized by cell size. The mechanical and thermal properties were compared with a commercial PUR foam.

EXPERIMENTAL

Materials

Crude castor oil Resinol 160/10 was supplied by Azevedo Óleos (Brazil), refined soybean oil Cocamar (Brazil), polyol-polyether Voranol 466N and *N,N*-dimethylcyclohexylamine were supplied by Arinos (Brazil), diphenylmethane diisocyanate Desmodur 44V 20L (NCO = 31.3%) was sourced from Bayer SA (Brazil). The surfactant Tegostab B8460 was obtained from Degussa Corp. (Germany), pentane, formic acid, and hydrogen peroxide 30% (w/w) from Vetec (Brazil), a trifunctional alcohol: glycerin or triethanolamine from Vetec (Brazil), and a strong base were used as received.

Soybean oil modification

Soybean oil was mixed with formic acid (1.0 mol of double bonds: 3.0 mols of formic acid) in a Büchi reactor at room temperature, hydrogen peroxide 30% was then added dropwise at a molar ratio (1.0 mol of double bonds: 1.5 mol of hydrogen peroxide) for 30 min under mechanical stirring. After the addition of peroxide, the temperature was kept at 65°C, for 2 h to obtain a formiated soy polyol with around 130 mg KOH/g. The remaining water was eliminated by vacuum distillation.[13]

Transesterification was performed in a 2-L round bottom glass equipped with heating, thermometer, and mechanical stirrer. Two molecules of triethanolamine was mixed with 1.0 mol of formiated soy polyol. Then, 0.2 w % of a strong base in relation to the total mass of the reagents was added into the vessel, and the reaction was performed at 150°C for 90 min. The oil conversion was verified by thin layer chromatography using a 1 : 1 solvent mixture (diethyl ether: cyclohexane). The obtained soy polyol was named (SO1), and the synthetic route was showed in Scheme 1.

Castor oil modification

Crude castor oil was transesterified with triethanolamine (CO1) or glycerin (CO2) under the same condi-
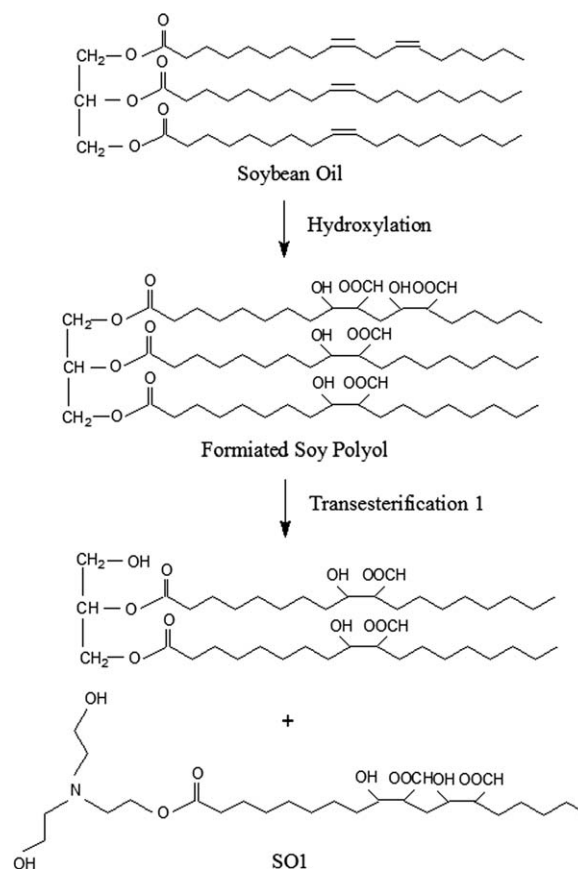
Scheme 1 Synthetic route to obtain soybean oil-based polyols.

tions described previously for soybean oil, with molar ratio 1.0 : 3.0 (oil : alcohol). The synthetic routes were showed in Scheme 2.

