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Mechanical Properties of Biocomposites Based on Enzymatically Treated Date Palm Fibers and PBS Matrix

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Mechanical Properties of Biocomposites Based on Enzymatically Treated Date Palm Fibers and PBS Matrix

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Abstract

Natural fiber-reinforced composites have garnered significant attention from researchers seeking to produce environmentally friendly materials and promote sustainable industrial development. The characteristics of the final composites, tailored for specific applications, depend not only on the properties of their constituents but also on the fiber/matrix interface. This is why soft fiber treatments are often recommended. This study aimed to assess the influence of the introduction of date palm fibers, having undergone an enzymatic treatment, on the mechanical characteristics of PBS/palm fiber biocomposites. The optimal enzymatic fiber treatment method and duration were determined based on reducing sugars released analysis. Fiber structure changes were determined by spectroscopic and morphologic analysis. The results showed that combined treatment with xylanase and pectinase for 8h contributed to higher amounts of reducing sugars released, indicating efficient removal of hydrophilic fractions. Microstructure tests showed an exposure of cellulose micro-fibrils that could enhance interfacial interaction fiber/matrix in the composite. Mechanically, composites with enzymatically treated fibers exhibited significantly increased stiffness modulus compared to the case of untreated fibers. The improvement in the composites rigidity is explained by the increase in the fibers cellulose rate with the biological treatment, which acts on the non-cellulosic components. The enzymatic treatment maintained the fibers natural morphology, enhancing fiber/matrix adhesion through increased contact surfaces.

Keywords

Fiber/matrix interface, PBS/palm fibers biocomposites, Mechanical characteristics, Enzymatic treatments.

1. Introduction

The utilization of plant fibers instead of synthetic ones to reinforce polymer composites presents a challenge for researchers aiming to manufacture ecological materials with excellent mechanical properties, which provide sustainable development in industries [1]. Thanks to their biodegradability, their abundance, their low cost as well as their low density conferring a high specific resistance for composites, these fibers are used as a reinforcing agent and have invaded many areas (aerospace, automotive, building, home appliances, …) [2]. However, some challenges remain, including the fibers' low thermal stability and hydrophilic nature which generates a high water absorption in the composite and that requires a coupling agent addition. The polarity difference between the hydrophobic polymer matrix and the hydrophilic fiber leads to insufficient interfacial adhesion, affecting the composite's mechanical behavior. Researchers have explored modifying natural fibers using physical and chemical methods like steam explosion, silane and peroxide treatments, corona treatment and NaOH treatment [3]. As an alternative to these commonly used methods, treatment with enzymes represents a more advantageous fiber surface treatment because it provides mild reaction conditions, non-destructive surface changes and high reaction specificity. Moreover, it is an environmentally friendly treatment methods that can be recycled after each use [4][5]. Enzymatic treatments act on non-cellulose components of the fibers like hemicellulose, pectin, waxes, ..., making it possible their extraction and obtaining fibers which are rich in cellulose [6]. Therefore, the mechanical characteristics of the treated fibers reinforced polymer matrix could be potentially enhanced [7]. Michael George et al. used different approaches (laccase, xylanase, polygalacturonase, pectinmethylesterase and Xylanase (10% cellulase)) in order to treat flax and hemp fibers. This study has shown the effectiveness of these enzymes in removing amorphous components. In addition, the hemicellulose fractions of the fiber are affected, particularly, by xylanase and pectinase enzymes [8]. The study conducted by Karaduman and Onal has shown that the treatment of fibers with the pectinase, laccase, xylanase and cellulase contributed to a reduction in the diameter and created rougher fiber surfaces. Thus, an increase in the fiber/matrix contact surface area as well as a stronger interfacial adhesion was obtained [7]. The aim of this study was to evaluate the influence of an enzymatically treated date palm fibers on the mechanical properties of PBS based composites. For that, different treatment approaches, including xylanase, pectinase, and a combination of both enzymes, were investigated in order to optimize fiber treatment and reduce the operation time. Biochemical and morphological analysis were employed to identify the most effective extraction method that exposes cellulose microfibrils by removing the maximum of amorphous constituents.

2. Materials and methods

2.1. Materials

The plant fibers utilized in this study were extracted from palm (comprising leaves + petioles) waste of the date palm tree, originating from the species Phoenix dactylifera in the Kebili region of Tunisia. The matrix used is the polybutylene succinate (PBS), specifically the PBE 003 type, supplied by Natureplast company in France. The enzymatic juices were produced at the Sfax Biotechnology Center (Molecular Biotechnology of Eukaryotes laboratory), with xylanases secreted by the fungus AX4 of Talaromyces thermophilus and pectinases by the strain CT1 of Penicillium occitanis.

