

Polyurethane Composites Synthesized Using Natural Oil-Based Polyols and Sisal Fibers

S. Michałowski¹, M. A. Mosiewicki^{2*}, M. Kurańska¹, M. I. Aranguren² and A. Prociak¹

¹*Department of Chemistry and Technology of Polymers, Faculty of Chemical Engineering and Technology, Cracow University of Technology, Warszawska 24, 31-155, Cracow, Poland*

²*Instituto de Investigaciones en Ciencia y Tecnología de Materiales- Universidad Nacional de Mar del Plata, Consejo Nacional de Investigaciones Científicas y Técnicas, Av. J. B. Justo 4302, 7600, Mar del Plata, Argentina*

Received July 03, 2017; Accepted August 8, 2017

ABSTRACT: Elastomeric polyurethanes were prepared from a reference polyurethane system modified with biobased polyols synthesized using rapeseed or palm oils. The reference material was modified by replacement of the commercial polyol by 10% of biopolyols and also by addition of sisal fibers up to 5 wt%. The higher functionality of the biopolyols increased the crosslinking density of the networks and this was reflected by an increase in hardness and a decrease in water absorption. The effect of the sisal fibers mainly improved the mechanical and thermomechanical properties of the system with rapeseed oil because of good dispersion and strong fiber-matrix interaction. The system containing palm oil polyol corresponded to an initial formulation of high viscosity and, consequently, the resulting composites presented lower densities than the theoretically expected ones. These results are associated with fiber dispersion problems in the initial reactive mixture.

KEYWORDS: Biopolyols, palm oil, rapeseed oil, polyurethane composites

1 INTRODUCTION

In the second half of the 20th century, the idea of sustainable development played a significant role in shaping the way of thinking about the relationship between the economy, society and environmental resources. Nowadays, to care for the quality of the environment, international-level initiatives are being undertaken in order to address global environmental problems [1]. Generally, petrochemical raw materials are mainly used in the production of polyurethanes (PUs). The polyaddition reaction of isocyanates with compounds that contain polyols with hydroxyl groups results in PUs [2]. Currently, PUs are one of the fastest developing groups of polymeric materials. According to the report, "Polyurethane Market – Global Forecast to 2021," the global PU market is projected to achieve ca. USD 60 billion by 2021 at a CAGR (compound annual growth rate) of 5.6% from 2016 to 2021.

A significant advantage of PU materials is the possibility to design their properties by applying compounds of diverse chemical structures in their

synthesis [3, 4]. Changing the type of raw materials, their relative volumetric ratio, as well as the appropriate design of the process of synthesis, enables the production of PU materials with apparent density in a range from 10 to 1100 kg/m³ [5–10]. The adequate selection of chemicals allows for the obtainment of porous (flexible and rigid), solid, structural, fibrous and leather imitation materials, as well as elastomers, adhesives and binders [5, 11–14]. The largest share in the production of PU materials corresponds to flexible foams used in the furniture and automotive industries.

The observed trends, legislative requirements and limited crude oil resources are forcing the producers of PU materials to use raw materials derived from renewable sources. In the case of PU foams, potential components are polyols derived from vegetable oils [15–20]. In the literature, there is an increasing number of studies regarding different methods of converting vegetable oils into reactive compounds which can be used as raw materials in the synthesis of different polymers [21–23]. Biopolyols may be obtained from a variety of vegetable oils, including rapeseed, linseed, sunflower, palm and castor oils [24–27]. The chemical modification is carried out through the transformation of double and/or ester

*Corresponding author: mirna@fi.mdp.edu.ar

bonds present in the structure of natural oils. The different strategies for functionalization of vegetable oils allow for the obtainment of natural oil-based polyols with various chemical structures. In the case of epoxydation and opening of oxirane rings, the structure is dependent on ring-opening reagents [21, 22, 28]. Water, the cheapest ring-opening agent, is used to obtain biopolyol through one-pot synthesis. In such a reaction, one oxirane ring generates two secondary OH groups [25, 26]. It is also possible to obtain biopolyols with primary and secondary hydroxyl groups by using, e.g., ethylene glycol, diethylene glycol and 1,2-propanediol [15]. Ozonolysis of unsaturated bonds allows for the obtainment of biopolyols with primary hydroxyl groups and functionality of 3. Higher functionality (ca. 4.0 or higher) can be obtained using other methods such as hydroformylation of fatty acid esters followed by a reduction reaction to introduce hydroxymethyl groups [16]. Hydroxyl derivatives of natural oils can be obtained in reactions of transamidization and transesterification with diethanolamine and triethanolamine, respectively [10, 13, 17].

In recent years, the development of natural fiber reinforced composites has also experienced large growth. The incorporation of natural fibers with competitive mechanical properties per unit weight into different polymer matrices allows for the reduction of manufacturing cost [29]. Different types of natural fillers, such as wood fibers, sisal fibers, flax fibers, hemp fibers and microcellulose, are being used for the modification of PU materials [30–34]. In particular, sisal fibers have been used in different polymeric structures, including polyurethanes, with the main focus being the mechanical properties [35–39]. However, the wide field of polyurethanes requires a study for each different matrix.

In this work, a commercial synthetic polyol was used to prepare the reference material, a flexible and unfoamed PU, which was modified with the addition of rapeseed oil and palm oil polyols in the formulation and also with the incorporation of unmodified sisal fibers. Physical, thermal and mechanical characterizations were carried out and the behaviors of the different materials were analyzed and compared.

2 MATERIALS AND METHODS

Petrochemical polyol JEFFOL® G-31-35 (properties are reported in Table 1) was supplied by Huntsman Polyurethanes. Rapeseed (RP) and palm (PP) oil-based polyols were synthesized at Cracow University of Technology. In the first step of the synthesis of the natural oil-based polyols, the unsaturated fatty acid

segments in triglycerides were reacted with peracetic acid to form epoxidized oil. Through the epoxidation, the double bonds of the triglycerides were transformed into oxirane rings [2, 12, 18]. The resulting mixture was neutralized with water. The remaining unreacted water was removed under vacuum. The conversion of double bonds was determined by measuring iodine values before and after epoxidation. In the second step, the epoxidized oils were converted into polyols using different ring-opening reagents, water in the case of PP and diethylene glycol in the case of RP. A scheme of synthesis of both polyols is shown in Figure 1. Titration method was applied to identify epoxy values in both epoxidized derivatives. Selected properties and gel permeation chromatography (GPC) results of the biopolyols as well as those of the petrochemical polyol are shown in Table 1.