Polyol characterization

Number average molecular weight (Mn) of the polyols was measured on a Waters 410 size exclusion chromatography equipped with a RI detector, using a PS calibration curve (eluent THF, flow rate 1 mL/min). The viscosity was measured on a Brookfield DV-II viscometer, and the OH-number was determined according to ASTM D1957-86. The acid value was measured by standard AOCS Te-2a-64. Differential scanning calorimetry (DSC) was performed on a Du Pont Instruments DSC 2910 and carried out under inert atmosphere (N$_2$). The samples were cooled to -150°C and heated to $+150$°C at a heating rate of 20°C/min.

Foam preparation

Modified castor oil, modified soybean oil or Voranol 466N were premixed at room temperature with surfactant, water, catalyst, foaming agent, and mixed with MDI using the hand mix method (1800 rpm) for 30 s at constant NCO/OH ratio 1.2 : 1 to guarantee
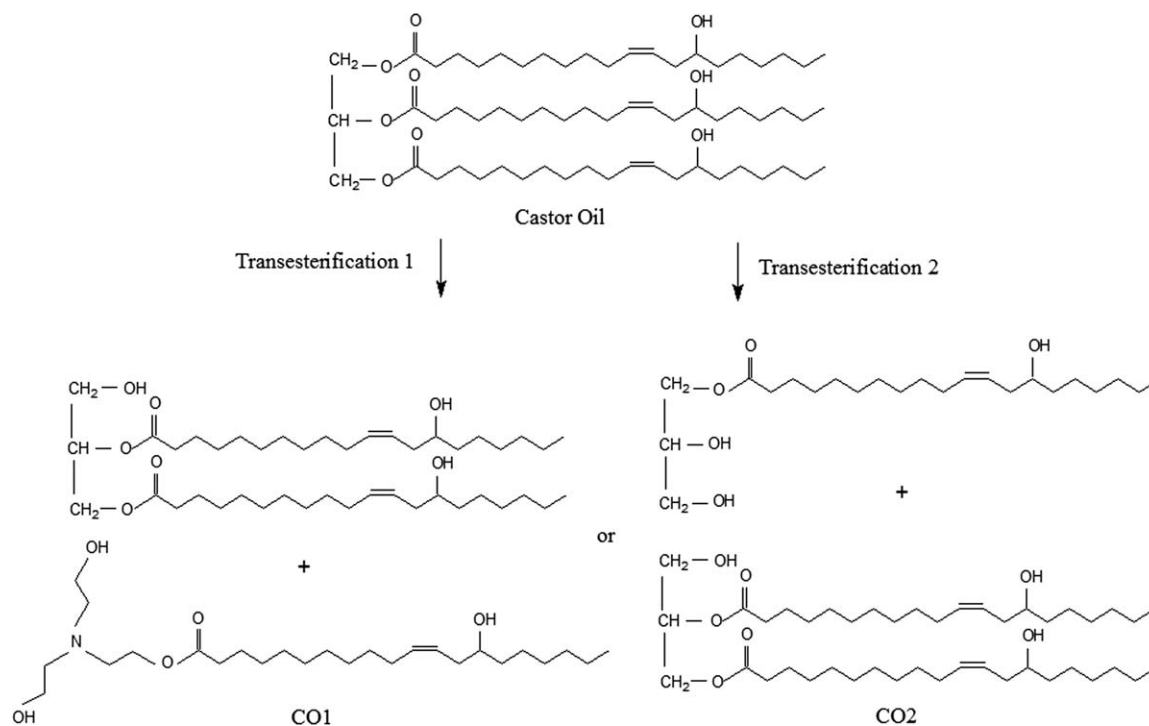
Scheme 2 Synthetic route to obtain castor oil-based polyols.

that each OH group will be reacted, and poured into a steel box (15 × 15 × 15 cm), closed during the foaming. The foams were then cured for 1 h at 100°C. These foams were named PU-CO1, PU-CO2, PU-SO1, and PU-VOR, and their formulations are shown in Table I. Because of the difference in polyol reactivity, the amount of catalyst was adjusted to guarantee a good mixture of the components before foaming.

