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Development of a Starch-based Biocomposite Reinforced by Natural Fibers Extracted from Sawdust: Biodegradability Study

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Abstract

In this work, natural biocomposites were developed from thermoplastic starch reinforced with natural fibers extracted from the sawdust, an industrial waste. The extracted fibers were thoroughly characterized for their chemical composition. To improve the adhesion properties, the fibers were treated with 5% NaOH solution at different time intervals of 2, 4, 6, 12, 24, and 48 hours. The resulting nanofibers were characterized using infrared spectroscopy. The starch/fiber biocomposites were then prepared using extracted fibers and starch and biocomposites were characterized comrehensively. For this purpose, various compositions of starch/nanofibers biocomposite were prepared and effect of different parameters were optimized. The effect of time for alkaline treatment of the fibers (2, 4, 6, 12, 24, and 48 h), mass percentage of added fibers (3%, 6%, 10%, and 12%), and fiber sizes (200 and 500 μm) on the moisture absorption rate of the synthesized biocomposites was studied. Finally, the biodegradability study of the synthesized biocomposite films (30 mm × 30 mm) was carried out by burial in the soil, in which a slurry in different proportions was incorporated. The samples lost their shape and became too fragile and brittle after 20 days of incubation, and after 30 days of burial, a total biodegradation of the films was observed, making it difficult to differentiate from the soil.

Keywords: Biocomposite, Sawdust waste, Starch, Natural fibers, Reinforcement, Biodegradation.

Introduction

Nowadays, plastics are present in our daily lives and used in many applications, such as shopping bags, packaging, etc. Inspite of their many advantages, they generate voluminous waste that poses enormous problems related to their end-of-life treatment [1, 2].

The solutions proposed so far are often expensive and require the implementation of an effective collection system. Due to the fact that these plastics are stable materials that decompose very slowly in nature (about 400 years), recycling seems to be the most adequate method, but the multiplicity of polymers used in plastic processing induces many difficulties, particularly during selective sorting, and unfortunately leads to recycled materials with poor and degraded properties

[3]. On the other hand, the incineration of plastics that have petrochemical origin is very polluting, as it releases enormous quantities of CO_2 and other toxic gases that are harmful to the environment and human health [4].

The recent awareness about environmental pollution and its adverse and prolonged impacts is promoting the new concept of "eco" or "bio" friendly materials among general population, scientific community and authorities. The concept of biocompatible or ecofriendly materials consists of elaborating materials from renewable resources (from biomass) with the aim of preserving the environment and better managing natural resources [5, 6]. Thus, new materials called eco-materials and biocomposites have emerged [7]. Among these biomaterials, bioplastics or biodegradable plastics are presented as a solution that can partially solve the problems of plastic waste, particularly by their ability to degrade naturally under the action of living organisms and their low rates of greenhouse gas emissions, which gives them a clear advantage over traditional plastics [8].

The development of these bioplastics is essentially based on the use of agro-sourced polymers, which exist in great diversity. Among them polysaccharides such as starch is a natural, abundant, biodegradable, and renewable polymer obtained from several sources such as corn, wheat, potato, cassava, etc. [9–11].

Starch-based polymers offer desirable physical properties such as thinness, flexibility, transparency, and impermeability to oxygen, with no discernible odor, taste, or color. However, they suffer from drawbacks like poor mechanical strength and water vapor permeability, limiting their applications when used alone [12]. To address these limitations, various methods have been employed, including starch modification methods like cross-linking with calcium and zirconium [13], as well as lignin [14], and blending with specific synthetic polymers like polyvinyl alcohol, polylactic acid, and polybutylene succinate [15, 16]. Additionally, incorporating lipids [17] into film formulations can enhance moisture resistance, although lipids are prone to oxidation. Furthermore, reinforcing thermoplastic starch with natural fibers presents another viable approach to improve its performance alongside other biodegradable materials.

In this context, blends of natural fibers with polymer materials are attracting significant attention because they offer favorable characteristics and performance at a reasonable price. Natural fibers, like hemp, wood, kenaf, jute, rice husk, and flax [18, 19], bring numerous economic and environmental benefits. They are readily available, cost-effective, lightweight, tough, biodegradable, and possess good heat resistance, while maintaining an acceptable strength-to-weight ratio. Compared to synthetic fibers [20], these natural alternatives stand out.

The natural fibers are commonly employed to reinforce various types of polymers, including thermosetting ones i.e. epoxy, urethane, vinyl ester, phenolic, polyester, polyamide, and polyurethane [21–23], as well as thermoplastics such as polyethylene, polypropylene, nylon, polycarbonate, polyvinyl chloride, polyether-ether ketone, and acrylonitrile-butadiene-styrene [24, 25], along with elastomers [26].

The high concentration of hydroxyl groups in natural fibers gives them hydrophilic characteristics. Therefore, their wettability with hydrophobic polymer matrices is very low. This fiber-matrix incompatibility not only makes the

distribution of fibers in the matrix non-uniform [27], but also increases the moisture absorption of composites, leading to swelling, high biological degradation, and low strength [28]. Fiber size and concentration in composites also have a direct influence on their ability to absorb moisture [29]. Consequently, natural fibers need to be pre-treated before being incorporated into polymer matrices. Various chemical, physical, and mechanical methods have been developed to modify the surface characteristics of natural fibers. Alkaline treatment (mercerization) is one of the most widely used chemical treatments. This treatment solubilizes fiber constituents such as lignin and hemicellulose from the surface and improves surface roughness, which in turn improves bonding with the matrix [30]. During chemical treatments, the hydroxyl groups in natural fibers reduce due to reaction with sodium hydroxide, resulting in decreased hydrophilicity of natural fibers.