The PUs were obtained by the reaction of the polyols with polymeric diphenylmethane diisocyanate (pMDI – Rubinate 5005, Huntsman Polyurethanes, equivalent weight of 131 g/eq). The catalyst used was dibutyltin dilaurate (DBTDL) (Sigma-Aldrich).

Sisal fibers (SFs) (Cellton, Brazil) were incorporated as natural fillers into the PU systems (Table 2). Firstly, sisal fibers were washed with a neutral detergent and then dried in a vacuum oven. After drying, the fibers were cut and then fractionated using proper sieves to obtain a fraction with a fiber length from 2 mm to 5 mm. This fraction of sisal fibers (Figure 2) was subjected to additional drying at 70 °C for 48 h prior to their addition to the PU systems.

Table 1 Selected properties of synthetic polyol (Jeffol G-31-35) and palm and rapeseed oil-based polyols (PP and RP, respectively).

| Property | Jeffol G-31-35 | RP | PP | |
|---|----------------|---------|-----------|-----------|
| Hydroxyl value, mgKOH/g | 35 | 264.2 | 102.0 | |
| Water content, % | 0.10 | 0.66 | 0.12 | |
| Iodine value, gI ₂ /100g | – | 3.2 | 7.8 | |
| Functionality | 4.4 | 6.6 | 3.0 | |
| Number-average molecular weight (Mn), g/mol | 6984 | 1410 | 1648 | |
| Weight-average molecular weight (Mw), g/mol | 9539 | 6014 | 5884 | |
| Polydispersity | 1.37 | 4.26 | 3.57 | |
| Viscosity, mPa·s. | 25 °C | 891 ± 2 | 8562 ± 45 | –* |
| | 50 °C | 273 ± 1 | 1385 ± 3 | 2319 ± 33 |

*At 25 °C PP polyol is a solid

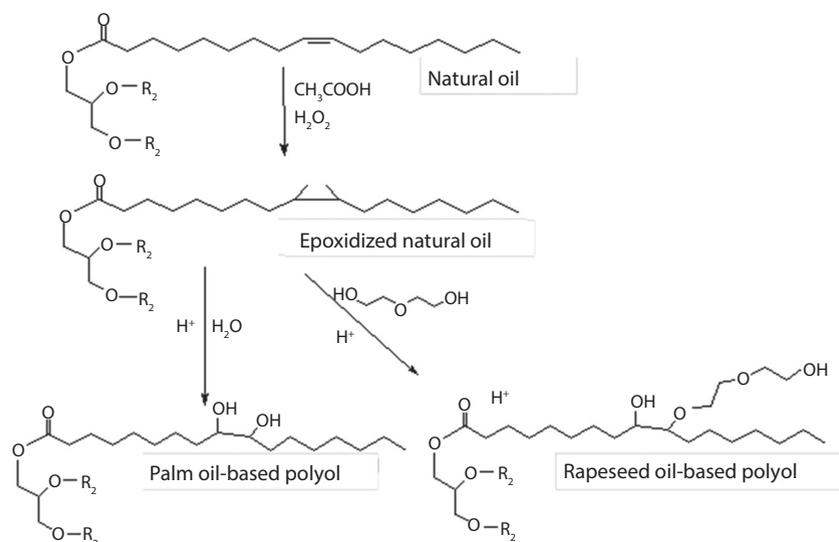


Figure 1 Scheme of synthesis of palm oil-based polyol (PP) and rapeseed oil-based polyol (RP).

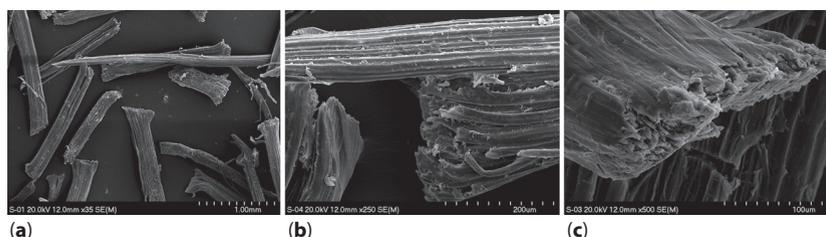


Figure 2 SEM microphotographs of sisal fibers at different magnifications: (a) x35, (b) x250, (c) x500.

2.1 Preparation of Elastomeric Composites

A mixture of polyols (Table 2) was stirred with the catalyst and the fibers in order to prepare the polyol premix (component A). Next, PU elastomeric biocomposites were obtained in a one-step mixing process of component A with component B that consisted of the polymeric diisocyanate (pMDI). Finally, the prepared mixtures were poured into a metal mold, which had a temperature of about 70 °C. Then, the mold was closed and placed in an oven at 70 °C for a period of 1 hour. After that, the mold was taken from the oven and elastomeric material was removed from the mold. Each sample was conditioned at 70 °C for 24 hours. The formulations used to prepare the different materials are shown in Table 2. The molar ratio of NCO to OH groups was adjusted to 1.05 in all cases.

The reference material (PU) contained only petrochemical polyol while the modified ones, PU/RP and PU/PP, were obtained by replacing 10 wt% of petrochemical polyol with the biopolyol based on rapeseed (RP) or palm (PP) oils, respectively.

Table 2 PU formulations of synthesized materials.

| Components | PU | PU/RP | PU/PP |
|--|---------------|-------|-------|
| Jeffol G-31-35, g | 100 | 90 | 90 |
| RP, g | – | 10 | – |
| PP, g | – | – | 10 |
| Catalyst, g | 0.1 | | |
| Isocyanate index* | 1.05 | | |
| Sisal fibers, wt% of polyurethane total mass | 1.0, 3.0, 5.0 | | |

*Molar ratio of NCO/OH groups

2.2 Characterization Methods

Selected properties of the obtained materials were evaluated according to the following methods.

The density of the materials was calculated as the weight/volume ratio of specimens cut in the shape of rectangular prisms of size ca. 40 mm × 5 mm × 1.5 mm, measured with a caliper.

The morphology of materials and fibers was analyzed using a scanning electron microscope (Hitachi

S-4700). The samples were cut at room temperature and sputter-coated with graphite before testing to avoid charging.

Thermogravimetric analysis (TGA) was performed using a Shimadzu TGA-50 thermogravimetric analyzer at a heating speed of 10 °C/min under air atmosphere. Samples of about 10 micrograms were used in the measurements and the scans were performed between 30 °C and 600 °C.

Water absorption (immersion) of the materials was determined according to ISO 62:1999 by immersing the samples in distilled water. The weight of the samples was recorded at different periods of time and until constant weight was achieved.