PUR foam characterization

Thermal properties

Thermogravimetric analysis (TGA) was carried out on a TA Q50 thermogravimetric analyzer under inert atmosphere (N_2) at a constant heating rate of 20°C/min from 25 to 800°C.

Glass transition temperature (Tg) was determined by dynamic mechanical analysis (DMA) on a DMA Q800 TA instrument equipped with a liquid nitrogen cooling apparatus, in compression cantilever clamp mode, with constant heating rate of 3°C/min from −120°C to + 250°C. Cylindrical samples were prepared in diameter and thickness with a special knife (32 mm × 10 mm). DMA measurements were performed at a fixed frequency of 1 Hz and fixed preload of 0.3 N.

Mechanical properties

PUR foam specimens were fabricated in the form of cubes with 50-mm sides for uniaxial compression tests. Static mechanical properties were investigated via compression loading. Tests were carried out using an EMIC universal testing machine (DL10000) with a displacement rate of 5 mm/min in the rise and transverse direction up to 10% core deformation at room temperature according to ASTM D1621. For each sample, five specimens were tested.

Scanning electron microscopy

After cryogenic fracture, the samples were coated with a thin layer of gold, and the micrographs were taken on a JEOL JSM 6060 scanning electron microscope (SEM). Cell area was analyzed using Image Tool 3.00 software. For each sample, 100 cells were measured.

Density

Density was determined by averaging the mass and volume measurements of five specimens per sample, following ASTM D1622-98 standard.

TABLE I
Rigid Foam Formulation

Formulation (part)	PU-CO1	PU-CO2	PU-SO1	PU-VOR
Polyol	100	100	100	100
Surfactant	3.7	3.7	3.7	3.7
Water	1.4	1.4	1.4	1.4
Catalyst	–	1.3	0.6	0.8
Foaming agent	4.0	3.8	4.1	3.5
Isocyanate	152	138	163	120

TABLE II
Characterization of Polyols Used in Polyurethane Preparation

Polyol	Mn (g/mol)	Viscosity (cP at 25°C)	OH number (mg KOH/g)	Acid number (mg NaOH/g)
CO1	894	52	441	0.77
CO2	1115	51	393	0.75
SO1	1205	2187	477	2.16
VOR	1402	7050	330	0.23

RESULTS AND DISCUSSION

PURs can be prepared using polyols obtained from vegetable oils in nature, such as castor oil, or from functionalized vegetable oils, such as hydroxylated soybean oil.[6,17,18] Soybean and castor oils are cheap and abundantly available in Brazil. Soybean oil consists of a triglyceride with number average molecular weight about 885 g/mol and around 4.5 double bonds/mol, and castor oil is a triglyceride consisting of about 90% ricinoleic acid, which contains one hydroxyl group and one double bond, having an OH-number around 164 mg KOH/g oil (OH functionality of 2.7).

The vegetable polyols were modified as shown in Scheme 1. Soybean oil was firstly hydroxylated[11] and further transesterified with triethanolamine giving a polyol named as SO1. Castor oil was transesterified with triethanolamine (CO1) or glycerin (CO2).

The obtained polyols are a mixture of mono-, di-, triacyglycerols, and unreacted polyfunctional alcohol and were used without further separation for PU preparation. Table II shows the characteristics of the polyols used in the foam formulations. An important characteristic for rigid foam preparation is the polyol OH-number, a range between 300 and 650 mg KOH/g being commonly requested. All modified vegetable polyols show an OH-number higher than commercial VOR polyols. For soybean oil, an increase from zero to 477 mg KOH/g demonstrates the efficiency of the modification to introduce OH groups into the molecule. The same effect can also be observed through the transesterification of the crude castor oil, where the OH-number increases from 164 to 441 and 393 mg KOH/g for CO1 and CO2 polyols, respectively.

The castor oil modification gives a majority of trifunctional products, however soybean oil can yield materials with higher or lower OH-functionality because of its heterogeneous composition.

