COMPOSITES BASED ON POLY(BUTYLENE SUCCINATE) (PBS) AND LIGNOCELLULOSIC FIBERS

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Abstract
Composites based on PBS and lignocellulosic fibers (coconut, sugarcane bagasse, sisal and curauá) were prepared via thermo-pressing. The effects of the lignocellulosic fibers on the mechanical and thermal properties of the composites were investigated by Izod impact tests, flexural tests and thermogravimetric analysis (TGA). The morphology of the samples was evaluated by scanning electronic microscopy (SEM), and the water absorption was also studied. The results showed that the composites reinforced with curauà and sisal exhibit very high resistance to impact and higher flexural strength than PBS/coconut and PBS/sugarcane bagasse. Moreover the SEM images of the fractured surface of curauá and sisal composites showed good adhesion at the interface fiber-matrix, as well as fibers filled and covered by the matrix. The influence of curauá fiber length and content was also investigated.

1 Introduction

In recent decades, researches focused on biodegradable polymers have received more and more attention due to promising applications and environmental considerations [1]. One of the most emerging biodegradable polymer is poly(butylene succinate) (PBS), a white semicrystalline thermoplastic, which is commercially available and that can be synthesized from bio-based renewable resources such as succinic acid and 1,4-butanediol. PBS has several interesting properties like good processability, excellent thermal and chemical resistance. Its melting point is similar to that of low density polyethylene (about 90-120 °C) and glass transition temperature is between those of polyethylene and polypropylene (about -45 to -10 °C) [2]. However, practical application of PBS has been limited because of its high price, softness and low mechanical and gas barrier properties.
In order to reduce the price of PBS and increase its performance, during the past few years, natural fibers reinforced PBS composites were prepared and studied. The introduction of a natural economic reinforcing agent contributes to a sensible reduction of the weight of the biocomposite resulting in a decreased cost of the polymeric matrix which is a critical limiting factor for a fully developed bio-based PBS [3]. Moreover, by using natural fibers instead of traditional reinforcing agents such as glass and carbon fiber, it is possible to get a fully biodegradable and recyclable material. The most studied natural fibers along with PBS were

jute [4], bamboo [5], kenaf [6], sisal [7], cotton fibers [8], etc. In the present paper the influence of four different lignocellulosic fibers (coconut, sugarcane bagasse, sisal and curauá) on PBS mechanical and thermal properties were studied. Moreover, considering that almost no paper concerning curauà fibers reinforced PBS has been published, we have focused our studies on this fiber which is one of the most promising in the field of composites, suggested as a suitable replacement for glass and carbon fibers reinforcements in thermoplastics composites especially in automotive devices [9].

2 Materials and testing methods

2.1 Materials

Sisal fibers were furnished by Sisal Sul Indústria e Comércio Ltda (São Paulo, SP, Brazil). Curauá and sugarcane bagasse fibers were kindly donated by Pematec Triangel do Brasil Ltda and Sítio São Judas Tadeu (São Paulo, SP, Brazil) respectively. Coconut fibers were supplied by Poematec Ltda- Comércio de Technologia Sustentável para a Amazônia (Ananindeua, PA, Brazil). All fibers were characterized in terms of lignin, hemicellulose, cellulose, ash and moisture content [10]. PBS (Natureplast PBE003) was purchased from Natureplast.

2.2 Composites preparation

Prior to use, the fibers were subjected to a pretreatment to remove waxes, fatty acids and other organic molecules [11]. Sugarcane bagasse underwent also a water washing and a defiber process to remove the pith. Then the fibrous polymeric composites with the different fiber length and content were produced trough the hand lay-up process followed by compression molding.

2.3 Characterization

TGA was performed in nitrogen using a Shimadzu TGA-50TA apparatus at 10 °C/min heating rate up to 800 °C. DSC measurements were conducted in a Perkin Elmer DSC-6 apparatus. Weighed samples (c.a. 10 mg) of the materials were encapsulated in aluminum pans and heated to 140°C at 20 °C/min (first scan), kept there for 1 min and then cooled to -60 °C at 20 °C/min (cooling scan). Then the samples were reheated from -60 °C to 140 °C at 20°C/min (second scan).

The XRD measurements were carried out using a RIGAKU Rotaflex apparatus, model RU-200B, operating at 40 kV, 40 mA and λ (Cu-Kα) = 0.154 nm at velocity of 2°/min in the range of Bragg angle 5-50°. For the fibers the crystallinity index (I_c) was calculated using the Buschle-Diller and Zeronian equation [12]:

$$I_c = 1 - (I_1/I_2) \times 100 \quad (1)$$

where I_2 is the intensity at the minimum of the crystalline peak ($18° < 2\theta < 19°$), and I_2 is the intensity at its maximum ($22° < 2\theta < 23°$).

Izod impact tests were carried out according to the ASTM D256-06a [13] using a CEAST Resil 25 equipment.

Flexural tests were performed using a three-point bending method according to ASTM D790-02 [14] using an Instrom Universal testing Machine, model 5569 equipped with a 50kN load cell. The SEM employed is a Zeiss-Leica, 440 model. The acceleration voltage used was 20 kV. The specimens were sputter-coated with gold before scanning.