Dynamic mechanical analysis of the cured samples was determined using an Anton Paar Physica MCR rheometer. Torsion geometry was used with solid rectangular samples of length 30 mm, width 10 mm and thickness 2 mm. Temperature sweep measurements were performed at a heating rate of 10 °C·min⁻¹, frequency of 1 Hz, and applied deformation of 0.1% to ensure working in the linear viscoelastic range.

Uniaxial tensile tests were carried out using an Instron 8501 universal testing machine, according to ASTM D638-94. Specimens were cut from each sample using a dog-bone shaped driller and tested at a cross-head speed of 1 mm·min⁻¹. Four specimens were tested for each sample. The elastic tensile modulus, the stress and the deformation to rupture were calculated from the obtained stress-strain curves and averaged over the replicate results.

3 RESULTS AND DISCUSSION

Figure 3 shows density and hardness values of the obtained materials. The results denote that density was not significantly modified in the system where the RP polyol was used to partially replace the petrochemical

one, even with the addition of sisal fibers. On the other hand, the partial replacement of synthetic polyol by PP in the PU formulation did not modify the density, but the further addition of fibers slightly decreased this property.

The density of the sisal fibers, taken as 1.45 g/cm³ [40], is considerably higher than that of unfilled polyurethane systems (PU, PU/RP and PU/PP). Thus, in a completely solid material (non-foamed and with the lumen of fibers completely filled), an increase in the density value is expected with the addition of sisal fibers. However, the low fiber concentrations used in the study were not enough to sensibly affect this property in the reference PU and PU/RP systems. Table 3 presents the comparison of the experimental densities and the theoretical ones calculated with the following rule of mixtures:

$$\frac{1}{\rho_c} = \frac{W_m}{\rho_m} + \frac{W_f}{\rho_f} \tag{1}$$

where ρ is the density and W is the weight fraction, and the subscripts c , m and f correspond to composite, matrix and filler, respectively. The value of ρ_m (1.09, 1.11 and 1.08 g cm⁻³ for the PU, PU/RP and PU/PP, respectively) was determined experimentally, and ρ_f was taken as 1.45 g cm⁻³, as was already indicated [40].

From the densities determined with Equation 1 and the data experimentally measured for this property, the void volume fractions (V_v) in the composites were calculated, assuming additivity of the volumes:

$$V_v = \frac{\rho_{c\text{theoretical}} - \rho_{c\text{experimental}}}{\rho_{c\text{theoretical}}} \tag{2}$$

The decrease in experimental density values with the incorporation of SF in the system of PU/PP could be due to the presence of additional holes (fiber empty lumens, trapped air, bubbles due to reaction of

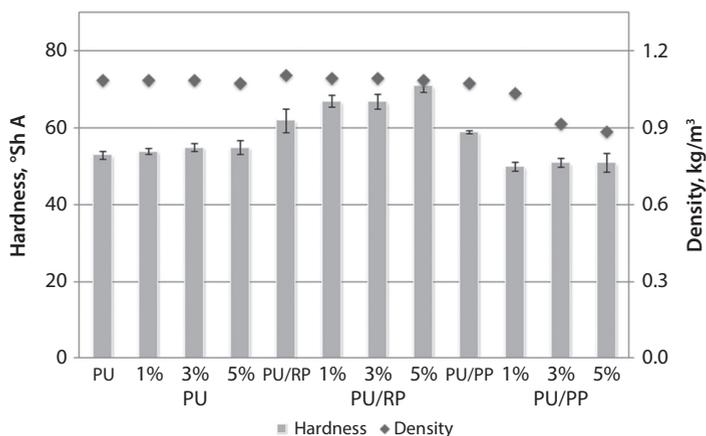


Figure 3 Hardness and density of synthesized materials.

humidity with the PU formulation) that would oppose the effect of the added fibers. As can be observed in Table 1, the viscosities of the biopolyols are considerably higher in comparison with the commercial polyol (at 25 and 50 °C), but this is especially so for the PP polyol. In fact, the PP polyol is solid at room temperature and its homogeneous incorporation into the initial reactive mixture is more difficult. Clearly, for this reason, the wetting of the fibers is also more difficult to achieve due to the higher viscosity of such composition. Results in Figure 4 agree with the previous discussion denoting a significant increase of void volume fraction with SF content in the system of PU/PP.

The replacement of the petrochemical polyol with the biopolyol RP to modify the PU system caused an increase in the hardness of the prepared materials. This fact is associated with a higher hydroxyl number of the biopolyol RP (in comparison with the Jeffol G-31-35 used in the reference system), added to the fact that this biopolyol has many primary OH groups, as the difference from the PP and both characteristics contribute to reach a higher crosslinking density. As expected, the addition of sisal fiber to the system modified with biopolyol RP increased the hardness of the materials as the content of rigid fibers was increased.

Table 3 Experimental and theoretical densities of the composites.

| Sisal fibers, SF (wt%) | Experimental Densities (g/cm ³) | Theoretical Densities (g/cm ³) |
|------------------------|---|--|
| PU | | |
| 0 | 1.09 ± 0.002 | *1.090 |
| 1 | 1.09 ± 0.002 | 1.092 |
| 3 | 1.09 ± 0.001 | 1.098 |
| 5 | 1.08 ± 0.002 | 1.103 |
| PU/RP | | |
| 0 | 1.11 ± 0.001 | *1,110 |
| 1 | 1.10 ± 0.001 | 1,112 |
| 3 | 1.10 ± 0.001 | 1,118 |
| 5 | 1.09 ± 0.001 | 1,123 |
| PU/PP | | |
| 0 | 1.08 ± 0.001 | *1.080 |
| 1 | 1.04 ± 0.001 | 1.083 |
| 3 | 0.92 ± 0.001 | 1.088 |
| 5 | 0.89 ± 0.001 | 1.094 |

*The densities of the unfilled polymeric matrices are taken equal to the experimental values.

A different trend was observed when the reference PU system was modified with the biopolyol PP and sisal fibers were added. Only in the case of the unfilled materials, the hardness of the PU/PP was higher than that of the reference material, which is directly related to the difference in the hydroxyl values and functionalities of the biopolyol and the petrochemical one (Figure 3). However, the addition of sisal fibers to the formulations containing PP resulted in a slight reduction of hardness irrespective of the fiber content, which is related to the reduced density of the materials modified with sisal fibers compared to the unfilled PU/PP. Figure 4 illustrates the changes in density of the composites as volume fraction of potential voids (empty lumens, incompletely wetted fiber surfaces, trapped air, etc.). The difference in the behavior of the PP-derived system is made clearly evident in this plot.