It is known that the hydroxyl groups generate strong interactions like hydrogen bonds, making shear between the oil molecules more difficult and increasing viscosity. However, after modification, the molecular weight and viscosity of the polyols were lower than Voranol 466N, as seen in Table II. This can be explained because of the formation of mono and

diacylglycerols, which decreases the molecular weight of the polyol, increasing its fluidity. This allows the foam to be processed at room temperature without defects such as bubbles, which frequently occur with high viscosity polyols. Polyols CO1 and CO2 had a lower viscosity than SO1, related to the lower OH number and molecular weight. Hydroxylation increased the molecular weight and viscosity of the soybean oil, probably because of the secondary etherification reaction.[13]

Otherwise, the higher viscosity of polyol-polyether VOR from petrochemical sources is due mainly to the higher molecular weight and linear chemical structure, because it has the lowest OH number. SO1 polyol also showed a higher acid number, resulting from the modification route used, which involves epoxidation-hydroxylation and further transesterification.

Figure 1 shows the DSC curves of polyols at second heating. Polyols CO1 and CO2 presented glass transitions (Tg) at −68 and −60°C, respectively, characteristic for amorphous material. The double bonds of fatty acids, which are in the majority in the cis configuration, do not keep the chains aligned, but entangled. These structures make crystallization more difficult and are responsible for the liquid character of oil at room temperature.

VOR polyol shows similar behavior with Tg at −49°C because of its linear structure. The SO1 curve shows a Tg at −46°C and an endothermic peak at 5°C, with a shoulder at 25°C, as result of the incorporation of functional groups into the molecule, which can interact strongly giving different melting peaks, probably because of the polymorphism of the triglycerides.[19]

