BIODEGRADABLE COMPOSITES OF SUGARCANE BAGASSE AND VEGETAL POLYURETHANE FOR BIOMEDICAL APPLICATIONS

COMPÓSITOS BIODEGRADÁVEIS DE BAGAÇO DE CANA DE AÇÚCAR E POLIURETANO VEGETAL PARA APLICAÇÕES BIOMÉDICAS

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Abstract: Due to the environmental problems caused by polymers, it is desirable to use biodegradable biopolymers such as vegetable polyurethane and sugar cane bagasse fibers. Therefore, the work aimed at the development of biodegradable biocomposites of sugarcane bagasse fibers for application in orthoses and evaluated their viability through mechanical, chemical, biodegradation and computational simulation tests. It was possible to obtain PU composites with sugarcane bagasse, which showed good interaction through the analysis of scanning electron microscopy images. It was observed that the addition of sugar cane bagasse fibers to the PU increased impact resistance, Young's modulus, there was a decrease in elongation and hardness and that the addition of fibers maintained the maximum tension value. The water absorption test showed that the fibers increased water absorption and biodegradation compared to polyurethane, which is advantageous for the orthosis, as it causes less accumulation of water between the patient's skin and the orthosis and reduces problems of infections and wounds. The computational simulation showed that it would be possible to make an orthosis with the PU composite with sugarcane bagasse and that for that it would be necessary to optimize the design of the orthosis. The use of PU composite with sugarcane bagasse in the medical field is promising, as it is a non-toxic material, from a renewable source and that uses agro-industrial waste with low added value, also presenting the advantage of providing better comfort to the patient.

Keywords: vegetable polyurethane; sugarcane bagasse fiber; biocomposites, bracing.

Resumo: Devido aos problemas ambientais causados pelos polímeros, é desejável a utilização de biopolímeros biodegradáveis, como poliuretano vegetal e fibras de bagaço de cana-de-açúcar. Portanto, o trabalho teve como objetivo o desenvolvimento de biocompósitos biodegradáveis de fibras de bagaço de cana-de-açúcar para aplicação em órteses e avaliou sua viabilidade através de testes mecânicos, químicos, de biodegradação e de simulação computacional. Foi possível obter compósitos de PU com bagaço de cana, que apresentaram boa interação através da análise de

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imagens de microscopia eletrônica de varredura. Observou-se que a adição de fibras de bagaço de cana ao PU aumentou a resistência ao impacto, o módulo de Young, houve diminuição do alongamento e da dureza e que a adição de fibras manteve o valor máximo de tensão. O teste de absorção de água mostrou que as fibras aumentaram a absorção de água e a biodegradação em comparação ao poliuretano, o que é vantajoso para a órtese, pois provoca menor acúmulo de água entre a pele do paciente e a órtese e reduz problemas de infecções e feridas. A simulação computacional mostrou que seria possível confeccionar uma órtese com o compósito PU com bagaço de cana e que para isso seria necessário otimizar o desenho da órtese. A utilização do compósito de PU com bagaço de cana na área médica é promissora, por se tratar de um material atóxico, de fonte renovável e que utiliza resíduos agroindustriais de baixo valor agregado, apresentando também a vantagem de proporcionar melhor conforto ao paciente.

Palavras-chave: Poliuretano; Bagaço de cana-de-açúcar; Biocompósitos; Órtese.

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1 INTRODUCTION

Due to problems related to improper disposal of polymeric materials in the environment, there is a constant search for the development of environmentally friendly materials that present quality and price compatible with conventional polymeric materials (commodity polymers). The use of environmentally friendly materials, such as biopolymers and biodegradable polymers, have the potential to partially replace biostable polymers, with the main advantage being a lower environmental impact due to saving natural resources and also reducing the accumulation of solid waste in fauna and flora (Geyer et al., 2017). Among the various existing biopolymers and biodegradable polymers, vegetable polyurethane and sugarcane bagasse stand out (Sabnis & Kaikade, 2023b; Chaudhary et al., 2021).

Polyurethane (PU), was discovered by Otto Bayer, in 1937, and is currently a large class of thermosetting materials whose properties obtained can be modified in the synthesis process. Currently, in the consumer market, the main polyurethanes used are adhesives (33%), flexible (31%), rigid (25%) and molded PU Foams (11%) (Sabnis & Kaiakade, 2023a). PU synthesis starts from the reaction of the hydroxyl groups of a polyol with an isocyanate group and PU's with different properties can be obtained through the use of different polyols or isocyanates, as well as varying the proportion between both or through the use of additives, such as expanding agents (Sabnis &

Kaikadeb, 2023; Sawpan, 2018). The isocyanates used can be aliphatic or aromatic, but the most used are aromatic, due to their greater chemical reactivity. Polyols, on the other hand, can be derived from petroleum or can be derived from vegetable oils such as soybean oil, sunflower, coconut, palm, cotton, castor oil, among others (Valero et al., 2018; Sabnis & Kaikade, 2023b; Sawpan, 2018; Rajput et al., 2022).

The great advantage of using polyols from vegetable sources is that they are non-toxic, renewable, highly available on the market and make the PU biodegradable. (Uscátegui et al., 2016; Sabnis & Kaikade, 2023a; Sawpan, 2018). The use of different vegetable oils for PU synthesis results in different mechanical and thermal properties, because each of the vegetable oils has different availability of hydroxyl groups to interact with the isocyanate. The PU derived from castor oil has a greater availability of free hydroxyls, which results in a higher density of crosslinks and produces greater thermal stability and higher mechanical property values, however, it generates a more rigid PU (Kessler et al., 2015). The density of crosslinks in vegetable PU is directly related to its biodegradability, since there is a relationship that the more flexible the PU is, the more biodegradable it will be due to the biodegradation process being facilitated by a lower density of crosslinks (Valero et al., 2018).