3.1 Morphological Analysis

Microphotographs obtained by SEM of selected materials are shown in Figure 5. The morphology of the unfilled materials presents a compact structure without bubbles. However, the samples prepared with the biopolyols show rougher fracture surfaces because of the higher heterogeneity in the PU networks (Figure 5a–c). The effect of the sisal fibers in the reference and modified PU systems is also shown in Figure 5. The pictures in Figure 5d–f (x50) corresponding to composites with 3 wt% of SF in the PU, PU/RP and PU/PP, respectively, denote that the introduction of fibers leads to macroscopically similar fracture surfaces (low magnification). However, the observation at higher magnification (Figure 5g–j) denotes that the lumens of the fibers are not completely filled with the matrix, mainly in the case of the PU/PP system in all the analyzed compositions. SEM micrographs suggest that the main source of voids in the composites is the empty lumens,

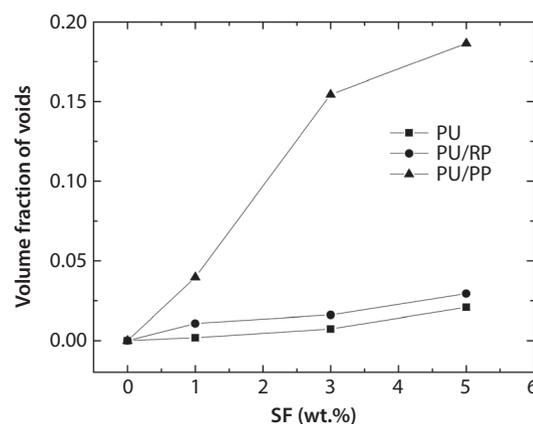


Figure 4 Void volume fraction as a function of SF content.

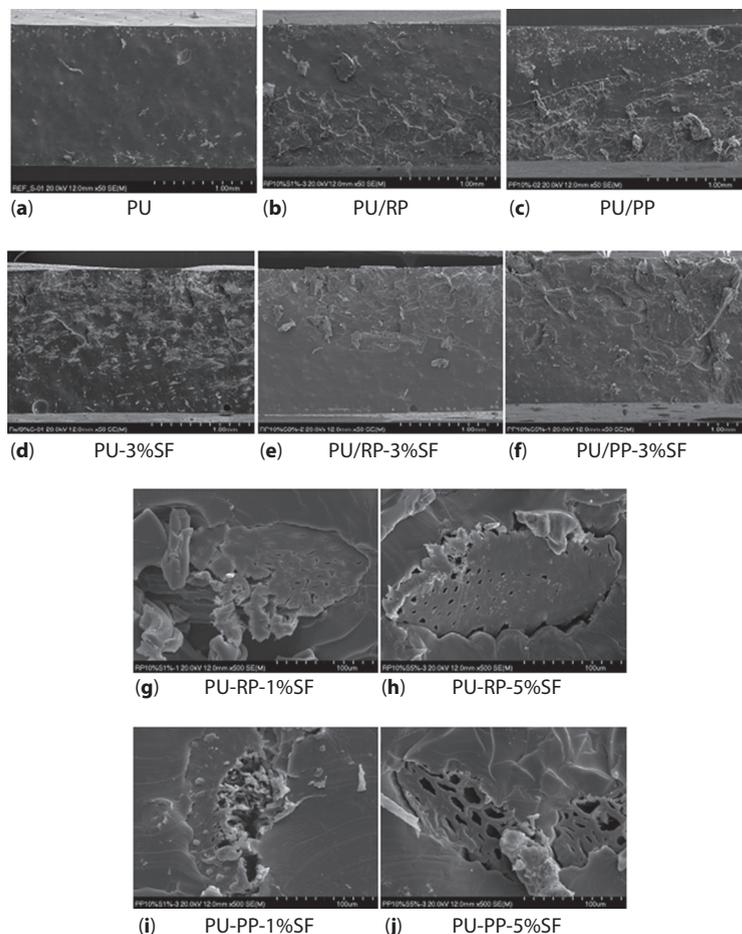


Figure 5 The SEM images of obtained PU materials with and without fibers.

a feature that appears to be more important in the PP system (Figure 4). These defects are caused primarily by a higher initial viscosity of the PU/PP formulation compared to the PU/RP and PU systems. With increasing content of sisal fibers in the composition, the initial viscosity becomes even higher and it is more difficult to wet and fill the interior of the fibers with the reactive liquid mixture. The result of such facts is reflected in the lower density of PU/PP modified with sisal fibers, as was previously discussed. On the other hand, good interfacial adhesion is observed around several particles and the fibers are cut at the level of the matrix fracture surface, which also indicates a rather good interfacial adhesion. The hydroxyl groups in the natural fibers can take part in the curing reaction with the isocyanate groups, a fact that can contribute to improve the strength of the fiber-matrix interactions [41].

3.2 Thermal Degradation Analysis

Figure 6 shows thermograms (residual weight (%) as a function of the temperature) for the sisal fibers,

unfilled polyurethane (reference, PU/RP and PU/PP) and filled polyurethane systems, all of them with 5 wt% of sisal fibers. All the curves (polyurethanes and its composites) present one single step of degradation in the range of 300 °C and 430 °C. The comparison of thermal degradation between the unfilled polyurethanes denotes that the replacement of the commercial polyol by the biobased polyols shifts the thermal degradation of the polyurethane to higher temperature (Figure 6a). The most important effect is observed in the PU/RP due to the higher functionality of the RP in comparison with the other polyols, increasing the crosslinking density and, consequently, the thermal stability of the material. Since the NCO/OH ratio was kept constant, the polyurethanes formulated with the polyols with higher hydroxyl values contained higher weights of isocyanate. Thus, besides the logical contribution of crosslinking, the increased concentration of aromatic pMDI (by weight) should have a positive effect on the thermal stability.