PUR foams were prepared by the hand mix method according to the formulations shown in Table I and were characterized according to SEM, mechanical properties, DSC, TGA, and thermal conductivity. Figure 2 presents the foam micrographs
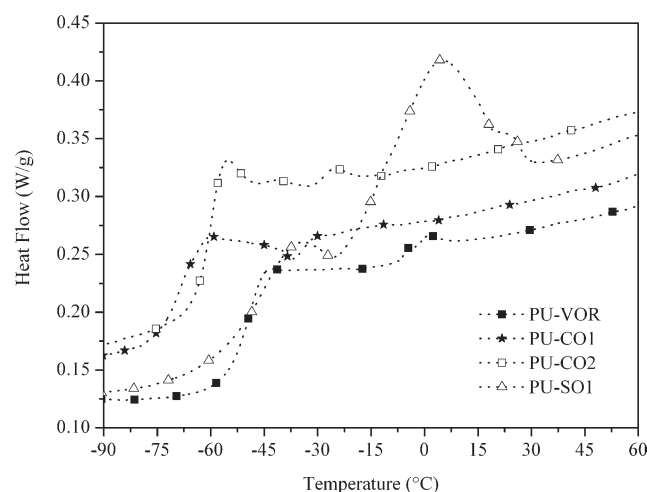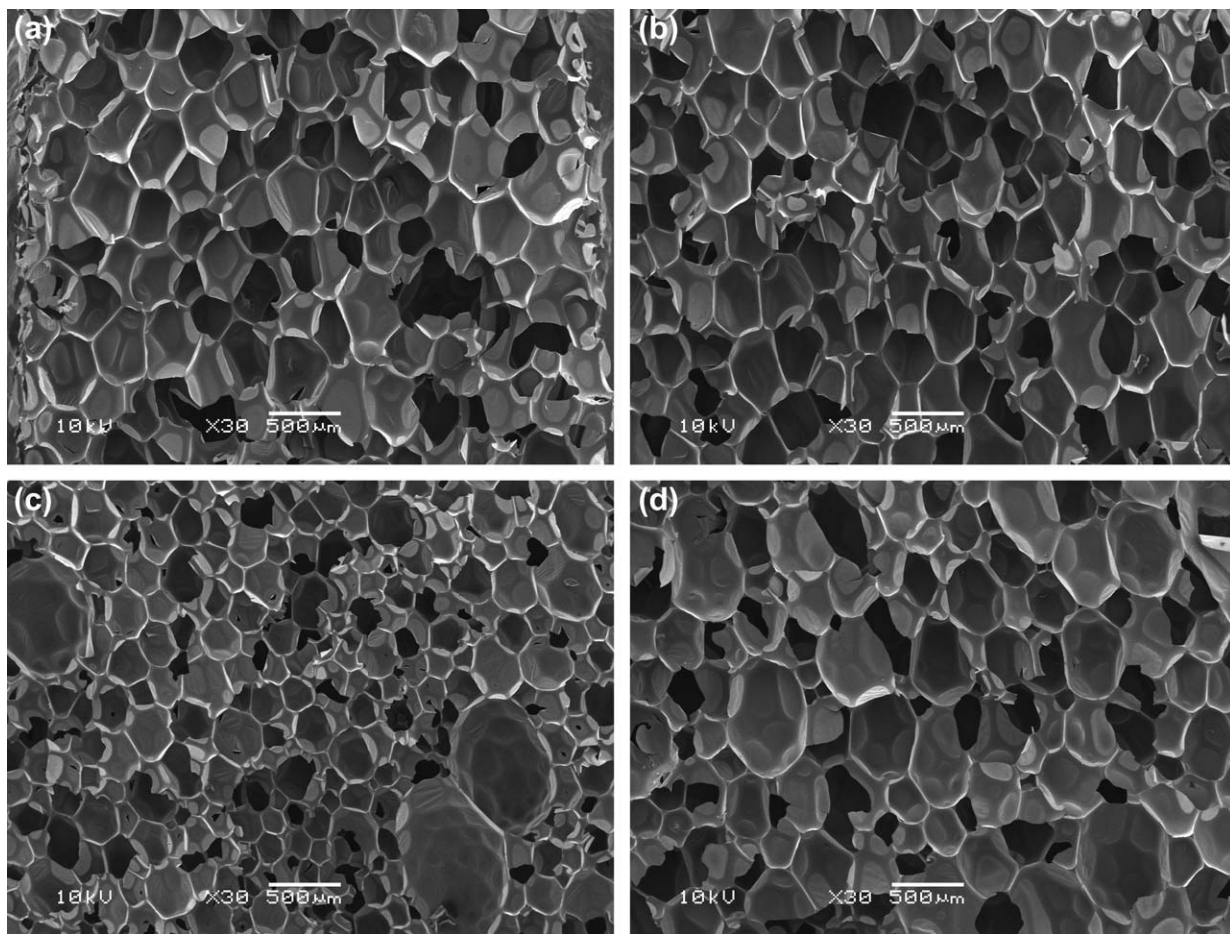

Figure 1 DSC curves of polyols.

Figure 2 Microphotographs of PUR foams in the rise direction (a) PU-CO1, (b) PU-CO2, (c) PU-SO1, and (d) PU-VOR.

and their cellular structures in the rise direction. The foams were prepared in a closed steel box and have a polygonal form because of the compression forces in the box. Microscopic examination of the resulting internal structure reveals that it comprises closed cells and that some open cells are observed because of the cutting effect of samples (black holes in Fig. 2). The cell walls of closed cells are thin membranes, whereas the cell edge struts are much thicker and generally elongated in the foam rise direction, exhibiting an anisotropic geometry.