Although the use of vegetable oils for the synthesis of PU makes it biodegradable, it will have a biodegradation period of up to two years, longer than that of other biodegradable polymers such as thermoplastic starch (TPS), which has a degradation period between 7 and 30 days in composted soil (Yin & Yang, 2020). Petrović et al., (2010) carried out the biodegradation test by respirometry following the procedures described in the D5291-02 standard for PU from the petrochemical segmented polyesterurethane, polyricinoleate diol (2,580 MW) and castor oil and also performed the same test with TPS, it was found that in over a period of 30 days the TPS degraded 50% of its mass, the PU derived from polyricinoleate diol mineralized less than 5% and the PU derived from castor oil degraded approximately 15%. It is observed that the use of castor oil makes the PU biodegradable, but that the biodegradation process is influenced by the crosslinks in the PU and also by its hydrophobic character, thus presenting a longer biodegradation time than TPS (hydrophilic and semicrystalline).

PU is currently used in several areas of industry, but in the medical field the first records of its applications date back to 1980, where this material was used in blood bags, catheters and small grafts. However, in the last decade, the number of publications on PU in medical applications has increased, currently being used in dentistry, tissue engineering (scafoolds), orthopedic devices (reconstruction of tendons and ligaments), surgeries to correct abdominal hernias and neural regeneration (Valero et al., 2018; Pedersen et al., 2022; Naureen et al., 2020). In addition to the applications described above, PU can be used in conjunction with other materials to improve its

properties, among which lignocellulosic fibers stand out.

Lignocellulosic fibers are natural fibers that have cellulose, hemicellulose and lignin as main constituents. Cellulose is formed by cellobiose mers, which are made up of two β-D-glucose units connected by a β-glycosidic bond (1□4), have the presence of free hydroxyls in their structure, which guarantees a hydrophilic character and capacity to carry out intra and intermolecular hydrogen interactions. Cellulose has a semicrystalline structure, which gives it good mechanical and thermal properties (Jacinto & Spinacé, 2019). Hemicellulose is an amorphous polymer composed of sugars such as glucose, mannose and xylose, which are connected through hydrogen interactions (Jacinto & Spinacé, 2019). Lignin is a polymer with an amorphous three-dimensional configuration consisting of a complex of aromatic and aliphatic groups (Dos Santos et al., 2019). It is produced in the cell wall of plants and is associated with cellulose in order to provide greater impermeability and chemical resistance (Jacinto & Spinacé, 2019).

For the use of lignocellulosic fibers with better mechanical and thermal properties, treatments for partial removal of hemicellulose and lignin can be carried out, among them, mechanical treatment with the use of ultrasound and microwaves; chemical treatments, which can be acidic, alkaline, ionic liquids, organosolv and biological treatments with the use of lignin degrading enzymes. Among the various existing treatments, the most used is mercerization (reaction in an alkaline medium - sodium hydroxide or potassium hydroxide), due to its lower cost-effective process associated with less formation of inhibitors (Alokika et al., 2021; Sukyai et al., 2021). The disadvantage of carrying out the alkaline treatment is the formation of black liquor, the name given to the residue that contains the alkaline medium with lignin and hemicellulose.

Lignocellulosic fibers can come from different sources such as wood, cotton and also from agro-industrial residues such as sugar cane bagasse. In this context, it is advantageous to use PU with lignocellulosic fibers.

Among the various applications of sugarcane bagasse, it can be used forming a composite with PU. Miléo et al., (2016) studied vegetable polyurethane composites derived from castor oil with cellulose and lignin derived from sugarcane bagasse. Sugarcane bagasse was previously subjected to an acid pre-treatment with sulfuric acid 10% (W/V), followed by an alkaline treatment with 1.5% (w/v) of sodium hydroxide, the lignin from the black liquor of the treatment alkali was precipitated and polyurethane composites were formed with 60 wt% lignin and with 40 wt% and 10 wt% cellulose. The SEM results showed that it was possible to form the composite using lignin and also cellulose and the TGA/DSC results showed that the addition of lignin and cellulose decrease the thermal stability of the composite.

Tran et al., (2022) also investigated the production of vegetable polyurethane using of the sugarcane bagasse-based-bio-oil produced from hydrothermal liquefaction (HTL) using glycerol as solvent and showed that sugarcane bagasse residue can also be used for the production of vegetable PU.

Yu et al., (2019) investigated the biodegradation process of rigid polyurethane prepared with 50% Petroleum-based polyol (Puranol RF 8238ª) and 50% (w/w) Soy oil-based polyol (YS-112) and polyurethanes using contents of 0, 2.5 %, 5.0%, 7.5%, 10.0% and 12.5% of agricultural waste (bagasse). By means of the mass loss test in composted soil (ASTM D5988) during a period of 10 weeks, it was possible to observe that the addition of bagasse increases the mass loss, which shows the advantage of using this material.

Dos Santos et al., (2018) studied PU composites derived from castor oil with bamboo powder, the addition of fibers increases water permeation and water absorption, which is desirable to reduce wound problems caused by muffling the prosthesis in constant contact with the skin. human skin.

Shahar et al., (2019) showed through a bibliographical review that Kenaf fiber has been used studied for biomedical orthoses with epoxy resin and polypropylene and that the use of fibers brings are cheaper, stronger, eco-friendly, user-friendly, and lighter could be developed and could also provide better mechanical properties.

Among the various lignocellulosic fibers that can be used with PU, in this work the sugarcane bagasse (BC) fiber stands out. Among the largest sugarcane producers are Brazil, India and China, whose production is mainly intended for obtaining sugar and ethanol (Chaudhary et al., 2021). About 28% of the entire mass of sugarcane produced becomes bagasse, which is an undervalued waste that is currently used for electricity production (burning), animal feed. The chemical composition of sugarcane bagasse is 32-45% cellulose, 20-32% hemicelluloses and 17-32% lignin, 1-9% ash and some extractives (Alokika et al., 2021; Sukyai et al., 2021). Due to the large amount of sugarcane bagasse produced and its majority composition of cellulose, it is advantageous to use it in applications that add value to this residue, such as packaging, cosmetics, textile and civil construction industries (Sukyai et al., 2021).