2.2. Fibers treatment

The fibers were processed by two treatments; a light alcalin pretreatment at low molar concentration (NaOH solution at 0.4M) followed by an enzymatic extraction method utilizing the xylanases, pectinases or a combination of both enzymes. The enzymatic treatment is basically based on a hydrolysis in an incubator at 50 ° C, for 8h and with continuous stirring under 120 rpm.

2.3. Composite preparation

The composite materials were manufactured using a twin-screw extruder of CLEXTRAL BC21 type. The extruded materials obtained at the outlet of the die were cooled in a cold water tank and subsequently cut into granules. After a 48h drying process at 50°C, the specimens underwent an injection molding process using a DK-Codim 50 multiprocessor system machine.

2.4. Characterization techniques

The treatment of fibers by enzymes generates a decrease in non-cellulosic components. In order to quantify the quantity removed of these constituents, an analy-

sis of the reducing sugars released was conducted. For the case of xylanase, the measurement protocol uses 50 mM of phosphate buffer at pH7. However, for the pectinase, a citrate buffer at a concentration of 50 mM and pH5 was used. A 10 min incubation period at 100 ° C was performed after adding 3ml of DNS to the test tubes. Then, a 20 ml distillate water was added. Finally, the optical density was determined at 550 nm.

The analysis of the particle size (diameter) distribution of crude and modified fibers was conducted using a FQA Kajaani FS300 Metso at the University of Quebec in Abitibi-Temiscamingue.

To examine the fiber microstructure following the various enzymatic treatments, SEM analysis were conducted using a scanning electron microscope of Jeol, JSM-540 type. A metallization step was carried out initially in order to ensure fiber conduction.

Fourier transform infrared analysis was performed in order to detect changes in the chemical composition of the fiber after enzymatic treatment. IRAffinity-1S FTIR spectrophotometer was served, by applying the ATR sampling technique and a resolution of 4 cm^{-1}.

Tensile tests were conducted using a universal Instron 33R4204 machine fitted with a 50 kN load cell and at 20 mm/min cross head speed. Formulations of 0%, 5%, 10%, 20% and 30% were considered for untreated fibers, while enzymatically modified fibers were set at a mass content of 20% in the composite. Moreover, Charpy impact tests were performed on all fabricated composites utilizing a pendulum with 4 Joules of capacity. For mechanical testing, five specimens were tested for each formulation.

3. Results and Discussion

3.1. Reducing Sugars Analysis

The AX4 strain of Talaromyces thermophilus and the CT1 mutant of *P.* occitanis produce juices rich in xylanase and pectinase activities, respectively. These enzymes are specific in that they don’t require further purification process as the fungis don’t secrete cellulase enzymes, responsible for cellulose degradation. The measurement of reducing sugars released is a technique used to quantify the depolymerization of non-cellulosic components during enzymatic hydrolysis. An optimization of incubation time and enzyme concentration was carried out. As shown in Fig. 1, the depolymerization rate of amorphous components increased with the incubation period. Regarding the treatment with xylanase or pectinase enzymes, the quantity of released sugars, as indicated by the curves' slopes, decreased after 8h of enzymatic reaction. This suggests that 8 hours is sufficient to liberate the maximum amount of sugars and that the fiber's three-dimensional

structure is destroyed after approximately 4 to 6h, making it easier to attack the target components. When combining xylanases and pectinases enzymes, a significant liberation of reducing sugars is observed after 8h of incubation. It is evaluated at 61 mg/g of fiber compared to 45 and 30 mg/g of fiber for pectinase and xylanase enzymes, respectively. A more efficient fiber treatment has, therefore, been obtained with the mixture of the two enzymes.