Castor PU foams, PU-CO1 and PU-CO2, show small pores with thin walls and mean areas of 132 $\pm$ 40 and 128 $\pm$ 37 ($\times 1000$) μm^2 [Fig. 2(a,b)] in a Gaussian size distribution of cells, as can be observed in Figure 3. In the case of soybean PU foam, PU-SO1, the cells have less uniform structures composed of larger elongated strip-like pores (area around 478 $\pm$ 30 [$\times 1000$] μm^2) and smaller pores of 55 $\pm$ 30 ($\times 1000$) μm^2 [Fig. 2(c)] in a non-Gaussian distribution giving an 85 $\pm$ 105 ($\times 1000$) μm^2 mean area (Fig. 4). This irregular distribution can be related to the higher branched polyol SO1, which has OH-groups at different positions, allowing greater elongation of some cells. The same is not true for the

CO1 and CO2 polyols, which consisted mainly of ricinoleic acid (around 90%), having OH-groups always at the same position (C-7). It is noted that the PU-VOR foam showed the largest mean cell
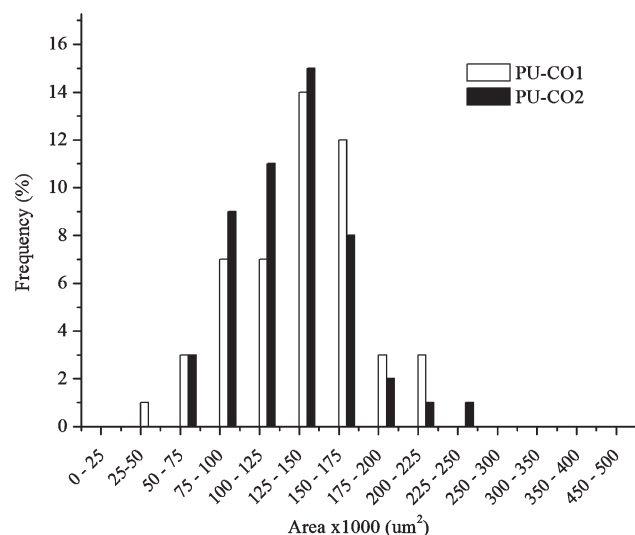

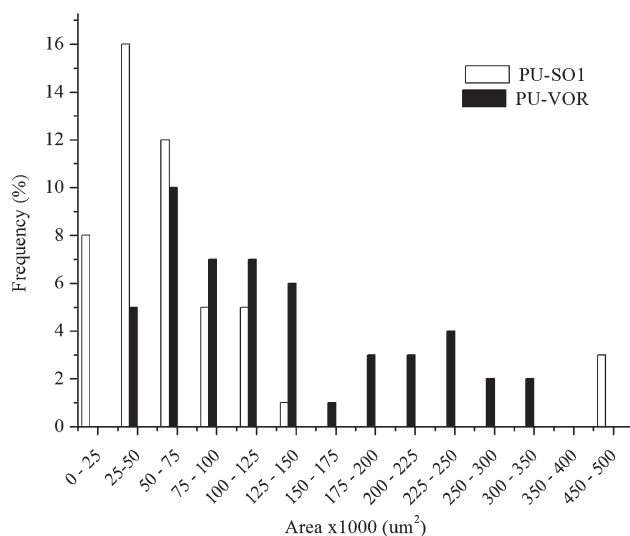**Figure 3** Distribution of measured cell area from PU-CO1 and PU-CO2.

Figure 4 Distribution of measured cell area from PU-SO1 and PU-VOR.

area, 138 ± 88 ($\times 1000$) μm^2, in a non-Gaussian distribution (Fig. 4), probably because of the higher molecular weight allied to the linear chain of Voranol 466N polyol, which stretches more than the branched polyols during foam growth. In this case, the lower pore area is 88 ± 33 ($\times 1000$) μm^2 and the higher pore area is 245 ± 63 ($\times 1000$) μm^2.