One of the possible applications of lignocellulosic fibers from sugarcane bagasse, with PU, is in biomedical equipment such as orthoses, which are medical devices that have the function of correcting some temporary or fixed disease in the orthopedic patient (Shahar et al., 2019). Currently, orthoses are produced with metals, plastics or composites using carbon fiber, however, their cost and production process are considerable disadvantages, so it is advantageous to use agro-industrial residues, such as sugarcane bagasse, in their manufacture, because presents potential for cost reduction (Shahar et al., 2019).

Orthotics and prostheses require user comfort due to the long period of use, which requires the study of new materials or the design of parts, however, this work is not always simple, since these devices are individual and require very personal perspectives of comfort (DeZeeuw & Dudek, 2019). Within this context, computer simulation is an advance and an ally for the evolution of medicine, as it allows, through finite element modeling, to produce effects similar to the use of the material, which facilitates the improvement of the product and also manages to solve problems. related to design and functionality. This simulation model can be applied to evaluate the functionality of orthoses and has satisfactory accuracy (Fiorentino et al., 2016).

Knowing that both vegetable PU and sugarcane bagasse can be used in the medical and biomedical field because they are non-toxic, renewable, easy to sterilize, compatible and functional (Valero et al., 2018), this work aimed to develop polyurethane biocomposites plant with short fibers of sugar cane bagasse and evaluate the viability of its use in an orthosis through mechanical tests and computational simulation.

2 METHODOLOGY

2.1 Materials

The sugarcane bagasse was obtained in a free fair in São Paulo City. The bicomponent vegetable polyurethane resin (component A and B) used was AGT 1315 Imperveg™, according to the supplier's specification, component A is a prepolymer and component B is vegetable oil extracted from castor oil (Ricinus communis). Sodium hydroxide used in the treatment of sugarcane bagasse fiber brand NOX - Lab solutions.

2.2 Preparation of sugarcane bagasse fibers

The sugarcane bagasse was collected at a local market in the municipality of São Paulo. The washing process was carried out following the procedures described by Dos Santos et al. (2018). Initially, the sugarcane bagasse was immersed in room temperature water (23 °C) for a period of 72 hours in a sealed glass container. It was then rinsed with running water to remove impurities. Subsequently, it was air-dried for 48 hours at room temperature. After drying, the fibers were ground using a food processor (PHILCO) and sieved. After drying, the fibers were sieved and designated as BC (none treated sugarcane bagasse fiber).

2.3 Alkaline treatment of sugarcane bagasse

The alkaline treatment was carried out using an 8% (w/v) sodium hydroxide solution at 80°C on a heating plate (Logen) for one hour with manual agitation every 5

minutes. The ratio used was 1 L of NaOH solution to 200 g of BC fiber. Subsequently, the fibers were rinsed with running water until the washing water reached pH 7 (measured using a pH strip). The drying process was conducted in a polypropylene tray in an oven (De Leo) at 70 °C for 48 hours. After drying, the fibers were sieved and designated as BCT (treated sugarcane bagasse fiber).

2.4 BCT fiber size distribution analysis

Optical microscopy of approximately 100 fibers was performed on a NIKON optical microscope (E100) at 4x magnification. Then, the optical microscopy images were analyzed in the ImageJ software, where the length and diameter of each of the 100 fibers were measured and the diameter and average length were obtained.

2.5 Moisture absorption from the air of sugarcane bagasse fibers

Air moisture absorption of sugarcane bagasse fibers were determined in quintuplicate following AOAC methodology. About 1 g of the sample was inserted into dry filters. The temperature of 110 (±5) °C for TPS and 120 (±5) °C for BC and BCP were used. After inserting the sample, the weighing filter remained open in the oven for 30 min, and then it was cooled and weighed. The procedure was repeated until the dough remained constant. The moisture content was determined according to Eq. (5), where m_i is the initial mass and m_f is the final mass.

$$\text{Moisture absorption (\%)} = (m_i - m_f / m_i) \times 100 \qquad (1)$$

2.6 Composites preparation

The composites were prepared using a biodegradable polyurethane resin IMPERVEG (AGT 1315) with a ratio of 1:1.2 (w/w) of Component A (pre-polymer) and Component B (polyol derived from castor oil). Components A and B of the resin were weighed in a polypropylene container and manually mixed for 2 minutes. After complete mixing of Components, A and B, 10% (w/w) of dried BC or BCT fibers, previously dried for 12 hours in an oven (DE LEO), were added and homogenized. The resin was cured in polycarbonate molds using soybean oil as a mold release agent. The total curing period for the resin was 7 days. The composite prepared with PU and BCT were referred to as PU/BCT and the composite prepared with PU and BC were referred to as PU/BC.

2.7 Shore A hardness test of PU and PU/BCT composite

The Shore A hardness test was performed using a durometer (HOMIS, HT - 6510OA), and the average hardness value was obtained by measuring the hardness

at 10 points on the specimen, according to ASTM-D-2240.

2.8 Impact Resistance

The charpy impact resistance test was carried out in accordance with ISO 179/1eA on 5 specimens with dimensions (80 x 10 x 4) mm. The test was performed on a Resil Impactor (6967 - Ceast), the base was used with a distance between the supports of 62 mm and a pendulum of 4J.

2.9 Tensile test of PU and PU/BCT composite

The tensile test was performed on Instron equipment (5566) in accordance with ISO Standard 527(2019) using Inston-Bluehill software. Five specimens of PU/BCT resin were tested, with dimensions of approximately (13 x 3 x 10 cm). During the tensile test, 100 mm of separation between the grips was used, a speed of 20 mm/min and a load cell of 20 KN.

2.10 Biodegradation test in fertilized soil of PU and PU/BCT composite

For the biodegradation test, the fertilized soil (West Garden) was manually sieved, and then 10 g of soil was diluted in 50 mL of water and homogenized on a magnetic stirrer (Logen) for 10 minutes. The pH was measured using a pH strip, and the obtained value was 7. Next, 2 Kg of sieved soil was added to a refractory container with dimensions of (30 x 20 x 7) cm, and 40% (w/w) water was added. Then, 5 samples of pure PU, PU with treated fiber, and PU with treated fiber were inserted into the soil. The container with soil and samples was kept at 36°C in a bacteriological incubator for 60 days, and the samples were removed from the soil and photographed after 7, 45, 85 and 120 days.