Standardized and non-standardized biodegradability tests applied to these composites [31, 32] have been reported in the literature. Standardized tests are essentially based on aerobic and anaerobic digestion. These tests use mass measurements, gases generated, and visual observations to assess the biodegradability of biocomposites.

Akhlaq et al. [33] reported that over the past 20 years, research studies have investigated the degradation of bioplastics under aerobic composting and anaerobic digestion conditions. This study provides critical insights into the topic. Pooja et al. [34] compared the biodegradation rates of potential bioplastics in soil from different sources, including biomass, microorganisms, and monomers. It highlights the biodegradable properties of these materials, making them promising alternatives to conventional plastics. The study investigated by Cai et al. [35] explored the biological degradation of plastics and microplastics. Although it covers various types of plastics, it sheds light on mechanisms and influencing factors relevant to bioplastics as well. Kubowicz and Booth [36] discussed the challenges and misconceptions related to plastic biodegradability. While they didn't focus solely on bioplastics, however, they provided valuable insights into the broader context of plastic degradation. Ghosh and Jones [37] reported that biodegradable plastics aim to safely return carbon to ecosystems by complete assimilation of the degraded product. This word discusses the current state of research and emphasizes the importance of understanding degradation mechanisms.

In this context, this study is devoted to the development of biocomposites based on biopolymers such as starch reinforced with natural fibers. The use of natural fibers was opted for their low cost, their availability, and especially to preserve the ecological advantages of the used biopolymers. Several natural fibers are used as substitutes for conventional fibers: hemp, flax, jute (in Europe) [38], bamboo (in Asia) [39], date palm, and esparto (in Africa) [40], but in this present investigation, the study was focused on sawdust.

The main objective of this study was to develop 100% natural bio-composites from biopolymers such as thermoplastic starch reinforced with natural fibers extracted from sawdust recovered by the local woodwork waste. The natural fibers derived from sawdust were examined along with their chemical composition. Then, improvements were made to the compatibility of natural fibers with starch-based matrices. Biodegradability tests were carried out in an anaerobic aqueous environment using digested activated sludge from municipal wastewater treatment plants.

Materials and Methods

Materials

For the fibrous reinforcement, the sawdust considered waste was used and collected from a local woodwork waste. The sawdust fibers serve as an excellent additive for biocomposite materials due to their renewable nature and biodegradability, reducing reliance on non-renewable resources and enhancing environmental sustainability. These fibers enhance mechanical properties such as tensile and flexural strength, while their lightweight nature contributes to weight reduction in several industrial applications. Additionally, utilizing sawdust fibers is cost-effective, as they are often low-cost or waste materials, reducing production expenses. Moreover, their inclusion improves thermal properties. By incorporating sawdust fibers, biocomposites offer reduced environmental impact, mitigating waste generation and promoting eco-friendly manufacturing processes.

The fibers were dried at 105 °C for 2 h to remove excess moisture. Then crushed and sieved using a sieve (NF.X11.501 standard). The final granulometry of the fiber obtained is between 200 and 500 µm as shown in Fig. 1. Starch was chosen as a matrix, which was provided by SARL.CEBON. Ethanol (CH_3CH_2OH), toluene ($C_6H_5CH_3$) acetic acid (CH_3COOH), hydrochloric acid (HCl), sulfuric acid (95-97% H_2SO_4), sodium hydroxide (NaOH), citric acid ($C_6H_8O_7$), and glycerol ($C_3H_8O_3$) were purchased from Sigma-Aldrich (Darmstadt, Germany). The chemical reagents were all analytical grade.

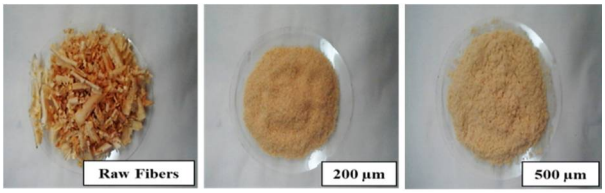

Figure 1. **Sawdust waste as a source of fiber for reinforcement of the synthesized biocomposite**

Physicochemical Analysis of Sawdust

Moisture and volatile matter content are determined according to the NFV03903 standard. The water content (H) corresponds to the weight loss undergone by the sawdust after drying at 100 °C until constant mass changes (around 3 h in this study). The dry matter content (M_S) is expressed as a percentage by mass of the sample, which is deducted from the water content [41].

$$H = \frac{W_1 - W_2}{W_1 - W_0} \quad (1)$$

$$M_S = 100 - H \quad (2)$$

Mineral and organic contents are determined by calcining the sample at 550 °C for 6 h in a programmable muffle furnace with a heating rate of 1 °C/min. The mineral and organic contents were calculated according to ASTME1755–61 procedures.

$$M_M = \frac{W_3 - W_0}{W_1 - W_0} \times 100 \quad (3)$$

$$M_O = M_S - M_M \quad (4)$$

Where, W_0 (g) is the weight of the crucible empty, W_1 (g) is the weight of the crucible and sample before heating and/or calcination, W_2 (g) is the weight (crucible + residue) after heating until constant mass changes, and W_3 (g) is the weight (crucible + residue) after calcination.