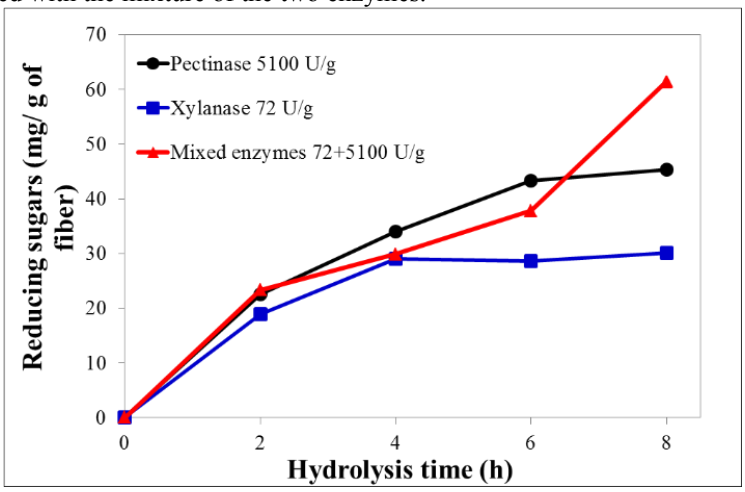

Fig 1. Optimization of time and enzymatic activities for palm fiber treatment

3.2. SEM Observation

Fig. 2 illustrate the changes in the surface morphology of the fibers following enzymatic treatments. The SEM image of the untreated fibers (Fig. 2a) shows the presence of non-cellulosic components on their surface that surround cellulose microfibrils, which constitute the fiber reinforcing element [9]. The treatment with xylanase (Fig. 2b) removed some impurities, oils and waxes and contributed to the reduction of hemicellulosic components. So, a cleaner and smoother surface was obtained. On the other hand, using pectinase enzyme also provided a significant reduction of cementing materials but didn't induce a fibers perfect separation (Fig. 2c). However, when a combination of enzymes (xylanase+pectinase) was employed, the cellulose microfibrils were fully exposed, resulting in a rough surface. This rough surface is believed to increase the contact area between the fiber and the matrix, facilitating better adhesion and polymer impregnation, which could enhance the overall performance of the biocomposites (Fig. 2d).

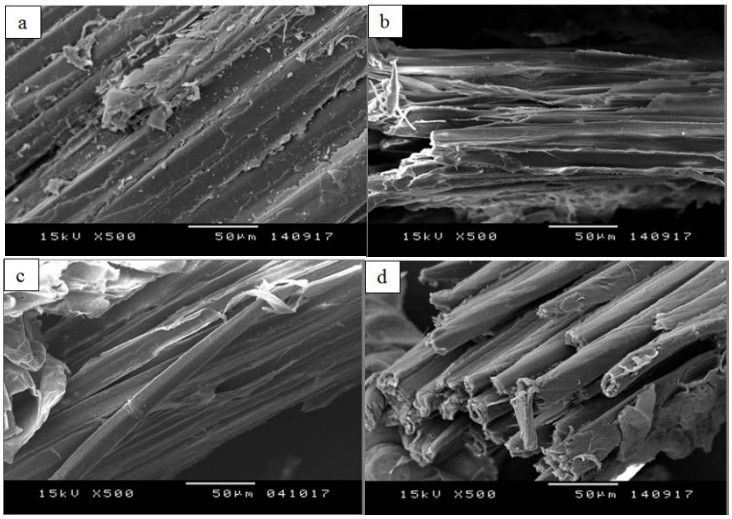

Fig 2. Micrographs of raw and treated palm fibers (a) control (b) xylanase (c) pectinase (d) xylanase + pectinase.

3.3. Particle size analysis

The diameter distribution of both untreated fibers and fibers which are treated with the mixture of enzymes is given in Fig. 3. The raw fibers obtained indicated that the majority of the mass distribution ranged from 31 to 40 µm, constituting 23.5% of the total. However, for the treated fibers, there was a reduction in the diameter where it is found that 20.9% of the fibers have a diameter within the interval of 21 and 30 µm. This reduction can be attributed to the decomposition of organic substances such as extractives and cementing compounds (like hemicellulose), which was initiated by the alkaline treatment and further promoted by the enzymatic treatment [10][11]. The resulting fibers became thinner and presented more separated cellulosic microfibrils [12]. Fatima Ezzahra et al., also reported that an alkaline pretreatment followed by enzyme treatment using cellulose and laccase activities contributed to a decrease in the fiber size [13]. Moreover, the non-modified fibers showed a larger surface area, with a diameter distribution ranging from 11 to 40 µm, compared to the modified surface fibers, suggesting a broader distribution of both bigger and smaller particles within the raw fibers. In contrast, the treated fibers displayed whereas a more homogeneously sized distribution. The diameter of the fibers significantly affects the biocomposite performance, and the reduction achieved through enzymatic modification of the lingocellulosic fiber allows for better dispersion and increased contact area with the polymer. This, in turn, is favorable for enhancing mechanical properties.