2.11 Scanning electron microscopy (SEM)

SEM imagens of PC/ABS blend before and after oil degradation was performed in a scanning electron microscope (FEI Quanta, 250), between 10 and 15 KV in high vacuum mode. The analyzed materials were covered with 20 nm of gold in a Sputtering equipment (LEICA ACE 200). For PC/ABS fracture microscopy, the cryogenic fracture was performed after insertion into liquid nitrogen for a period of 15 min.

2.12 Fourier transform infrared spectroscopy (FTIR-ATR)

The FTIR measurements were performed in attenuated total reflectance (FTIR-ATR) mode on a Perkin Elmer Frontier spectrophotometer (100 FT-IR) from 4000 to

650 cm^{-1} with 4 cm^{-1} resolution and 32 scans.

2.13 PU/BCT composite water absorption test

The samples, in triplicate, previously dried at 100 °C for 2 hours, were weighed on an analytical balance (Marte, AL 500C). The samples were placed in recipients containing 50 mL of water at room temperature (25 °C). After 96 hours the samples were removed from the water, dried on absorbent paper and weighed. The calculation of water absorption occurred according to Equation 2, where m_x is the mass of the sample after 96 hours immersed in water and m_i is the initial mass before immersion in water.

$$\text{Water absorption (\%)} = ((100 \times m_x)/m_i) \quad (2)$$

2.14 Density of PU and PU/BCT composite

Density analysis was performed on an Archimedes stand, using a Mars analytical balance (AW220) following the procedures described in ASTM D792. Initially the samples were cut and weighed (m_c). Then, the Archimedes support and a 200 mL beaker with distilled water at 25.6 °C were inserted, after zeroing the balance with the Archimedes support, the sample was inserted into the beaker with water and the apparent mass was measured (m_{ap}). Density was calculated using Equation 3, where d is the density of water at a temperature of 25.6 ºC (dH_20= 0.9970479 g/cm^3).

$$\boldsymbol{dc = \left(\frac{m_c}{m_c - m_{ap}}\right) . d^{H2O}} \quad \textbf{(3)}$$

2.13 Computacional simulation

The software used to create the mathematical geometry of the orthosis was NX (version 12.0, 2017), using the function 101 Linear statics – Global Constraints, which manages to simulate displacement, tension and reaction at the support points. An evaluation of the application of a tension of 200 N on the X, Y and Z axes was carried out.

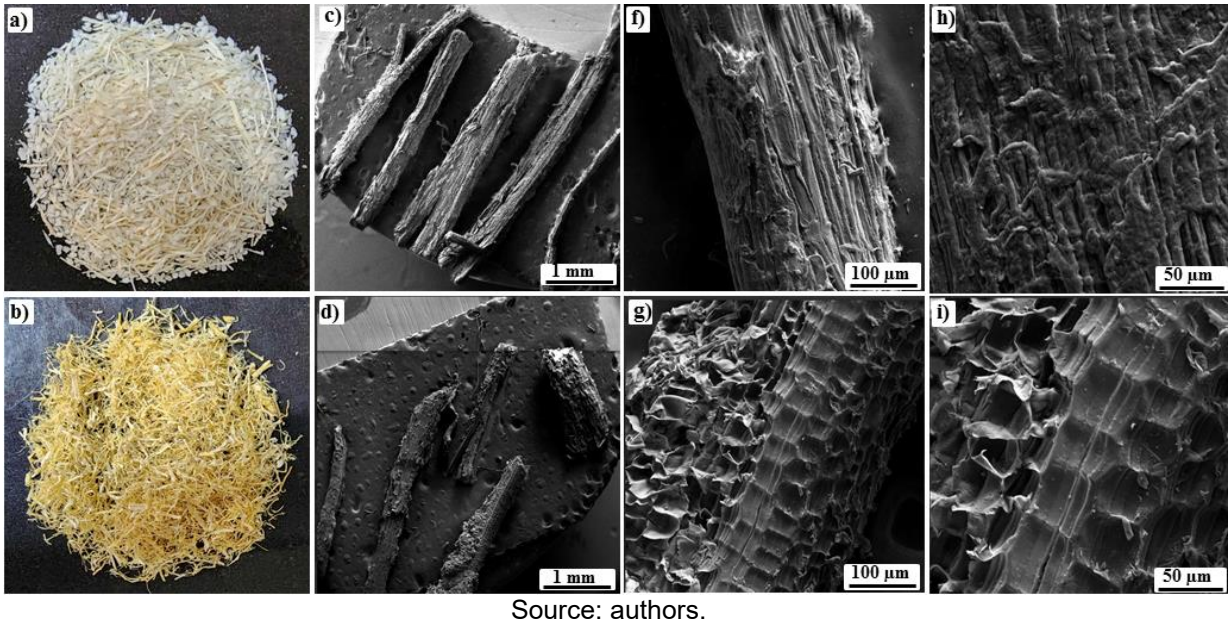
3 Results and Discussion

3.1 Fiber treatment: morphological analysis, moisture absorption, size distribution and FTIR

The analysis of the visual morphology of the fibers through photographs (Figure 1 a and b) showed that there was yellowing of the fibers after the alkaline treatment, a

characteristic alteration of this type of treatment (Gallos et al., 2017). The alkaline treatment was carried out with the objective of removing components such as waxes, lignin and hemicellulose, which makes the fiber rougher, as observed in the SEM images of Figure 1 c – i . The greater roughness of the fiber results from the partial disruption of the fiber caused by the removal of hemicellulose and lignin, which favors interface interactions by mechanical adhesion (Cao et al. 2006; Gallos et al., 2017). The alkaline treatment increases the surface roughness of the lignocellulosic fibers and tends to reduce the hydrophilic characteristics of the fibers, having a greater compatibility with matrices that are hydrophobic (Kabir et al., 2012).
The visual change observed in the photographs and through the SEM images is an indication that the treatment achieved the expected objective.