In order to determine the chemical composition of the sawdust fibers, a series of extractions were carried out to isolate the different substances contained in the material, such as greases and wax, pectin, hemicelluloses, and lignin. All the tests were performed according to the procedures described in the literature, which are mostly based on the American Society for Testing and Materials (ASTM).

Treatment of the fibers in an ethanol-toluene mixture (ASTM D 1107-96 procedure) was used to remove grease and wax [42]. 4 g of the dried fibers were treated with 400 mL of an ethanol-toluene mixture (in volume ratio 1:2) in a Soxhlet apparatus. The extraction was carried out for 8 h. The residue was then filtered and dried in an oven at 100 °C up to constant weight changes.

$$\%\ \text{grease \& wax} = \frac{(W'_1 - W'_2)}{W'_1} \times 100 \quad (5)$$

Treatment of the fibers in hot water (ASTM D1110-84 procedure) was used to remove wax and some other inorganic substances. 2 g of the dried fibers were treated twice per 100 mL of reflux water at 85 °C for 3 h. Then the residue is filtered and washed with water and dried in an oven at 100 °C. After drying, the residue was weighed to determine the change in fiber weight.

$$\text{Wax}\ (\%) = \frac{(W'_1 - W'_2)}{W'_1} \times 100 \quad (6)$$

Lignin content was evaluated using standard method (APPITA P11s-78 standard) [41]. Precisely, 1 g of wood fibers recovered after treatment with the ethanol-toluene mixture were immersed and agitated in a 75% H_2SO_4 solution for 2 h. Then 560 mL of water was added to reduce the acid content to 3%, and the solution was boiled under reflux for 4 h. The residue was then filtered and washed with 500 mL of water, dried at 100 °C, and weighed. As lignin is insoluble in 75% sulfuric acid, this residue consists essentially of lignin.

$$\text{Lignin}\ (\%) = \frac{W'_1}{W'_2} \times (100 - W'_3) \quad (7)$$

Holocellulose content was also estimated using standard method (NFT 12-008). This test includes cellulose and hemicelluloses [41]. 3 g of the fibers recovered after treatment with an ethanol-toluene mixture were placed in a flask containing 150 mL of distilled water, 0.2 mL of glacial acetic acid, and 1 g of sodium hypochlorite ($NaClO_2$). This flask is heated in a water bath maintained at 70-80 °C for 5 h with stirring. Every hour, 0.2 mL glacial acetic acid and 1 g $NaClO_2$ were added. After five hours, the flask was placed in an ice-water bath until the temperature of the solution reached 10 °C.

The flask contents were then filtered, and the residue was washed with 500 mL of distilled water (the residue changed color from yellow to white). The residue was then dried at 100 °C until constant weight.

$$\text{Holocellulose}\ (\%) = \frac{W'_2}{W'_1} \times (100 - W'_3) \quad (8)$$

Cellulose content of the fibers was studied using Kurshner and Hoffer's method [41]. Initially, 2 g of dried holocellulose, obtained from the previous test, was treated with a 17.5% sodium hydroxide solution for 30 min. 50 mL of distilled water was then added, and the mixture was stirred for 5 min. Then the residue was filtered and washed with 8.3% soda solution, then with 40 mL of 10% acetic acid, per 1000 mL of water, and finally dried at 100 °C until constant weight.

$$\text{Cellulose}\ (\%) = \frac{W'_2}{W'_1} \times W'_4 \quad (9)$$

Where W'_1 and W'_2 are the fibers weights before and after treatment, respectively and W'_3 is the result obtained after the solubility test of the fibers in the ethanol-toluene mixture (%). The W'_4 is the percentage of holocellulose obtained from the previous test.

Alkaline Treatment (Mercerization)

The sawdust fiber was immersed in a sodium hydroxide solution of 5% (w/v). The chemical treatment was held for different times: 2, 4, 6, 12, 24, and 48 h at room temperature. After treatment, the fiber was washed several times with distilled water, and the NaOH residues were neutralized by an acetic acid solution of 2% (wt/v). Then the neutralized fibers were again rinsed abundantly with distilled water. Finally, the fibers were dried at room temperature for 48 h and in a hot air oven at 100 °C for 3 h.

FTIR was carried out to identify the type of bonding, components, and structure changes in the wood fiber resulting from the different treatment times using FTIR (SHIMADZU IR Prestige-21). The samples were crushed and well mixed with potassium bromide (95% KBr + 5% samples), then pressed in the form of thin pellets. The infrared spectrum was recorded in the range from 4000 to 400 cm^{-1} at a resolution of 1 cm^{-1}. Thermal stability is one of the limiting characteristics of natural fibers as the reinforcing agent in producing structural composite materials. To determine the thermal behavior of various chemical constituents present in the sawdust fiber, thermogravimetric (TGA) and differential thermal (DTA) analyses were performed in the nitrogen gas atmosphere (flow rate 20 mL/min) at a heating rate of 10 °C/min starting from room temperature (25 °C) to 900 °C. The TGA and DTA curves were obtained using Perkin Elmer/TGA 4000.