The effect of the fibers (5 wt%) on the thermal degradation of the modified materials can be observed

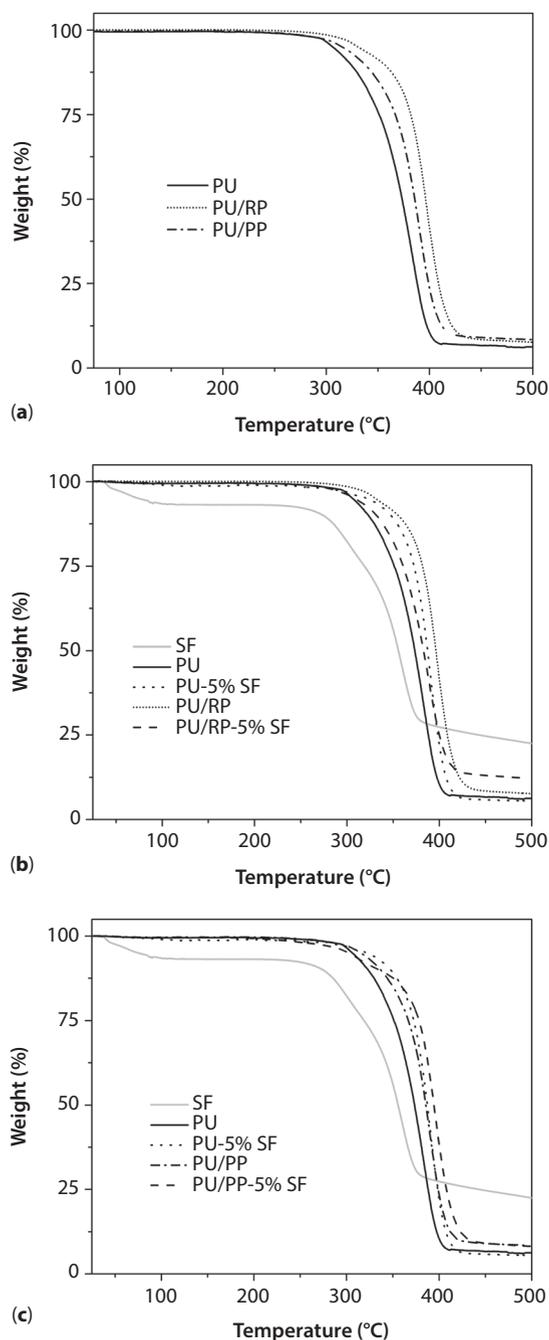


Figure 6 TGA curves of reference PU (a) and modified elastomers (PU/RP and PU/PP) with and without SF (b,c).

in Figure 6b,c. At temperatures below 120 °C the sisal fibers lose the moisture absorbed because of the hydrophilic nature of natural fibers. However, the unfilled polyurethane systems and the corresponding composites do not show this loss. This could be associated with the fact that the content of fibers is small enough to not modify the more hydrophobic nature of the unfilled PUs.

For the reference PU system, the main degradation step starting at temperatures higher than 300 °C shifts to some extent to higher temperatures with the addition of sisal fibers, denoting higher thermal stability. The reaction between the pMDI and the hydroxyl groups of the fibers originates new covalent bonds, contributing to the higher thermal stability of the filled films.

The effect of the fibers in the PU/RP is not significant in this step of degradation; however, it can be observed that at temperatures higher than 400 °C the PU/RP with 5% of sisal fiber present higher residual mass (char) than the unfilled material. The amount of char corresponding to the composite is intermediate between that of the matrix and the SF, although the value is higher than that which can be calculated from the weighed cumulative contributions of the polyurethane and the fibers. In the PU/PP system, the incorporation of fibers does not significantly modify the thermograms. The poor dispersion of PP in the initial reactive mixture can provoke incomplete reaction of the hydroxyl groups in the polyol with the isocyanate. This last component can react with the available OH groups in the SF, and in this way the composite can degrade as a unique component (matrix and fibers taking part in a chemical network) showing a char close to that of the unfilled matrix. Comparatively, in the PU/RP system the crosslinking of the biopolyol and pMDI was more efficient, leaving free NCO to react with the natural fibers. On the other hand, the wetting of the fibers and lumen filling was good in this system and the final outcome is an intermediate onset temperature and increased char.

3.3 Water Absorption

A study of the effect of biocomponents on water absorption behavior of the final materials was also performed (Table 4). The application of both biopolyols had a beneficial impact by reducing water absorption. It can be explained as an effect of decreasing polarity in the case of samples modified with natural oil derivatives. Additionally, higher crosslinking density in the PU/RP and PU/PP in comparison with the reference PU generates tighter structures with less polar groups available to interact with water. The increasing addition of fibers to PU/RP mildly increases the water absorption. In the system with PP, the incorporation of fibers largely increases the water absorption but without a clear trend with increasing amount of fibers. It is apparent that the main reason for the large difference in this series is the reduced density of the composites, which, as was already discussed, is related to the high viscosity of the palm oil and the resulting high void volume fraction.

Table 4 Water absorbance of obtained PU materials.

| Sisal fibers, SF (wt%) | 24 h | 48 h | 130 h | Increase with respect to the corresponding unfilled PU at 130 h (%) |
|------------------------|--------------|--------------|--------------|---|
| PU | % vol | % vol | % vol | |
| 0 | 13.5 ± 0.4 | 15.0 ± 0.3 | 15.8 ± 0.3 | |
| 1 | 13.5 ± 0.1 | 14.8 ± 0.0 | 15.8 ± 0.1 | 0.0 |
| 3 | 15.5 ± 0.2 | 16.4 ± 0.4 | 17.9 ± 0.0 | 13.3 |
| 5 | 15.7 ± 0.3 | 17.2 ± 0.3 | 18.1 ± 0.2 | 14.5 |
| PU/RP | | | | |
| 0 | 7.7 ± 0.4 | 8.5 ± 0.7 | 8.9 ± 0.7 | |
| 1 | 7.8 ± 0.3 | 8.4 ± 0.9 | 9.1 ± 0.9 | 2.2 |
| 3 | 7.9 ± 0.5 | 8.8 ± 0.3 | 9.5 ± 0.6 | 6.7 |
| 5 | 8.5 ± 0.0 | 8.9 ± 0.4 | 9.9 ± 0.2 | 11.2 |
| PU/PP | | | | |
| 0 | 8.1 ± 0.2 | 9.3 ± 0.5 | 10.0 ± 0.5 | |
| 1 | 10.1 ± 0.0 | 11.7 ± 0.4 | 13.6 ± 0.3 | 36.0 |
| 3 | 9.5 ± 0.7 | 11.1 ± 0.3 | 12.7 ± 0.8 | 27.0 |
| 5 | 9.8 ± 0.5 | 11.1 ± 0.0 | 13.4 ± 0.6 | 34.0 |

3.4 Dynamic Mechanical Analysis

Figure 7 shows the dynamic-mechanical properties of the different PU systems with sisal fibers. Figure 7a,c,e shows the shear storage modulus for the reference PU, the PU/RP system and PU/PP system, respectively. In the three systems, differences in crosslinking density in the matrix, dispersion of the fibers into the matrices and reaction between OH groups in the SF and free isocyanate seem to be the most important factors affecting the dynamic-mechanical properties.