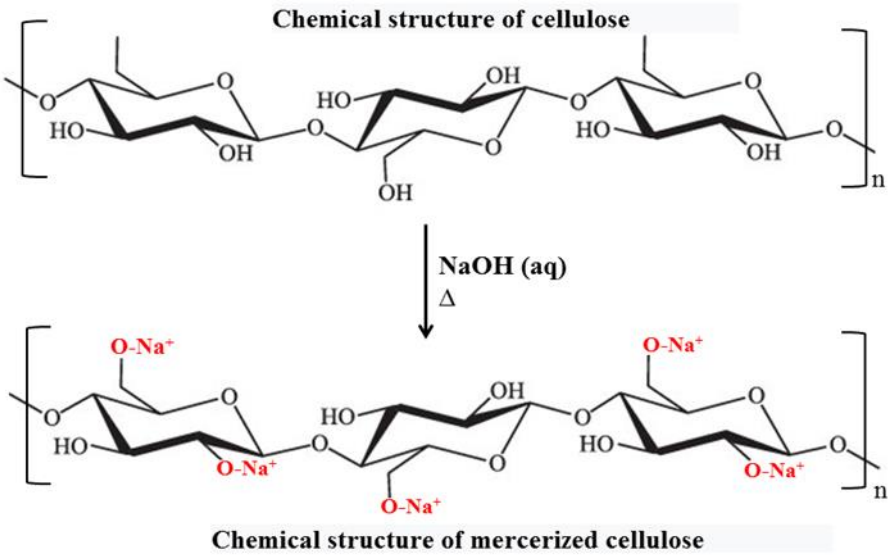
Figure 1 - Photographs a) BC, b) BCT; SEM images c, f and h) BC and d, g and i) BCT.



Source: authors.

The air moisture absorption content for BC was 24.2 (± 1.1)% and for BCT it was 13.6 (± 0.4)%. It is observed that the alkaline treatment reduced 77% of the absorption of moisture from the air of the sugarcane bagasse fiber. In addition to altering the surface of the fiber, as shown in Figure 2, during alkaline treatment with NaOH, partial replacement of cellulose hydroxyl groups (-OH) by -O-Na+ groups occurs. The hydroxyl groups are responsible for absorbing water from the fiber, with the decrease in hydroxyl groups caused by the alkaline treatment, there is a reduction in the hydrophilic character of the cellulose, which decreases its moisture absorption (Ferreira et al., 2019; Jacinto & Spinacé, 2019).

Figure 2 - Representation of the effect of alkaline treatment with NaOH on the chemical structure of cellulose, where n is the degree of polymerization.



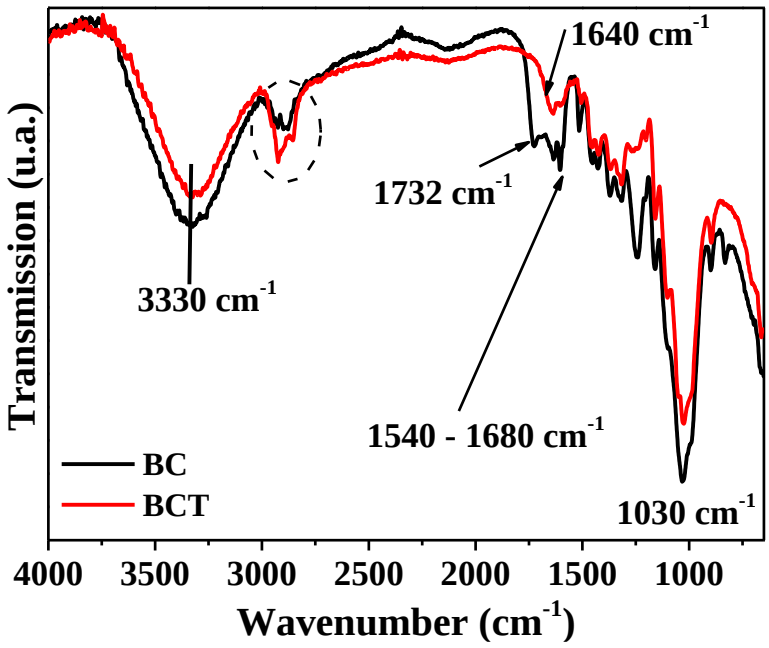
Source: adapted from d'Almeida et al., (2005).

The fiber size distribution analysis showed that the average length of the fibers was 0.57 (± 0.27) mm and the average diameter was 0.14 (± 0.06) mm. sizes and diameters of the fibers, which was caused due to the absence of the process of separating the fibers by size. It is important to evaluate the length and average diameter of the fibers, since the fiber size interferes with the mechanical properties of the composite, as observed by Dos Santos et al. (2018) who verified the influence of the different sizes of sugarcane bagasse fiber on the thermoplastic starch (Dos Santos et al., 2018).

The graph of the FTIR-ATR analysis for the BC and BCT fiber is shown in Figure 3. The band located at 3330 cm^{-1} refers to the O-H stretching vibrations of the intra and intermolecular bonds, it is noted that there is a decrease in the intensity of this peak in the fiber subjected to treatment, this fact can be attributed to the partial replacement of the hydroxyl groups by the $O\text{-}Na^{+}$ group (as shown in Figure 2) (Dos Santos et al., 2018; Spinacé & Santos, 2021). The bands between 3000 and 2800 cm^{-1} (indicated with a circle in Fig. 3, refer to the asymmetric and symmetric vibrations and stretching of the CH_2 and CH_3 of the cellulose, the profile change in these peaks for the fiber after treatment (BCT) is indicative of hemicellulose and lignin removal. The peak at 1740 cm^{-1} is attributed to vibrations of the carbonyl group present in the lignin structure and also in hemicellulose and The peaks between 1540 and 1680 cm^{-1} refer to C=C bonds and C-O that are present in the aromatic rings of lignin, it is observed that for the untreated fiber these peaks are more evident, which is an indication that the chemical treatment was effective in removing hemicellulose and lignin. The peak in 1030 cm^{-1} refers to the C-OH stretching present in the cellulose, it is noted that the

peak is less intense for the treated fiber, which indicates less presence of these groups and confirm what was observed in the air humidity absorption test (Dos Santos et al., 2018).