Preparation of starch/fiber composites
Starch matrix

Corn starch (5 g) was dispersed in 100 mL of distilled water under magnetic stirring. 1.5 g of glycerol (30% by weight), 3 mL of HCl (0.1 M), and 0.5 mL of citric acid (10%) were added successively. The mixture was heated up to 80 °C in a water bath for about 45 min until the mixture became translucent. At the end of heating, 3 mL of NaOH (0.1 M) was also added. Once the mixture cooled down, it was poured into rectangular glass molds and placed in an oven at 35 °C for 48 h. The films were unmolded after cooling down to room temperature (Fig. 2).

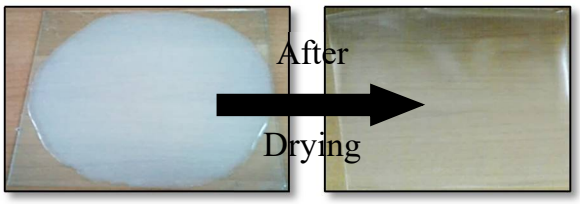

Figure 2. **Starch strips basic matrix for the synthesized biocomposite**

Fiber-reinforced Starch Composite Strips

The same procedure used for the matrix preparation was carried out. Different amounts of treated and untreated fiber (3%, 6%, 10%, and 12%) were added. The details in proportions of each composite manufactured are given in Table 1.

Table 1. Proportions of chemical compounds for film preparations.

Strips	Label	Fibers (%)	Starch (g)	H_2O (mL)	Glycerol (g)	HCl [0.1 M] (mL)	NaOH [0.1 M] (mL)	Citric acid (g)
Starch	SS0	0	5.00	100	1.50	3	3	0.50
Strips by untreated Fiber	SntF3	3	4.85	100	1.45	3	3	0.48
	SntF6	6	4.70	100	1.41	3	3	0.47
	Snt10	10	4.50	100	1.35	3	3	0.45
	SntF12	12	4.40	100	1.32	3	3	0.44
Strips by treated Fiber	StF3	3	4.85	100	1.45	3	3	0.48
	StF6	6	4.70	100	1.41	3	3	0.47
	StF10	10	4.50	100	1.35	3	3	0.45
	StF12	12	4.40	100	1.32	3	3	0.44

Water Absorption

In order to study the hygroscopicity effect of the ambient air on the prepared composite materials, especially those based on starch due to its high affinity to water, water absorption tests were carried out according to the ASTM E104 procedure [43].

Different composite strips (20 mm × 20 mm) were made up by adding different amounts of untreated and treated fibers: 3%, 6%, 10%, and 12%. The dried strips were placed into a controlled relative humidity conditioning chamber, which contains 75% of a saturated NaCl solution. Thereafter, the samples were removed at specific intervals and weighed until a constant weight was obtained. The content of water uptake was calculated as follows:

$$\text{Water uptake (\%)} = \frac{M_0 - M_t}{M_t} \times 100 \quad (10)$$

Where, M_0 and M_t represent the initial weight of samples and the weight after time t (days) exposure of the samples to a relative humidity of 75%, respectively.

Results and Discussion

Physicochemical Characteristics of Sawdust

The mechanical, crystalline, and thermal properties of natural fibers are greatly influenced by various chemical constituents existing on their surface. The obtained results of the physical and chemical analysis of sawdust showed that the sawdust contains 99.2 wt% of dry matter while the moisture is less than 0.1 wt%. The sawdust fiber consists of organic matter (99.24 wt%) mainly, whereas, the mineral matter (ash) is around 0.67 wt%.

The amount of cellulose found in the sawdust was around 45 wt%, which contributes significantly to the improved mechanical and crystalline properties by providing strength, toughness, rigidity, and structural constancy to the cell walls of the fibers [44]. The higher weight percentage of the cellulose content was found in the sawdust fibers when compared to some other natural fibers, for instance, coconut tree leaf sheath fiber (27 wt%), bamboo fiber (26–43 wt%), and *Althaeaofficinalis* L. fiber (44.6 wt%). However, the cellulose content of sawdust was found lesser than *Grewiadamine* fiber (57.78 wt%), *C. quadrangularis* root fiber (77.17 wt%), jute fiber (72 wt%), *Sidarhombifolia* fiber (75.09 wt%), and *C. quadrangularis* stem fiber (82.73 wt%) [45].

The higher amount of hemicellulose content in the natural fiber can disintegrate microfibrils present in the fibers and deteriorate the mechanical strength of fibers [46, 47]. In this study, sawdust contains 29.06 wt% of hemicellulose, which is near to the bamboo fiber (30 wt%) and lower than the seagrass fiber (38 wt%), but higher than *K. Africana* fiber (9.34 wt%), *C. quadrangularis* root fiber (11.02 wt%), *F. religiosa* fiber (13.86 wt%), and *P. pusilla* leave fiber (18.56 wt%) [48].