Table III shows the physical mechanical properties of PUR foams with similar densities (50 ± 1 kg/m³). Young's modulus and yield stress in the transverse direction are smaller than their values in the rise direction for all foams. This difference in deformation is attributed to anisotropy in the internal cellular structure, arising from the preparation process.[20]

The mechanical response is directly influenced by the chemical structures and functionality of the polyol. PU-VOR presented the best resistance to compression, highest Young's modulus (7.05 MPa) and compressive strength in the rise direction (363 kPa) and in the transverse direction (240 kPa). This probably occurs because of the linear chain of Voranol 466N polyol leading to a high proportion (72%) of pores with a little mean area of 88 ($\times 1000$) μm^2. PU-CO1 and PU-CO2, which have similar molecular structure, density and cell area distribution, pre-

sented similar mechanical behavior, but lower than PU-VOR. It is possible because the internal OH groups of modified polyols have only partly reacted with isocyanate, which explain worse mechanical properties. It was observed during the development of this work, because the foams based on vegetable polyols prepared at NCO/OH ratio lower than 1.2 : 1 showed defects as shrinking.

The lower mechanical response of PU-SO1 can be related to the plasticizing effect of the dangling chains[8] of the SO1 polyol, which has OH-groups in different positions, resulting in a small fraction of cells with higher sizes (6%), which decreases compression strength in the rise direction.

Figure 5(a) shows the TGA curves of the PU foams performed in nitrogen atmosphere. The corresponding derivative curves [Fig. 5(b)] reveal two or three main distinct regions of weight loss for all foams. The weight loss in the first stage is related to urethane bond rupture in the range of 245–284°C for all foams (Table IV). PU-VOR shows a different curve profile and higher thermal stability (Tonset at 284°C) because the VOR polyol is a polyether, whereas the vegetable polyols are polyesters. However, it shows a lower temperature at 50% weight loss (T50%; Table IV).

PU-SO1 presented the lowest Tonset, 245°C, because of the initial decomposition of formiate groups, PU-CO1 and PU-CO2 showed lower weight loss at the first stage, associated with their lower OH-number and consequently fewer urethane bonds formed. The further degradation stages between 325 and 550°C were governed by the decomposition of the polymer chains for all foams. While the decomposition of PU-CO1, PU-CO2, and PU-VOR was almost complete at around 600°C, the decomposition for PU-SO1 was incomplete at 800°C, with 24 w % of residue remaining.

Figure 6 shows tanδ curves of PUR foams, and the presence of γ, β, and glass (α) transitions can be observed. The γ-transitions between -120 and -20°C can be related to the backbone chain motion of the soft segments and the β-transitions, around -21 and -69°C, are related to the rotation of the short groups in the fatty acid chains.[11] The broad peaks on tanδ at higher temperatures are related to

TABLE III
Physical-Mechanical Foam Properties

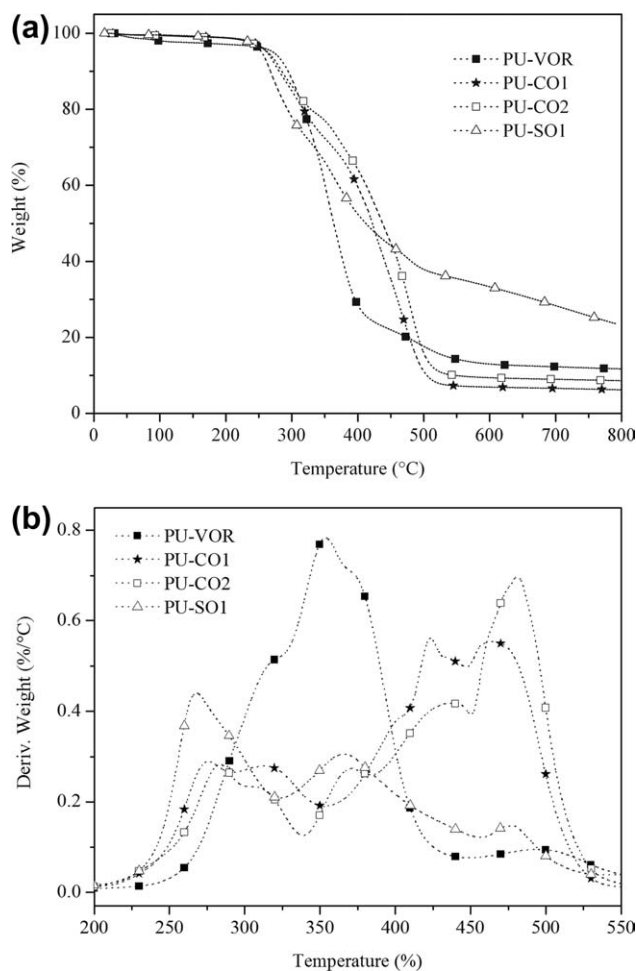|	Density (kg/m³)	Young's modulus rd (MPa)	Young's modulus td (MPa)	Yield stress rd (kPa)	Yield stress td (kPa)	Yield strain rd (%)	Yield strain td (%)
PU-CO1	50	4.1 ± 0.8	2.8 ± 0.8	247 ± 9.0	152 ± 9.0	6.2 ± 0.4	6.6 ± 0.7
PU-CO2	49	5.2 ± 0.1	3.8 ± 0.2	261 ± 2.0	184 ± 13.0	5.8 ± 0.2	5.8 ± 0.5
PU-SO1	49	3.1 ± 0.4	1.7 ± 0.5	179 ± 7.0	167 ± 7.0	7.0 ± 0.9	6.5 ± 0.5
PU-VOR	51	7.1 ± 0.6	4.3 ± 0.8	363 ± 0.7	240 ± 0.4	5.6 ± 0.2	7.2 ± 0.6