Figure 3 - FTIR-ATR analysis graph for BCT and BC.



Source: authors.

3.2 Obtaining the PU/BC and PU/BCT composite

Uniform composites were successfully obtained using BCT fiber, as shown in the PU/BCT composite photo (Fig. 4 a). However, for the PU/BC composite, which utilized BC fiber, the formation of composites was not possible due to swelling during the curing period, resulting in an irregular surface with numerous bubbles (Fig. 4b and c), rendering it unsuitable for testing. The successful production of the PU/BCT composite was attributed to the alkaline treatment, which partially replaced the hydroxyl groups in the fiber chains and removed amorphous regions. This treatment led to reduced moisture absorption from the environment and improved adhesions between the fiber and the matrix, enabling the successful fabrication of the composites (Oushabi, 2019; Tita et al., 2002). On the other hand, when using untreated fiber, water absorption occurs during the hardening period (removal from the mold after a minimum of 8 hours of curing and full hardness achieved after 1 week), resulting in composite swelling, irregularities, and the formation of bubbles. Therefore, despite generating waste, the alkaline treatment in this case allowed for the production of high-quality composites.

Figure 4 - Photographs of a) PU/BCT composite and b) and c) PU/BC composite.

Source: authors.

3.3 Mechanical properties of PU and PU/BCT composite: hardness, impact resistance and tensile test

The results of the Shore A hardness, Charpy impact resistance tests and tensile essay conducted on the PU samples and PU/BCT composite are presented in Table 1. The hardness of the PU is consistent with values reported in the literature for conventional PU (derived from the mixture of a polyol and diisocyanate), indicating that the biodegradable PU used in this study possesses similar properties (Rosa & Guedes, 2003). It is noteworthy that the hardness of the PU is slightly higher than that of the PU/BCT composite, which can be attributed to the fibers used, as they contribute to a decrease in hardness due to their predominant composition of cellulose, hemicellulose, and lignin.

The impact resistance results demonstrate that the PU/BCT sample exhibits approximately 2.8 times higher impact resistance compared to PU, indicating that the fibers act as reinforcement agents and contribute to a reduction in stiffness in the composite. This finding aligns with previous studies on alkali-treated short sugarcane bagasse fibers (Tita et al., 2002). Alkali treatment not only reduces the hygroscopic nature of the fiber but also decreases the content of hemicellulose and lignin, thereby enhancing the reinforcement effect on PU and resulting in a significant increase in impact resistance (Tita et al., 2002).

Table 1 - Results of Shore A hardness, impact resistance and tensile tests for PU and PU/BCT, where σmax (MPa) is the maximum tension, ε (%) is the elongation and E(MPa) is the Young modulus obtained from the tensile test.

Sample	Shore A hardness (A)	Impact resistance (J)	$\sigma_{máx.}$ (MPa)	ε (%)	E (MPa)
PU	93,6 (± 3,6)	0,2 (± 0,1)	4,9 (± 0,9)	54,9 (± 7,4)	12,5 (± 0,6)
PU/BCT	84,9 (± 4,8)	0,6 (± 0,2)	5,1 (± 2,1)	6,9 (± 2,0)	114,0 (± 20,0)

Source: authors.

For the maximum tension value obtained in the tensile test, observe that there was no significant increase, which indicates that the fiber does not act as a reinforcing agent. This fact may be related to the size of the fiber, which did not favor the increase in mechanical property. However, even without increasing the maximum tension value, the use of BCT in the PU is advantageous, as the BCT fibers act as a filler, avoiding the cost of producing the composite and also contributing to the reuse of the agro-industrial discharge of sugarcane bagasse.

However, it is observed that there was an approximately 9-fold increase in the Young's Modulus value (MPa) and an approximately 8-fold decrease in the elongation value (%) for the PU/BCT compound when compared to the PU. The presence of sugarcane fibers can increase the stress of the PU, making it less deformable, this is due to the rigid nature of the sugarcane bagasse fibers (John & Thomas, 2008).

3.4 Water absorption and density of PU and PU/BCT

The PU absorbed 0.67 (± 0.28)% of water after 96 hours, while the PU/BCT composite absorbed 5.11 (± 0.48)% of water after 96 hours. fibers in PU increases water absorption by about 7 times.

In general, when a composite absorbs more water, this is indicative of greater permeation, in this case the greater water absorption is due to the presence of hydroxyl groups in the BCT fibers (Jacinto & Spinacé, 2019). This result is in line with what was reported by Dos Santos et al., (2018), who studied PU composites derived from castor oil with bamboo powder and observed that the addition of fibers increases water permeation and water absorption.

For biomedical application of orthoses, the greater water absorption of the composite is advantageous, as it has the potential to reduce wounds caused by the accumulation of water between the patient's skin and the prosthesis/orthesis, helping to prevent infections (Dos Santos et al., 2018).

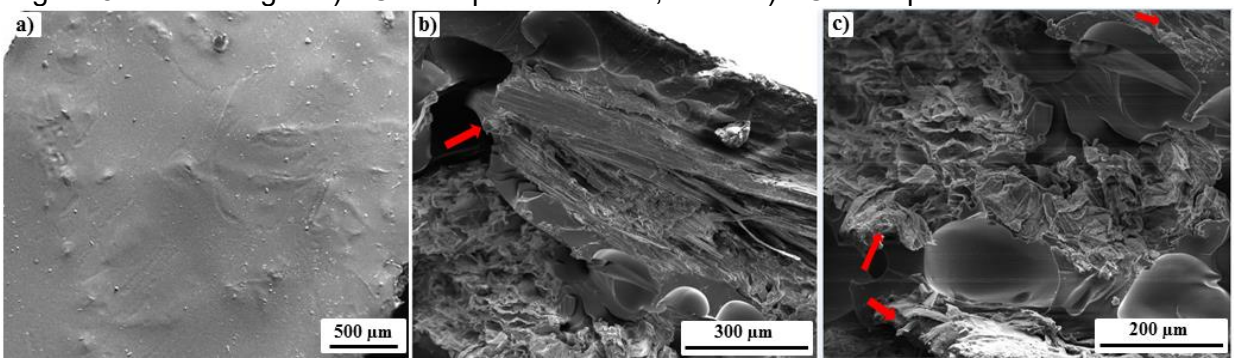
The density value obtained for the PU was 1.07 g/cm^3 and for the PU/BCT composite it was 0.88 g/cm^3. It is observed that the addition of fiber decreases the density by 17.8% compared to PU, which is advantageous, mainly for biomedical applications in which the patient will have to carry the material for a long period of time. The decrease in density provides greater comfort to the patient.