In the reference PU system, the presence of sisal fibers slightly increases the G' in the rubbery region associated with the incorporation of rigid fibers in a polymer of low modulus. However, the PU/RP denotes an increase in this property in all the analyzed temperature ranges with a more important change in the rubbery modulus. This fact could be associated with good dispersion of the particles into the matrix and strong interaction between them. The PU/PP system does not suffer an important change in the storage modulus through the whole temperature range. Poor dispersion and low filling of the lumens of the particles because of the high viscosity of the initial reactive mixture are the effects that counterbalance the expected effect of adding rigid fibers to the polymer, leading to the observed final dynamic-mechanical behavior.

With respect to T_g (determined as the temperature corresponding to the maximum in the $\tan \delta$ peak),

the reference PU system shows a small decrease in the T_g with the addition of SF (-54.2 °C to -55.5 °C for 0^g and 5 wt% of SF, respectively). On the other hand, the PU/RP suffers an important increase in T_g with the addition of just 1 wt% SF (from -54.2 °C to -49.5 °C), however, higher amounts of filler (3 and 5 wt%) do not modify the T_g values. The increase in T_g , as mentioned previously for the G' increase, is related to good distribution and interaction of the particles and the matrix generating high cohesive density.

Finally, in the PU/PP system (as was observed from the trend of the storage modulus) the T_g values are almost the same with or without SF.

In all cases, as was expected, the height of the $\tan \delta$ peak decreases with the presence of SF with a more pronounced effect in the PU/RP system because of the reduced mobility of the polymer in the presence of well-distributed fibers, leading to decrease of the damping capacity (energy dissipation). The heterogeneity of the networks also results in the widening of the peak.

The comparison of the $\tan \delta$ curves of the unfilled PUs shows that the height of the peak in the system modified with PP is lower than in the other ones (PU and PU/RP). In this case, the less homogenous network and lower damping capacity result from the reduced dispersion of the polyol of very high viscosity (solid polyol at room temperature) in the reactive blend.

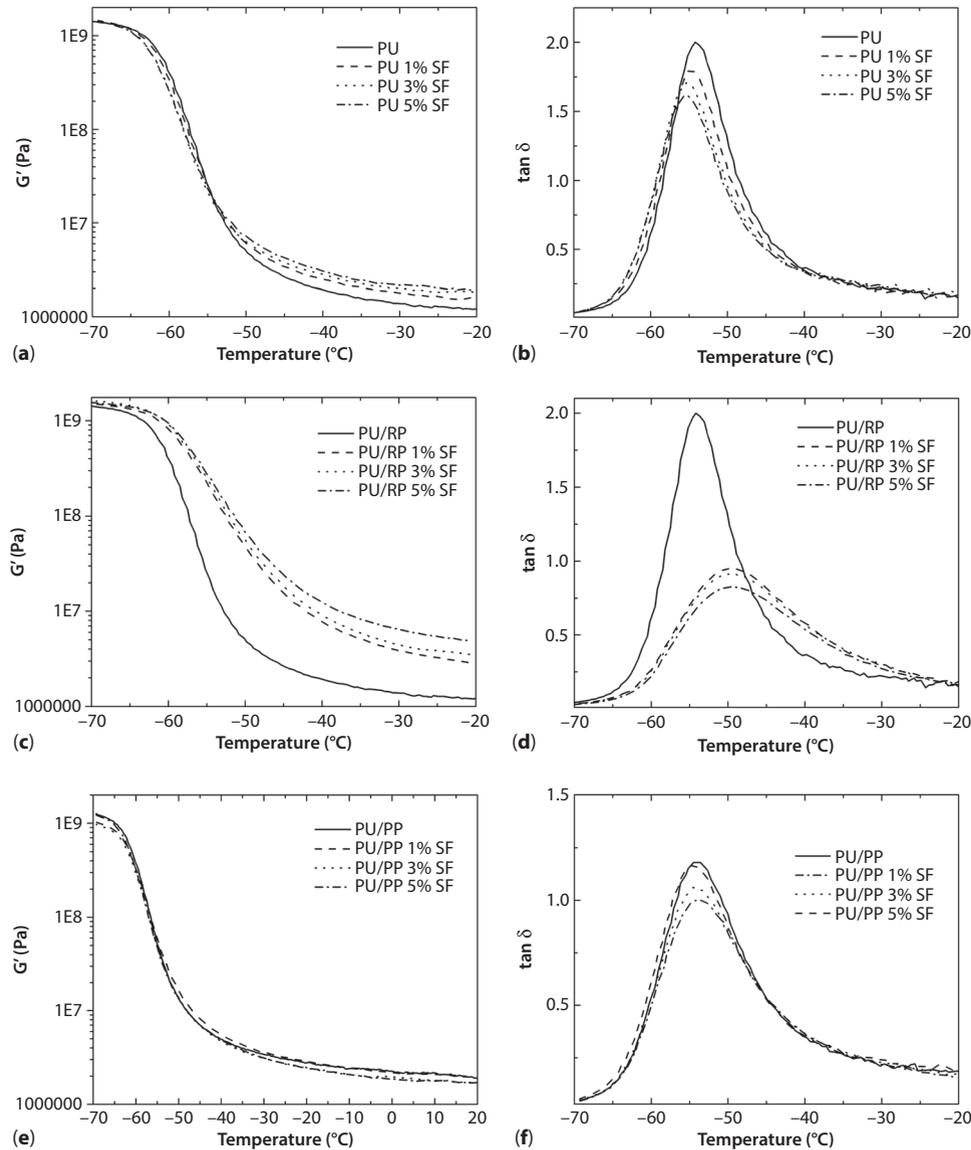


Figure 7 Temperature scans of G' and $\tan \delta$ for PU system (a,b), PU/RP system (c,d) and PU/PP system (e,f) with and without SF.