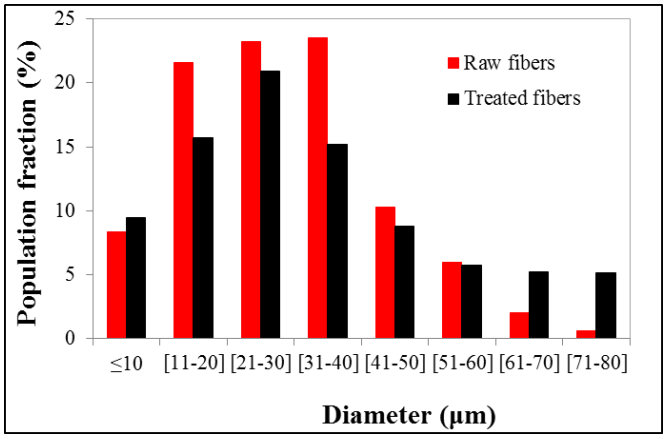

Fig 3. Diameter distribution of raw and treated palm fibers

3.4. FTIR Analysis

The treatment of fibers with mixed enzymes induced changes in the chemical composition, primarily due to the removal of amorphous constituents that represent the adhesive materials of the fibers. This change was confirmed by the FTIR spectrum, as shown in Fig. 4. The obtained results revealed specific absorbance peaks that provide insights into the structural modifications. The peaks observed at 1043 cm^{-1} and 1141 cm^{-1} correspond to the stretching of C-O bonds and antisymmetric bridge
C-O-C groups, respectively, in both cellulose and hemicellulose [14][15]. A -COO bond of hemicellulose was also associated with the 1238 cm^{-1} absorption band [16][17]. Moreover, the peak at 1595 cm^{-1} is linked to the C-O band related to the benzene ring, present in lignin [16]. The decrease in this peak indicates a reduction in lignin content, which is particularly evident with NaOH pretreatment. Finally, the absorption peak ranging from 1650 cm^{-1} to 1750 cm^{-1} correspond to the -C=O bond, which is assigned to aliphatic and aromatic aldehydes and esters [16][18][19].

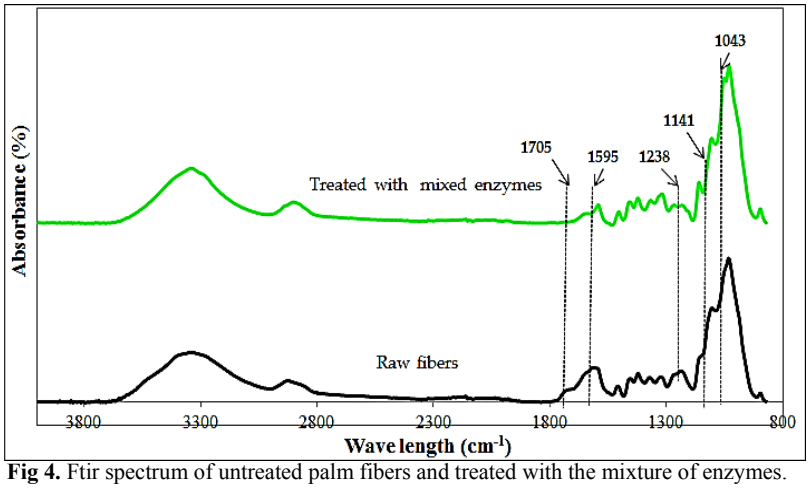

Fig 4. Ftir spectrum of untreated palm fibers and treated with the mixture of enzymes.

3.5. Mechanical Properties

Mechanical tests were carried out on biocomposites loaded with untreated and enzymatically treated palm fibers (Fig. 5). The treatment method adopted is that with the simultaneous enzymes action, which has proven to be effective in eliminating amorphous components and enhancing fiber separation. According to the Young modulus property, Fig. 5a) shows that the addition of fibers generates an increase in the composite's rigidity, due to better fibers dispersion in the PBS matrix [20]. bioomposites filled with surface-modified fibers exhibited the highest elasticity modulus, reaching approximately 1600 MPa. Consequently, the improvement of the fibers cellullose rate contributed to improving the composites rigidity, which indicates the effectiveness of the treatment undergone to the fibers. With regard to the tensile strength (Fig. 5b), the incorporation of raw palm fibers resulted in a decrease in this property from 40 MPa for pure PBS to 26 MPa for composites based on 30% raw fibers. This fact is linked to the restriction of the mobility of the polymer chains as more fibers are introduced into the matrix [21]. Composites with treated fibers exhibited, however, a slight increase in tensile strength compared to those with 20% raw fibers. Charpy shock tests (Fig. 5c) demonstrated that the virgin PBS polymer experienced only a slight deformation without rupture. Upon the addition of fibers, the energy required to fracture the specimens decreased. In the case of composites reinforced with treated fibers, the energy decreased by up to 33% compared to composites with untreated fibers at the same loading percentage (20%). This decrease in shock resistance is attributed to the improved rigidity of the composite, leading to crack propagation and embrittlement [22].