The composite density analysis and the water absorption analysis showed that the composite became lighter and more permeable, this result is important to guarantee greater comfort to the patient who uses orthosis and prosthesis.

3.5 SEM and biodegradation test for PU and PU/BCT

The SEM image in figure 5a shows the surface of the PU/BCT composite, it can be seen that it was possible to obtain a homogeneous surface. The fracture SEM (Figure 5 b and c) indicates, on the red arrows, a good adhesion of the BCT fiber with the PU matrix, which is in line with what was expected due to the fiber treatment and also the adhesive property of the PU (Sabnis & Kaiakade, 2023a). The good interaction between the phases of the composite is important to distribute applied mechanical stresses and also favor the permeation of water in the material.

Figure 5 - SEM images a) BCT composite surface; b and c) BCT composite fracture surface.

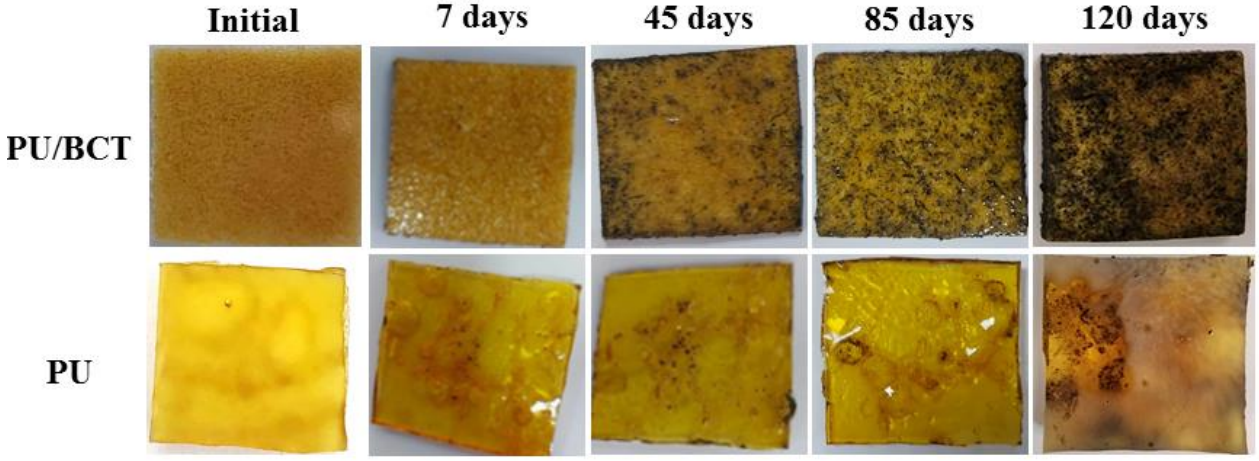


Source: authors.

The photos of the biodegradation test (Fig. 6) showed that the initial signs of material degradation began after 45 days of biodegradation testing. By the 45th day of the test, degradation was evident through the appearance of erosions, color changes, and soil strongly adhered to the specimens. After 120 days of biodegradation testing, it is visually observed that there was greater darkening of the sample and formation of erosions, however, there was no complete biodegradation of the PU and PU/BCT samples, which indicates that complete degradation occurs in a period longer than 120 days. This result is expected for the PU, since the vegetable PU, despite being biodegradable, has cross-links, which makes the biodegradation process difficult.

It is noted that the PU/BCT composite showed greater darkening when compared to the PU, indicating greater biodegradation, this is caused by the addition of BCT fibers, it is also noticeable that the degradation starts with the fibers, which is expected due to their higher hygroscopic nature compared to PU (Kale et al., 2015).

Figure 6 - Photographs of the biodegradation test in composted soil for the PU and PU/BCT samples in the period of 7, 45, 85 and 120 days of testing.

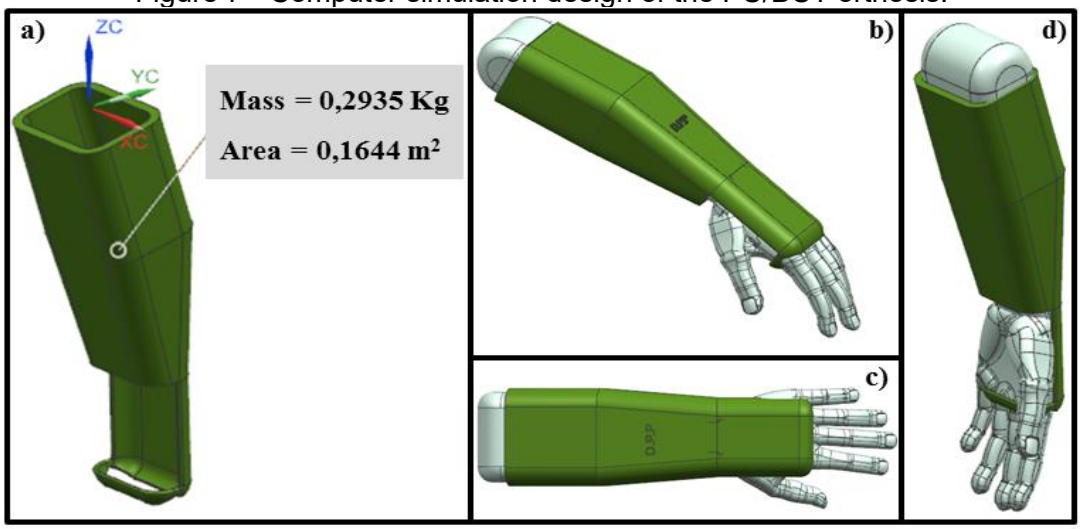


Source: authors.