rd, rise direction; td, transverse direction.

Figure 5 TG curves (a) and derivative TG (b) of PURs prepared from polyols having different OH functionality with MDI in nitrogen.
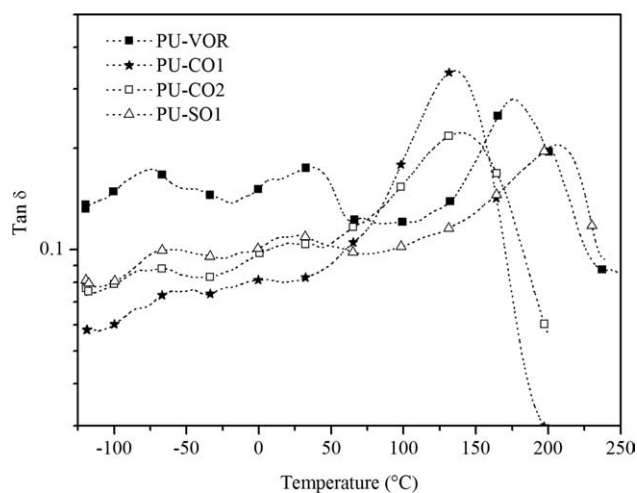

Figure 6 Tan δ curves of oil-based PURs.

CONCLUSIONS

Vegetable oils provide a viable alternate source for polyols in PUR preparation. Through simple organic reactions, we can produce polyols based on castor oil with higher OH-number, allowing direct application in rigid foam preparation. After transesterification with polyfunctional alcohol, an additional increase of the OH-number could be obtained, associated with a decrease in molecular weight and viscosity. These facts allow the modified oil to be processed in the same way as commercial polyols to prepare rigid foam.

In relation to the mechanical response of the foams, it can be concluded that the rigid foams from modified vegetable oil presented behavior slightly lower than the commercial one, showing excellent potential as renewable raw materials for rigid PUR foam production.

the glass transition of rigid isocyanate segments. The PU-VOR prepared with linear polyol presented a Tg at 176°C, because of the high functionality of this polyol. For PU based on branched vegetable polyols, the glass transition increases as the OH-number increases. This can be observed for PU-SO1, which, at 205°C, presented the highest Tg among the vegetable PUs, mostly because of the greater polyol OH number and also to having these groups at different positions, increasing the crosslink density and consequently the Tg. PU-CO1 and PU-CO2 showed lower Tg, at 134 and 139°C, respectively, corresponding to a lower crosslink density.

TABLE IV
Tonset and T50% of Samples

Sample	Tonset (°C)	T50% (°C)
PU-CO1	253	437
PU-CO2	255	421
PU-SO1	245	412
PU-VOR	284	362

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