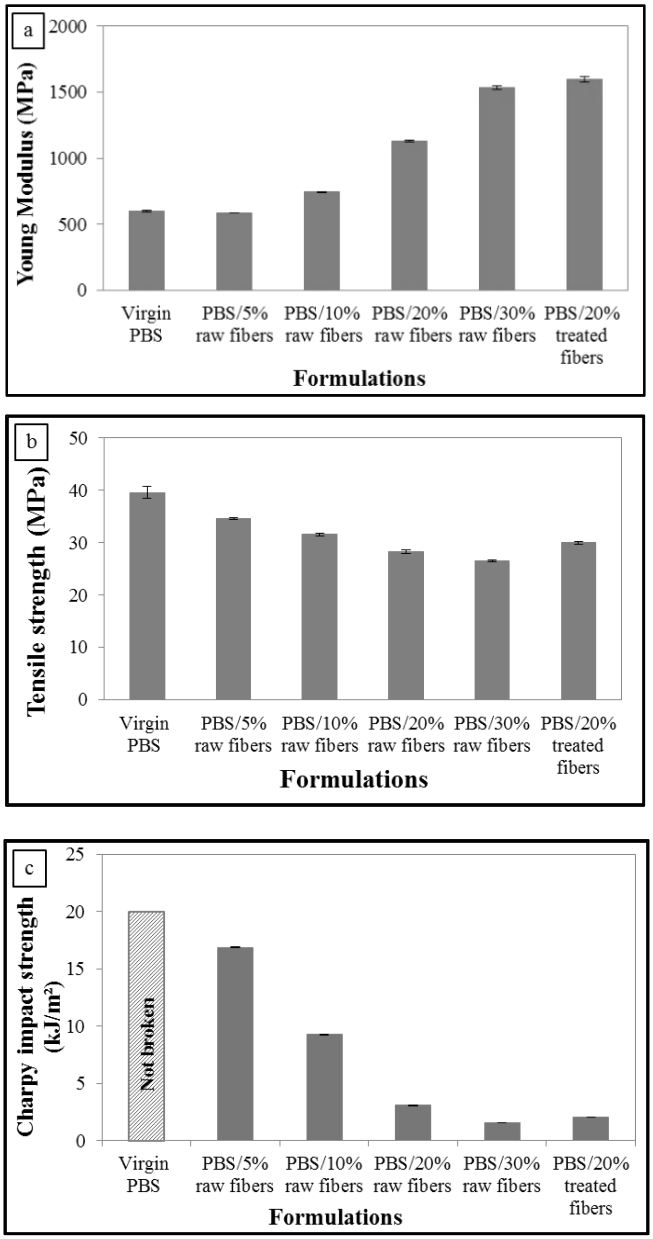

Fig 5. Mechanical results (a) Young's modulus (b)Tensile strength and (c) Charpy impact strength of pure PBS and raw and treated fibers reinforced PBS polymer

4. Conclusions

This study has demonstrated the effectiveness of enzymatic treatments in selectively removing disordered fiber components, which are non-crystalline in nature, while preserving the fiber structure and morphology. Specifically, the combination of xylanase and pectinase enzymes proved to be beneficial and profitable, resulting in the extraction of fibers rich in cellulose while reducing the processing time. The biocomposites filled with treated fibers exhibited significant improvements in rigidity compared to those containing raw fibers, along with enhanced tensile strength. These findings highlight the potential of enzymatic treatments as a promising approach for improving the mechanical characteristics of palm fiber-reinforced biocomposites. By optimizing the enzymatic treatment, it is possible to produce biocomposites with improved performance, contributing to the development of sustainable and friendliness materials for various industrial applications.

Competing Interests

The authors have no conflicts of interest to disclose in relation to this article.

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