Mechanical Behaviour of Polyurethane from Castor oil Reinforced Sugarcane Straw Cellulose Composites


Abstract

Ecological concerns have resulted in a renewed interest in natural, renewable resources-based and compostable materials. For this reason, material components such as natural fibres and biodegradable polymers can be considered as interesting alternatives for the development of new biodegradable composites. The aim of this work was the obtainment of castor oil polyurethane reinforced with cellulose fibres from sugarcane straw. For the obtainment of cellulose, sugarcane straw was pretreated by steam explosion, followed by a delignification with NaOH 1.5% (wt/v). For the production of the polyurethane, the mass ratio between polyol (castor oil) and diisocyanate was 1.5:1.0. Reinforcement of the matrix was done changing the concentration of cellulose fibres (5,10,15,20% wt/wt). Chemical characterization of the materials obtained during the process was carried out. SEM micrographs of the fibres and fractured surfaces of flexural tests were done. SEM images of the fibres corroborate the results of chemical analysis, which showed a large solubility of components, making the fibres more exposed. The incorporation of cellulose fibres in the matrix showed that the composites stiffness increased, the Young's modulus also increased when compared to the pure matrix. SEM analysis of the fractured surfaces showed a poor dispersion of fibres in the matrix, and high interaction fiber-matrix.

Keywords: Castor oil; Sugarcane straw; Biocomposites; Polyurethane; Mechanical Behaviour

* Corresponding author. Tel.: +5512 31595033; fax: +5512 31533165.
E-mail address: patriciamileo@debiq.eel.usp.br
1. Introduction

Composites materials formed by natural fibres and polymeric matrices constitute a current area of interest in composites research [1]. Polyurethane resins are attractive due to their structural versatility (as elastomer, thermoplastic, thermosetting, rigid and flexible foams), as well as the fact that they can be derived from either petroleum or vegetable oils. They still present the particularity to be more compatible to vegetable fibres in relation to other resins, due to possible reaction of hydroxyl groups of the fibers and the isocyanate groups of the polyurethane [2].

Biopolymers as its polyurethane derived from castor oil can serve as matrices for composites reinforced with vegetable fibres. Castor oil is readily available as a major product from castor seeds. Castor oil-based polyurethane is a useful, versatile material and widely used as an individual polymer possessing network structure because of its goof flexibility and elasticity [3]. It contains about 90% (wt/wt) of ricinoleic acid. This triglyceride contains hydroxyl groups in its chain which react with isocyanate groups to form urethane links.

Brazil is the greatest sugarcane producer in the world [4]. The sugarcane is cultivated in the southeast and northeast portions of the country, and for 2009–2010, the production was over 604 million tons. The material removed before the cane is crushed, is called straw. One ton of sugarcane cultivated produces 140 kg of sugarcane straw. Sugarcane straw is comprised of the dried leaves, fresh leaves, and the top of the plant. Most of this residue is burned, thus losing energy and causing significant pollution. From 2005 onward, environmental concerns and legislation forbid the burning of sugarcane fields prior to harvesting in São Paulo State, making a great amount of sugarcane straw. Sugarcane straw, as any other biomass, consists of three main macromolecules: cellulose, hemicellulose and lignin, cellulose is the most abundant and best studied. Cellulose-based fibers are the most widely used, as biodegradable filler. Intrinsically, these fibers have a number of interesting mechanical and physical properties [5,6]. With their environmentally friendly character and some technoeconomical advantages, these fibers are of interest in an increasing number of industrial sectors (e.g. automotive) to replace glass fibers [7].

The aim of this work is to develop and investigate a new biomass composite material composed by a polyurethane resin derived from castor oil reinforced with cellulose fibres from sugarcane straw, pretreated by steam explosion, followed by a delignification. The fibres and the obtained composites were SEM and chemical analysis, in order to elucidate the morphological characteristics of composite fracture surfaces, fibre distribution and microstructure.