3.5 Tensile Tests

The modification of the reference system with biopolyols also caused significant changes in the mechanical properties of the materials (Table 4). The replacement of petrochemical polyol with the biopolyol RP caused an increase of the tensile strength, while modification with the biopolyol PP resulted in the reduction of this parameter relative to the reference PU material. Although the functionality of the PP was the highest, the material could not fully benefit from this fact because of the high viscosity of the oil that prevented good mixing to obtain a homogeneous sample. The additional decrease of tensile strength and elongation at break for PU/PP composites can be related to

a higher content of void volume and, consequently, lower density of the corresponding composites, as already reported. The incorporation of 1 wt% sisal fibers leads to the reduction of the modulus (the effect of the resultant reduced density is more important than the increased content of fibers). However, as more sisal is added the modulus moderately increases as a response to the addition of the fibers of high modulus. Clearly, the effect of the sisal fibers is closer to the expected behavior for the reference system and the RP series. That is, the polyurethane series that is prepared from the high functionality RP has higher modulus (higher crosslinking density) and the addition of the fibers into the composites produces an increase of the modulus (Table 5). The contribution of the void

Table 5 Mechanical properties of elastomers modified with biopolyols based on rapeseed and palm oil and sisal fibers.

| Sisal fibers, SF (wt%) | Modulus, E MPa | Tensile strength, MPa | Elongation at break, % |
|------------------------|----------------|-----------------------|------------------------|
| PU | | | |
| 0 | 1.45 ± 0.04 | 0.54 ± 0.03 | 52.4 ± 4.1 |
| 1 | 2.04 ± 0.13 | 0.55 ± 0.04 | 37.8 ± 5.5 |
| 3 | 2.03 ± 0.13 | 0.55 ± 0.03 | 39.0 ± 3.0 |
| 5 | 2.15 ± 0.17 | 0.53 ± 0.03 | 36.3 ± 4.1 |
| PU/RP | | | |
| 0 | 2.43 ± 0.20 | 0.89 ± 0.08 | 51.7 ± 2.8 |
| 1 | 3.48 ± 0.27 | 0.73 ± 0.04 | 27.7 ± 3.2 |
| 3 | 4.00 ± 0.25 | 0.80 ± 0.06 | 25.9 ± 2.5 |
| 5 | 4.38 ± 0.45 | 0.79 ± 0.07 | 24.0 ± 2.4 |
| PU/PP | | | |
| 0 | 1.88 ± 0.12 | 0.41 ± 0.14 | 31.1 ± 9.7 |
| 1 | 1.32 ± 0.13 | 0.28 ± 0.07 | 30.6 ± 4.7 |
| 3 | 1.60 ± 0.11 | 0.37 ± 0.07 | 31.2 ± 5.9 |
| 5 | 1.79 ± 0.14 | 0.30 ± 0.07 | 24.8 ± 3.5 |

volume was much lower in this series of composites and closer to that observed for the petrochemical PU series.

4 CONCLUSIONS

The investigations confirmed a possibility to modify a commercial polyurethane-based elastomer formulation with biopolyols from rapeseed oil and palm oil in order to obtain biocomposites with different mechanical properties. The addition of sisal fibers to the polyurethane systems was also evaluated.

The differences in viscosity and functionality of the biopolyols are critical characteristics affecting the final properties of the materials. This highlights the importance of considering the characteristics of the biopolyol to be incorporated as well as the interaction with filler/reinforcement being considered in the formulation of the composites.

The composites prepared with rapeseed oil polyol presented the best dispersion and interaction between the sisal fibers and the polyurethane matrix, leading to the largest overall improvement in final properties of the obtained composites.

ACKNOWLEDGMENTS

This research had financial support in the frame of the People Programme (Marie Curie Actions – International Research Staff Exchange Scheme) of the European

Union's Seventh Framework Programme under REA grant agreement n° PIRSES-GA-2012-318996, titled "Bio-based polyurethane composites with natural fillers" (Acronym: BIOPURFIL). Thanks also go to the National University of Mar del Plata, CONICET and ANPCyT in Argentina and Cracow University in Poland.

REFERENCES

1. P. Kosmela, L. Zedler, K. Formela, J. Haponiuk, and L. Piszczyk, Recent developments in polyurethane foams containing low-cost and pro-ecological modifiers. *Chem. Chem. Technol.* **10**, 572–580 (2016).
2. M. Kurańska and A. Prociak, The influence of rapeseed oil-based polyols on the foaming process of rigid polyurethane foams. *Ind. Crop. Prod.* **89**, 182–187 (2016).
3. K. Mizera and J. Ryszkowska, Polyurethane elastomers from polyols based on soybean oil with a different molar ratio. *Polym. Degrad. Stab.* **132**, 21–31 (2016).
4. W. Karalus, J.R. Dąbrowski, M. Auguścik, and J. Ryszkowska, Tribological properties of biodegradable polyurethanes of various structure and content of rigid elements. *Polimery* **61**, 509–518 (2016).
5. E. Malewska, S. Bąk, M. Kurańska, and A. Prociak, The effect of various rapeseed oil-based polyols on selected properties of flexible polyurethane foams. *Polimery* **61**, 799–806 (2016).
6. A. Prociak, M. Kurańska, and E. Malewska, Porous polyurethane plastics synthesized using bio-polyols from renewable raw materials. *Polimery* **62**, 353–363 (2017).
7. J. Ryszkowska, M. Auguścik, M. Kurańska, R. Oliwa, J. Czech-Polak, and A. Prociak, Preparation and