The lignin content was noted to be 15.56 wt%, which is higher than the lignin content of *Furcraeafoetida* (11.46 wt%) and lower than *Pennisetumpurpureum* (20 wt%). Lignin has useful and reasonable adhesive and hydrophobicity properties that serve as a defensive agent against biological attack and significantly contribute to the fiber's structure and characteristics [49].

The wax tenor of sawdust was 12.16 wt.%, which is considerably higher than *Furcraeafoetida* (0.24 wt%), *Prosopis Juliflora*, *Acacialeucophloea*, etc. The high amount of wax and moisture contents adversely influence the interfacial bonding

characteristics during the preparation of composite materials[27].

Infrared Spectra of Treated Fibers

The FTIR spectra of treated and untreated fibers are shown in Fig. 3. A wide band at 3317 cm^{-1} was observed corresponding to the hydroxyl groups (-OH), which may belong to either cellulose, hemicellulose, or lignin. A band around 2919 cm^{-1} was observed, which is attributed to the asymmetrical elongation vibrations of the (C-H) groups of cellulose and lignin. The peak at 1737 cm^{-1} is assigned to the elongation vibration of the carbonyl groups (C=O) from esters or acetyl funtionalities of hemicellulose substances (especially hexuronic acids), pectin, and wax [43]. The vibration at 1653 cm^{-1} represents the adsorbed water, due to the hydrophilic character of the cellulosic fibers. The peaks at 1507 cm^{-1} and 1456 cm^{-1} both reflect the symmetrical elongation of the bonds (C=C) of the aromatic ring present in lignin, the peaks at 1316 cm^{-1} and 1366 cm^{-1} correspond to the vibrations of the bonds (C-H) in cellulose and hemicelluloses [50, 51]. While the peak at 1263 cm^{-1} is assigned to the ether groups (C-O-C) elongation of lignin. Finally, a characteristic band at 1027 cm^{-1} translates the elongation vibrations of the (C-O) groups in cellulose, and the alcohols in lignin and wax [52].

After alkaline treatment, the band at 1735 cm^{-1} assigned to carbonyl groups (C=O) elongation vibration esters or acetyl groups of hemicelluloses, pectin, and wax disappeared [53]. The disappearance of the peak at 1263 cm^{-1} corresponds to the elongation of ether groups (C-O-C) of lignin [54]. These disappearances are mainly due to lignin, wax, and pectin solubilization in sodium hydroxide solution. The obtained spectrum also shows a lowering in the intensity peaks at 1653 cm^{-1} (adsorbed water), 1027 cm^{-1} (C-O), and 3317 cm^{-1} (-OH). The decrease in intensity of the peaks was attributed to the decrease in hydroxyl groups (-OH) and lignin solubilization [55].

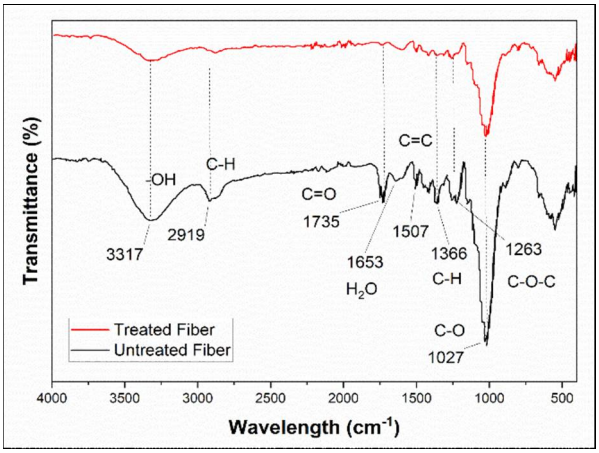

Figure 3. **FTIR spectra of untreated and treated sawdust fiber**

Thermogravimetric Differential Thermal Analysis (TG/DTA)

Usually, the manufacturing of thermoplastic composites reinforced with natural fibers requires high temperatures. Thus, it is crucial to examine the strength and thermal stability of these fibers at various temperatures to (i) determine the most suitable temperature range for processing these composites, and (ii) avoid deterioration of fiber characteristics [47].

The DTG and DTA curves of sawdust fibers are shown in Fig. 4 (a). In the first phase of degradation at temperature around 120 °C, the DTG curve shows a loss of moisture with a mass loss of approximately 8.57%. This phase is accompanied by an endothermic peak of dehydration [56]. Then, a stability level between 120 °C and 230 °C was recorded, from which no loss of mass was recorded. In the second phase, a strong degradation occurred between 230°C and 370 °C with a significant mass reduction of 60.44%. This weight loss is related to the reduction of hemicellulose and glycosidic

bonds of cellulose [57]. The DTA curve shows an intense peak at 340 °C, which results in thermal degradation of cellulose I and extreme degradation of α-cellulose. A comparable peak was detected in various natural fibers such as *Lygeumspartum* (338.7 °C) [47], the root of *Cissusquadrangularis* (328.9 °C) [45]. The complete decomposition of cellulose and the maximum amount of volatile matter completely decomposed between 370 °C and 640 °C, the remaining mass disappeared is around 30.99%.

From the above results, it can be confirmed that sawdust fibers are a suitable additive material playing an important role in the reinforcement of composites in which the working temperature can reach 350 °C.