2. Experimental

2.1. Pretreatment and alkaline delignification of sugarcane straw

Steam explosion pretreatment was carried out in a 2.5 m³ reactor designed for this purpose. The reactor is equipped with a heating device, which has a live steam valve and sudden decompression. Sugarcane straw was pretreated in the reactor with a pressure of 15.3 kgf/cm² (equivalent to 200°C) for 15 min. The material collected in the cyclone was washed with water until complete removal of hydrolyzed sugars. Ten kilogram of pretreated sugarcane straw (dry matter) was transferred to a 350 L stainless steel reactor with 80 L of water and 20 L of aqueous solution containing 1.5 kg NaOH. The reaction was performed at 98-100°C for 1 h under stirring at 100 rpm. Final concentration of the mixture was 1.5 wt/v% NaOH and a solid/liquid ratio of 1:10 (w/v). After delignification, the mixture was carried to centrifugation at 1100 rpm. Cellulose was washed and dried under at 4°C for chemical characterization.
2.2. Obtainment of Polyurethane composites reinforced with cellulose

For the preparation of polyurethane and composites the following materials were used: polyl from castor oil (Ricinus communis) and polyurethane prepolymer based on MDI (diphenylmethane disiocyanate), and cellulose fibres extracted from sugarcane straw. The polyurethane based on castor oil was obtained by mixing by the polyl with diisocyanate at ratio of 1.5:1.0. This polymerization reaction is exothermic, around 45°C. The composites were prepared by compression molding. The components of the polyurethane resin were mixed handly. After that the pulp was added. The concentrations of cellulose added were 5,10,15 and 20% of the final mass of the polymer. After the cure, around 48 h, the material was removed from the mold and was submitted to the flexural test. It was also prepared the polyurethane matrix without the addition of cellulose reinforcements. All the process was performed at room temperature.

2.3. Chemical composition of sugarcane straw, pretreated sugarcane straw and pulp

The modified Klason method was utilized [8,9]. Samples (1,0g) of in natura, pretreated and delignified sugarcane straw were treated with 10.0 mL of 72% H₂SO₄. After 7 min stirring at 45°C, 25 mL of water was added to the mixture, which was post-hydrolyzed under 1.05 bar for 30 min. The product was filtered and the insoluble portion (Klason lignin) was quantified. The pH of the hydrolysate was adjusted to 1-3 with 6.5 mol.L⁻¹ NaOH, filtered in a Sep-Pak C₁₈ cartridge, and analysed by high-performance liquid chromatography in a Shumadzu LC10 chromatograph with Aminex HPX-87H column at 45°C. The mobile phase was 0.005 mol.L⁻¹ H₂SO₄ at 0.6 mL.min⁻¹. The hydrolysis products were determined by refractive index and quantified by using calibration curves. Soluble lignin was determined as described by Gouveia et al. [9] using absorption at 280 nm of alkaline solutions obtained from the hydrolysate. The concentration of cellulose was determined by the addition of anhydrous – glucose, cellobiose and HMF, besides the amount of polyoses was determined through the sum of the anhydrous – xylose, arabinose and furfural [8,9].

2.4. Mechanical properties of composites - Flexural tests

Composites were analyzed in an EMIC testing machine (model DL2000), equipped with pneumatic claws. In the flexural tests, a load was applied on the specimen at 1.3 mm.min⁻¹ crosshead motion rate. Five specimens were analyzed with dimensions in agreement with the ASTM D 790 standard: 25 mm width, 76 mm length and 3.2 mm thickness. The adopted flexural test was the 3-points method.

2.5. Scanning electron microscopy (SEM)

The fibres (sugarcane straw, pretreated straw and delignified pulp) and the specimens submitted to flexural tests, preserving composite intact fracture surface, were analyzed in JEOL JSM5310 scanning electron microscopy with tungsten filament operating at 20 kV, employing low vacuum technique and secondary electron detector.

3. Results and Discussion

3.1. Chemical composition of sugarcane straw, pretreated sugarcane straw and pulp

Analysis of chemical composition of in natura and pretreated straw by steam explosion, reported in
Table 1, together with the process yield 56.6%, revealed that 91.8% of hemicelluloses (Figure 1) present in crude straw was solubilized. This type of pre-treatment causes the degradation of hemicellulose and lignin transformation by high temperature [10]. During the steam explosion, hemicelluloses are partially hydrolyzed by acetic acid formed at high temperatures, from the acetyl groups present in polyoses (auto-hydrolysis). Moreover, there was also a great loss of cellulose during pretreatment, which was 25.2% (Figure 1), probably because of amorphous or low crystallinity cellulose, making cellulosic fraction more susceptible to the action of other reagents.