3.6 Computer simulation

Figure 7 shows the design that was used to carry out the computational simulation, it can be seen that the simplest design was used for a wrist and arm orthosis. The design on the orthosis can be adjusted according to the patient's needs and also to save material. The orthosis weighed 0.29935 Kg and is within the weight values obtained in orthoses currently sold on the market.

Figure 7 - Computer simulation design of the PU/BCT orthosis.



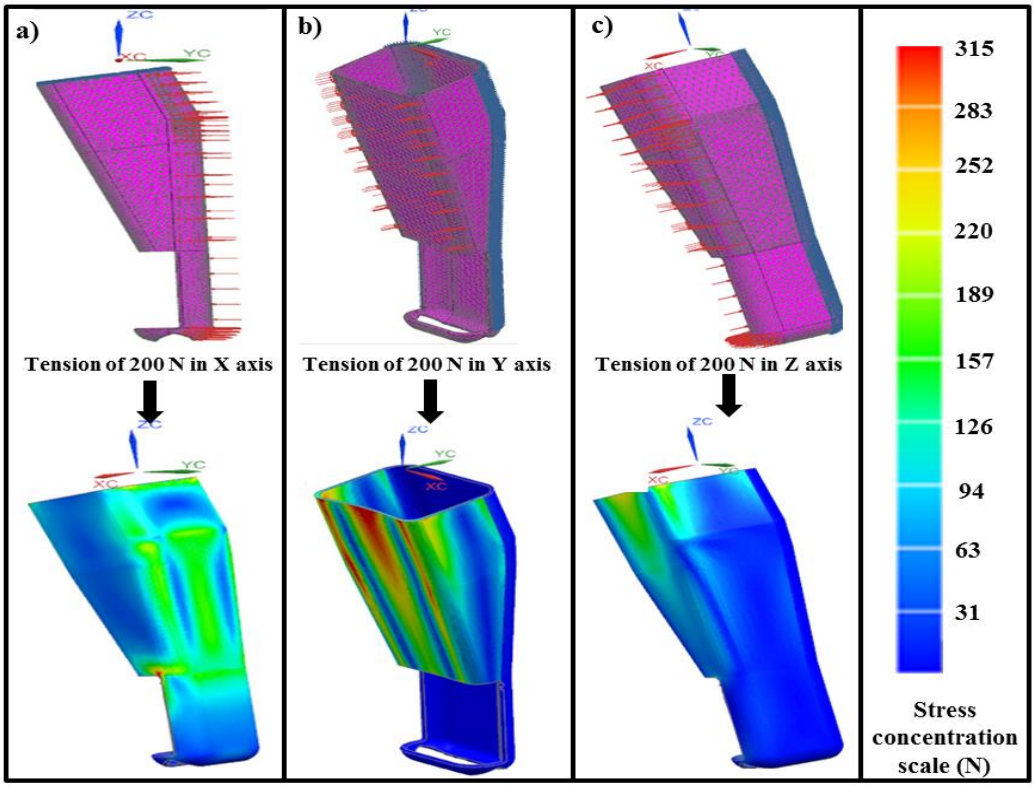
Source: authors.

Figure 8 shows the results of the computer simulation obtained for an orthosis made of PU/BCT when a tension of 200N is applied on the X, Y and Z axis. For the computer simulation, the resistance value of the PU/BCT was used as of maximum tension obtained in the tensile test (Table 1). It can be seen that there are different colors that indicate points of stress concentration (Fig. 8), but in this case they do not

lead to breakage of the product. In order to reduce stress points, it is possible to optimize the design or change the thickness of the product.

Based on the results of the stress analysis, it is possible to assess whether the orthosis meets the strength requirements. With the simulation analysis, it was possible to notice some points of stress concentration in the orthosis, however, within the expected range for this application.

Figure 8 - Results of the computational simulation for the orthosis made of PU/BCT after applying a tension of 200 N in the X, Y and Z axes.



Source: authors.

4 CONCLUSION

The treatment of the BC fiber was effective, as a change in the morphology and color of the fiber after treatment was observed by SEM. There was a decrease in the moisture absorption of the treated fibers, which made it possible to later manufacture the PU/BCT composite. The fiber size distribution was wide, which can influence the mechanical properties of the composite. The FTIR showed a decrease in the band at 3330 cm-1 referring to the vibrations of the hydroxyl group for the BCT fiber compared to BC, caused by the alkaline treatment.

The tensile test showed that there was no significant increase in the maximum tension value, however, there was an increase in stiffness evidenced by the increase in the Young's modulus value and reduction in the elongation of the PU/BCT composite

compared to the PU. The tensile test indicates that the fiber acted as a filler in the composite, reducing the cost compared to the PU matrix. The impact strength of the PU/BCT composite improved compared to the PU and there was a decrease in hardness.

The density of PU/BCT decreased by 17.8% compared to PU, which is advantageous for medical applications. The addition of fibers in the PU increases water absorption by about 7 times, which contributes to better water dispersion, reducing the formation of wounds in medical applications of orthoses/prostheses.

The SEM images of the composite showed that the fracture surface showed good adhesion between BC and PU fibers. The biodegradation test showed that the fibers are more susceptible than the PU and that the biodegradation of the composite occurs in a period greater than 120 days. The computer simulation analysis showed that there are some points of stress concentration in the orthosis, however, they can be minimized with the optimization of the orthosis design.

The objectives of the work were achieved, and it was possible to observe that the PU/BCT composite presents a promising character for application in orthoses due to its low density, atoxicity, satisfactory mechanical properties and also due to its renewable and biodegradable source that collaborates to reduce the deposition of polymeric waste in the environment.

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