The treatment with NaOH can have several effects on the chemical composition and structure of sawdust fibers. This treatment can eliminate certain components, such as hemicelluloses, modify or partially remove lignin, and can influence the properties of cellulose. These chemical changes can influence the thermal stability of the material [58, 59].

The effect of the time of alkali treatment on the thermal stability of sawdust fibers is shown in Fig. 4 (b). It can be observed that the loss on ignition of the treated fibers was reduced significantly with increasing treatment time. Indeed, the minimum loss on ignition was obtained after 6h of impregnation (35% remained weight).

The impact of time of alkali treatment on thermal properties of fibers is also crucial. Longer treatment may result in greater modification of sawdust fiber components, leading to increased thermal stability due to the removal of lignin and hemicelluloses, which are an amorphous components and are soluble in alkali solution. However, excessively long treatment could also damage the cellulose structure, which could be observed as a reduction in thermal stability [60].

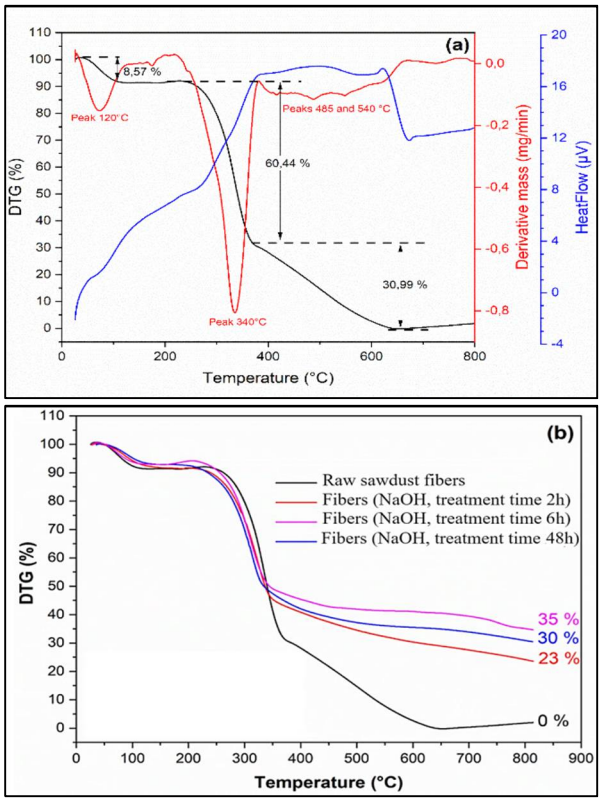

Figure 4. **Thermogravimetric and Thermo-Differential analysis of (a) raw sawdust fibers, (b) alkaline treated fibers**

Characterization of Composite Materials
Effect of Alkaline Treatment on the Fibers

The effect of alkaline treatment of the fiber on water absorption of the composites is illustrated in Fig. 5. Both treated and non-treated fibers showed the rapid increase in water absorption during first few days and reached equilibrium at the beginning of the second week when same percentage of fiber content was added. Composite samples containing 3%, 6%, and 10% of treated fibers had a lower moisture absorption rate than the untreated fibers. After two weeks, composites with 12% treated fibers reached a moisture content of 16%, while the untreated fibers reach 20%.