- characterization of poly(urea-urethane) elastomers synthesized from rapeseed oil-based polyols. Part II. Thermal properties. *Polimery* **62**, 136–143 (2017).
8. M. Kirpluks, U. Cabulis, A. Ivdre, M. Kuranska, M. Zieleniewska, and M. Auguscik, Mechanical and thermal properties of high-density rigid polyurethane foams from renewable resources. *J. Renew. Mater.* **4**, 86–100 (2016).
 9. 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).
 10. K. Pietrzak, M. Kirpluks, U. Cabulis, and J. Ryszkowska, Effect of the addition of tall oil-based polyols on the thermal and mechanical properties of ureaurethane elastomers. *Polym. Degrad. Stab.* **108**, 201–211 (2014).
 11. V.M. Wik, M.I. Aranguren, and M.A. Mosiewicki, Castor oil-based polyurethanes containing cellulose nanocrystals. *Polym. Eng. Sci.* **51**, 1389–1396 (2011).
 12. M. Kurańska, A. Prociak, M. Kirpluks, and U. Cabulis, Polyurethane-polyisocyanurate foams modified with hydroxyl derivatives of rapeseed oil. *Ind. Crop. Prod.* **74**, 849–857 (2015).
 13. A. Fridrihsone-Girone and U. Stirna, Characterization of polyurethane networks based on rapeseed oil derived polyol. *Polimery* **59**, 333–338 (2014).
 14. M. Auguścik, M. Kurańska, A. Prociak, W. Karalus, K. Lipert, and J. Ryszkowska, Production and characterization of poly(urea-urethane) elastomers synthesized from rapeseed oil-based polyols. Part I. Structure and properties. *Polimery* **61**, 490–498 (2016).
 15. H. Dai, L. Yang, B. Lin, C. Wang, and G. Shi, Synthesis and characterization of the different soy-based polyols by ring opening of epoxidized soybean oil with methanol, 1,2-ethanediol and 1,2-propanediol. *J. Am. Oil Chem. Soc.* **86**, 261–267 (2009).
 16. E. Głowińska and J. Datta, Polyurethane biomaterials produced with the use of modified natural oils: A literature review. *J. Elastomers Plast.* **46**, 33–42 (2014).
 17. A. Fridrihsone, U. Stirna, B. Lazdiņa, M. Misāne, and D. Vilsone, Characterization of polyurethane networks structure and properties based on rapeseed oil derived polyol. *Eur. Polym. J.* **49**, 1204–1214 (2013).
 18. M. Zieleniewska, M.K. Leszczyński, M. Kurańska, A. Prociak, L. Szczepkowski, M. Krzyżowska, and J. Ryszkowska, Preparation and characterisation of rigid polyurethane foams using a rapeseed oil-based polyol. *Ind. Crop. Prod.* **74**, 887–897 (2015).
 19. A. Prociak, M. Kurańska, U. Cabulis, and M. Kirpluks, Rapeseed oil as main component in synthesis of bio-polyurethane-polyisocyanurate porous materials modified with carbon fibers. *Polym. Test.* **59**, 478–486 (2017).
 20. A. Hejna, M. Kirpluks, P. Kosmela, U. Cabulis, J. Haponiuk, and Ł. Piszczyk, The influence of crude glycerol and castor oil-based polyol on the structure and performance of rigid polyurethane-polyisocyanurate foams. *Ind. Crop. Prod.* **95**, 113–125 (2017).
 21. M.A. Mosiewicki and M.I. Aranguren, A short review on novel biocomposites based on plant oil precursors. *Eur. Polym. J.* **49**, 1243–1256 (2013).
 22. A. Guo, Y. Cho, and Z. Petrovic, Structure and properties of halogenated and nonhalogenated soy-based polyols. *J. Polym. Sci., Part A: Polym. Chem.* **38**, 3900–3910 (2000).
 23. A. Paruzel, S. Michałowski, J. Hodan, P. Horák, A. Prociak, and H. Benes, Rigid polyurethane foam fabrication using medium chain glycerides of coconut oil and plastics from end-of-life vehicles. *ASC Sustain. Chem. Eng.* **5**, 6237–6246 (2017).
 24. M.A. Mosiewicki, P. Rojek, S. Michałowski, M.I. Aranguren, and A. Prociak, Rapeseed oil-based polyurethane foams modified with glycerol and cellulose micro/nanocrystals. *J. Appl. Polym. Sci.* **132**, 1 (2015).
 25. N.E. Marcovich, M. Kurańska, A. Prociak, E. Malewska, and K. Kulpa, Open cell semi-rigid polyurethane foams synthesized using palm oil-based bio-polyol. *Ind. Crop. Prod.* **102**, 88–96 (2017).
 26. N.E. Marcovich, M. Kurańska, A. Prociak, E. Malewska, and Sonia Bujok, The effect of different palm oil-based bio-polyols on foaming process and selected properties of porous polyurethanes. *Polym. Int.* (2017).
 27. M. Kurańska, A. Prociak, U. Cabulis, M. Kirpluks, J. Ryszkowska, and M. Auguścik, Innovative porous polyurethane-polyisocyanurate foams based on rapeseed oil and modified with expandable graphite. *Ind. Crop. Prod.* **95**, 316–323 (2017).
 28. D. Ji, Z. Fang, W. He, Z. Luo, X. Jiang, T. Wang, and K. Guo, Polyurethane rigid foams formed from different soy-based polyols by the ring opening of epoxidised soybean oil with methanol, phenol, and cyclohexanol. *Ind. Crop. Prod.* **74**, 76–82 (2015).
 29. S. Geller, O. Weissenborn, M. Gude, and A. Czulak, Impregnation studies and mechanical characterization of cellular, natural, fiber-reinforced, composite structures. *Polimery* **61**, 125–132 (2016).
 30. M. Kurańska and A. Prociak, Porous polyurethane composites with natural fibers. *Compos. Sci. Technol.* **72**, 299–304 (2012).
 31. M. Kurańska, A. Prociak, U. Cabulis, and M. Kirpluks, Water-blown polyurethane-polyisocyanurate foams based on bio-polyols with wood fibers. *Polimery* **60**, 705–712 (2015).
 32. M. Kurańska, A. Prociak, S. Michałowski, U. Cabulis, and M. Kirpluks, Microcellulose as a natural filler in polyurethane foams based on the biopolyol from rapeseed oil. *Polimery* **61**, 625–632 (2016).
 33. P. Rojek, M.I. Aranguren, A. Prociak, and M.A. Mosiewicki, Solid polyurethanes based on rapeseed oil polyol and modified with glycerol and microcellulose. *J. Renew. Mat.* **4**, 266–274 (2016).
 34. A. Santamaria-Echart, L. Ugarte, A. Arbelaiz, F. Barreiro, M.A. Corcuera, and A. Eceiza, Modulating the microstructure of waterborne polyurethanes for preparation of environmentally friendly nanocomposites by incorporating cellulose nanocrystals. *Cellulose* **24**, 823–834 (2017).
 35. E. Głowińska, J. Datta, and P. Parcheta, Effect of sisal fiber filler on thermal properties of bio-based polyurethane composites. *J. Therm. Anal. Calorim.* 1–10 (2017). DOI: 10.1007/s10973-017-6293-5.
 36. R.V. Silva, M.M. Ueki, D. Spinelli, and J.R. Tarpani, Thermal, mechanical, and hygroscopic behavior of sisal

- fiber/polyurethane resin-based composites. *J. Reinf. Plast.* **29**, 1399–1417 (2010).
37. M. Cardoso Vasco, S. Claro Neto, E. Mauro Nascimento, and E. Azevedo, Gamma radiation effect on sisal/polyurethane composites without coupling agents. *Polimeros* **27**(2), 165–170 (2017).
38. I.O. Bakare, F.E. Okieimen, C. Pavithran, H.P.S. Abdul Khalil, and M. Brahmakumar, Mechanical and thermal properties of sisal fiber-reinforced rubber seed oil-based polyurethane composites. *Mater. Des.* **31**, 4274–4280 (2010).
39. A.C. Milanese, M. Odila Hilário Cioffi, and H.J.C. Voorwald, Flexural behavior of Sisal/castor oil-based polyurethane and sisal/phenolic composites. *Mat. Res.* **15**, 191–197 (2012).
40. N. Chand and M. Fahim, *Tribology of Natural Fiber Polymer Composites*, 1st ed., pp. 88, Woodhead Publishing, UK (2008).
41. M.A. Mosiewicki, J. Borrajo, and M.I. Aranguren, Mechanical properties of woodflour/linseed oil resin composites. *Polym. Int.* **54**, 829–836 (2005).