The water absorption test was performed according to ASTM D570-98 [15]. The dimension of the samples were 76.2 mm × 25.4 mm × 3.2 mm. After drying the samples were

completely immersed in distilled water at room temperature. The percentage of weight increase due to water absorption was calculated according to the following equation:

$$A\% = [(m_t - m_0)/m_0] \times 100 \quad (2)$$

where is A% is the percentage of water absorbed, m_t is the mass of the specimen at the time t and m_0 is the mass of the dried specimen.

3 Results and discussion

PBS is a semicrystalline material, characterized by high thermal stability, a glass transition temperature at -27 °C, a melting temperature at 115 °C and a crystallization temperature at 68 °C during the cooling scan.

To improve the physical properties of PBS four different types of lignocellulosic fibers with the same length and content, were investigated: sugarcane bagasse, coconut, curauá and sisal. The chemical characterization of the fibers revealed that curauá and sisal are the fibers with the highest content of cellulose; in accordance with these data, XRD analysis proved that they are also the most crystalline due to the presence of cellulose which is a semycristalline polysaccharide.

3.1 Effect of fiber types

All the composites were studied in terms of thermal stability, mechanical properties and morphology. TGA proved that the addition of the different kind of fibers has no effect on the thermal stability of PBS which is maintained very high independently of the fiber kind.

The results of Izod impact resistance specimens and of the flexural strength tests proved that the samples with sugarcane bagasse and coconut fibers are the weakest both in term of impact resistance and flexural strength. In the case of sugarcane bagasse the lower flexural strength can be due to the low flexural strength of the pure fiber (35.1 MPa [16]). However, the bending modulus of PBS is increased even for sugarcane bagasse and coconut. In agreement with this results, SEM micrographs showed the poor wettability of bagasse and coconut fibers by PBS indicating a lower compatibility with the PBS matrix. As a consequence the fibers can be easily pulled-out from the interfacial region resulting in a rapid partial collapse of the composites due to an insufficient dispersion and transfer of the applied load.

On the other hand, curauá and sisal fibers bring a higher reinforcement on PBS matrix; moreover, in the case of the impact test, some specimens of curauá and sisal composites don't break, indicating a better reinforcement and compatibility arising from these two fibers. The higher cellulose content of curauá and sisal may generate a stronger interface due to the interaction of the hydroxyl groups of cellulose and PBS. Besides the lower lignin percentage implies a small concentration of aromatic rings making these fibers more compatible with the aliphatic matrix. The higher compatibility of curauá and sisal with the polymer matrix was also evidenced by the SEM micrographs in which the fracture surface image revealed a strong interaction with the interface and a better wettability.

Regarding the results of the water uptake studies, as it was expected, the introduction of lignocellulosic fibers increases the water absorption capability of the matrix due to their hydrophilic nature. Bagasse and coconut fibers show the greatest saturation level which is likely due to the poor interface and to the lower crystallinity of these fibers, containing lower cellulose crystalline domains. On the contrary sisal and in particular curauá have the lowest water saturation levels. The intimate contact between the fiber and the matrix in this case is able to generate a smaller number of microvoids with the matrix filling the hollow structure of the fibers thus decreasing the amount of water that can be stored in the bulk of the material.

3.2 Effect of curauá fiber content

The values of Izod impact resistance and flexural strength for composites loaded with different amount of curauá but same length indicated the relevant effect of the addition of curauá fibers in PBS. In fact, an increase in the fiber content enhances the impact resistance and flexural strength of the polymer. Probably a further increase would decrease the resistance due to an incomplete wetting of the fibers surface by the polymer leading to a weak interfacial adhesion.

3.3 Effect of curauá fiber length

Values of Izod impact resistance of composite reinforced with curauà fibers at different lengths but same proportion proved that shorter fibers enable the composites with the best impact resistance. Indeed a reduction of size, implying an increase in surface area, leads to a greater interface available for close contact between the fibers and the polymer. On the other hand when longer fibers are used, a non uniform dispersion with local clumping of fibers into the matrix may have been generated leading to either fibers-rich or matrix-rich region. As a consequence the uneven microstructure with polymer-rich areas may have been the cause of the lower mechanical properties due to a poor stress transfer efficiency favoring crack initiations. Contrary to what was found for the impact resistance, the increase in fibers length enhanced the flexural strength. SEM images show no noticeable changes in the interface characteristics meaning that the high Izod impact resistance, for shorter fibers, are caused by the greater surface area available for the mechanical interlocking.

4 Conclusions

In this work novel biocomposites were produced by the traditional thermo-pressed molding technique introducing into a PBS matrix different lignocellulosic fibers (sugarcane bagasse, coconut, curauà, and sisal). Due to the relatively low processing temperature of PBS it was possible to prepare composites by thermo-pressed molding technique without affecting the thermal stability of the fibers which often restricts the choice of the polymer matrix mainly to polyolefins. Izod impact test and flexural test proved that curauá and sisal fibers sensibly improve the polymer mechanical characteristics. SEM images reveal the stronger interfacial adhesion between PBS and these fibers likely due to a better chemical compatibility and surface roughness. Moreover, since no chemical modification of fibers surface was performed, mechanical interlocking was essential for an intimate contact between the two phases. The polarity of the functional groups present in the PBS chain favors the interactions with the polar groups of the lignocellulosic fibers creating the conditions for an intimate contact between the matrix and the fibers which are essential for a proper load transfer.

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