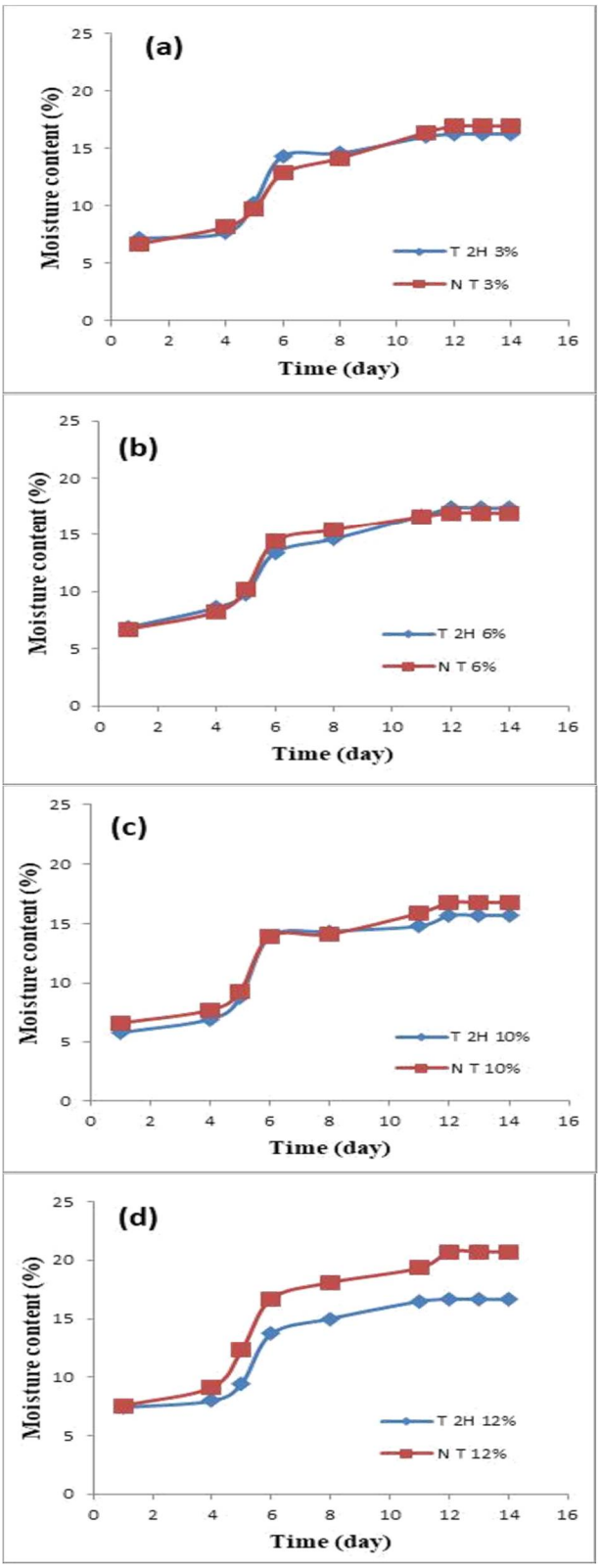

Figure 5. **Moisture content of the films (200 µm) (T = Treated fibers for 2 h, and NT = Untreated fibers), (a) 3%, (b) 6%, (c) 10%, and (d) 12%**

Effect of Time Treatment

Different alkaline treatment times were applied to the sawdust fibers at 2, 4, 24, and 48 h. Moisture absorption rates of the composites were plotted in Fig. 6. It can be seen that the treatment from 2 h to 4 h results in lower moisture content absorption of the composites compared with untreated fibers. Beyond 24 h of treatment, the moisture content of composites with treated fibers is much higher than those with untreated fibers.

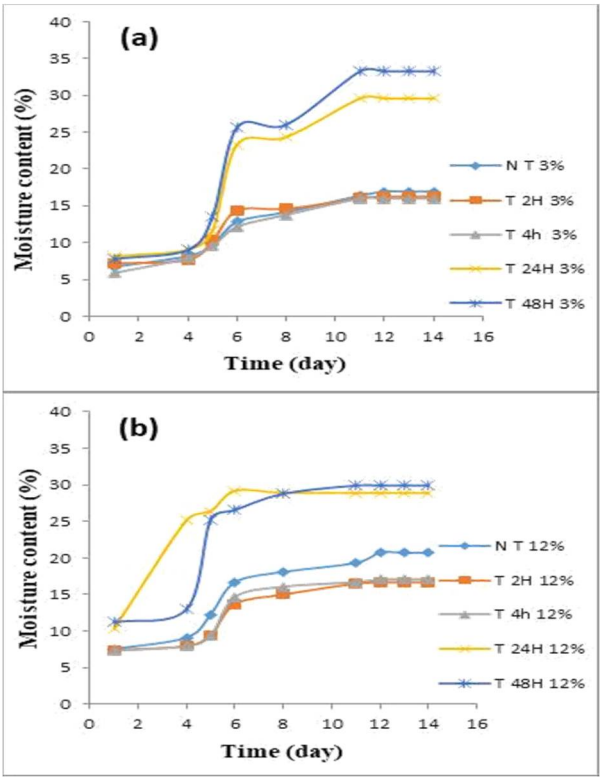

Figure 6. **Effect of treatment time on the absorption moisture content of films (200 µm) (NT = Untreated fibers, and T = Treated fibers for 2 h, 4 h, 24 h, and 48 h), (a) 3%, (b) 12%**

Effect of Fiber Content on Composites

Moisture absorption rates of the prepared composites with treated and untreated fibers containing different percentages of 3%, 6%, 10%, and 12% of

fibers are shown in Fig. 7. It can be seen that the percentage of fibers in the composites does not affect the moisture absorption rate.

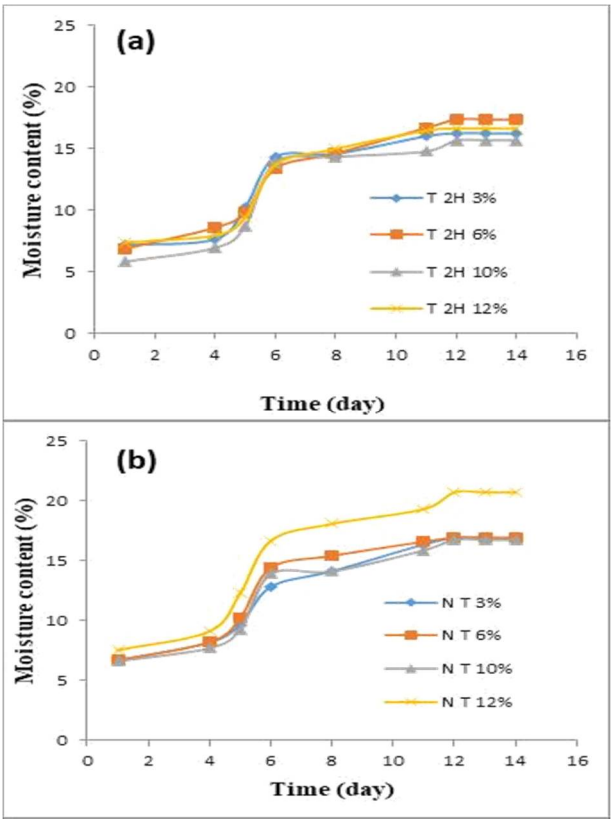

Figure 7. **Effect of fiber (200 µm) content on moisture rate (T = Treated fibers for 2 h, and NT = Untreated fibers), (a) fiber treated film (b) film not treated**