Table 1. Chemical composition of sugarcane straw, pretreated straw and pulp

<table>
<thead>
<tr>
<th>Components</th>
<th>In natura Straw</th>
<th>Pretreated Straw</th>
<th>Delignified pulp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>38.1 ± 0.2</td>
<td>50.3 ± 0.5</td>
<td>77.3 ± 1.2</td>
</tr>
<tr>
<td>Polyoses</td>
<td>29.2 ± 0.3</td>
<td>4.3 ± 0.1</td>
<td>4.9 ± 0.1</td>
</tr>
<tr>
<td>Lignin</td>
<td>24.7 ± 0.2</td>
<td>40.4 ± 0.2</td>
<td>14.8 ± 0.2</td>
</tr>
<tr>
<td>Ashes</td>
<td>3.4 ± 0.1</td>
<td>5.1 ± 0.1</td>
<td>3.4 ± 0.1</td>
</tr>
<tr>
<td>Extractives</td>
<td>4.7 ± 0.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Process yield (%)</td>
<td>100</td>
<td>56.6</td>
<td>54.2</td>
</tr>
</tbody>
</table>

The pulp obtained after delignification showed about 14.8% of lignin (Table 1), a value much lower if compared to the amount of lignin present in the in natura straw. Approximately 80% (Figure 1) of the lignin present in the pretreated straw was solubilized during the delignification process. It was also noticed a removal of 37.5% (Figure 1) of hemicelluloses, but the solubilization of about 17% of cellulose (Figure 1) at this stage indicates that the this process was very drastic, resulting in a substantial loss of cellulose for degradation, which will help to decrease the pulping process yield.

3.2. Scanning electron microscopy (SEM) of sugarcane straw, pretreated sugarcane straw and pulp

SEM is an excellent technique for examining the surface morphology of fibres. Photomicrographs of in natura sugarcane straw, pretreated straw and pulp (cellulose) are shown in Figure 2. It can be notice in a comparative analysis, a significant change in the morphological structure of sugarcane straw after the processes of pretreatment and delignification. When the sugarcane straw is pretreated, there is the breakdown of lignocellulosic structure, and a large fraction of hemicellulose is removed, increasing the accessibility to cellulose fibres.
After the stage of alkaline delignification it is possible to observe a great number of free cellulose fibres, showing that the stage of pretreatment followed by delignification can provide a better availability of cellulosic fibres for subsequent processes, such as the use of the fibres as reinforcement in biocomposites. Photomicrographs corroborate the chemical analysis, which showed a large solubility of components, making the fibres more exposed in each stage of processing of biomass and thus increasing their surface area.

3.3. Mechanical properties of composites – Flexural tests

The flexural modulus is related to the material rigidity. For the pure PU(matrix) flexural modulus was 163.7 ± 25.1 Mpa. These values in MPa for cellulose/PU composites, being the %cellulose 5%, 10%, 15% and 20%, were, respectively, 171.0 ± 9.7; 182.2 ± 22.9; 314.8 ± 36.5 and 354.5 ± 25.1. The Young’s modulus was higher for the composites when compared with the pure matrix. If the fibres are well distributed and aggregated to the matrix, a higher flexural modulus for the material can be obtained. Better performance of composites is attained due to homogeneous distribution of fibers in the matrix, as a result the stress transference between fibre and matrix is more effective, affecting positively the performance.
It was observed that the specimens used in tests of the pure polyurethane resin and the composites did not fracture at maximum load. As the specimens showed low resistance to bending and large displacement without rupture, the polyurethane resin can be characterized as ductile-brittle material.

The addition of cellulose fibres in the matrix showed that the composites became more rigid when compared to the pure matrix, as the Young's modulus, increased with increasing percentage of reinforcement added to the matrix, making it clear that the inclusion of cellulose fibres influence mechanical properties.

To perform the fractographic analysis, specimens of the flexural test were carried to rupture. Figure 3 shows the fracture region, where it was evident that there was a poor dispersion of fibers in the matrix, fractured fibres and a good fiber-matrix adhesion. There was no evidence of the presence of pull out. It was also observed energy dissipation during the frictional process mechanics.

4. Conclusions

Results revealed that the route chosen for obtaining cellulose was promising, but changes in the process must be carried in order to avoid losing large amounts of cellulose. The steam explosion pretreatment was efficient in the solubilization of hemicellulose, but there was also a significant loss of cellulose. The addition of cellulose fibres to the matrix improved the flexural modulus, making it clear that the inclusion of cellulose fibers influence mechanical properties. The fracture region showed a poor dispersion of fibers in the matrix, fibres fractured along the polymer and a good fiber-matrix adhesion. Moreover, there was no presence of pull out.

Acknowledgements

Authors are grateful for the research support by CAPES and FAPESP.

References