Effect of Fiber Size

The addition of fibers at different sizes (200 and 500 µm) was also studied. The results of moisture absorption as a function of the fiber content incorporated in the matrix are presented in Fig. 8. During the first week, it was observed that composites with 500 µm fibers absorbed less moisture than the composites with 200 µm fibers, and beyond this week, the absorption of composites with 500 µm exceeds largely as compared to composites with 200 µm fibers.

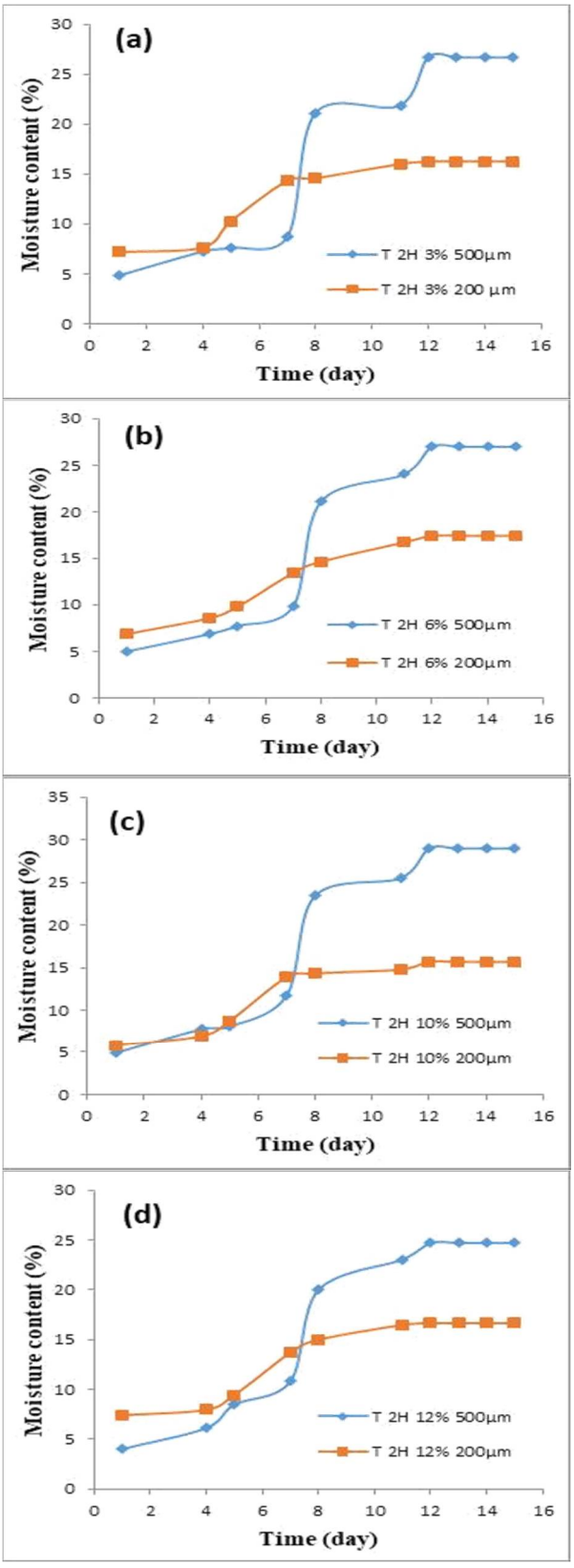

Figure 8. **Effect of fiber size on moisture rate (T = Treated fibers for 2 h), (a) 3%, (b) 6%, (c) 10%, and (d) 12%**

One of the major disadvantages of starch-based materials is their sensitivity to moisture. This hydrophilicity is related to the presence of hydroxyl groups that interact with water molecules and establish strong hydrogen bonds. The incorporation of fibers allows, therefore, replacing the hydroxyl groups with more hydrophobic functions. These results are in good agreement with those of FTIR analysis.

In Vitro Biodegradability Tests of Biopolymer Films in the Soil

The biodegradability of the composites performed in the present study was evaluated by the method of undergrounding the biopolymer films in the soil. This technique permits getting closer to the real conditions of the natural environment.

Under small-scale laboratory conditions, the biodegradation tests were carried out in aluminum cans of dimension 6 cm ×6 cm ×3 cm, filled with 100 g of natural soil and others containing soil with different percentages of sludge: 5%, 15%, 20%, and 30%, respectively, to the mass of the natural soil (Fig. 9). The sludge used was collected from the residues of the wastewater treatment plant (domestic discharge) of Mostaganem City (Algeria). Films with dimensions of 30 × 30 mm were undergrounded in these containers and sprinkled every 5 days with water to ensure a high enough moisture content to activate the bacteria present in sludge. After every 5 days of undergrounding, the composite films were removed and carefully stripped from the soil and photographed. This method allows the monitoring of the degradation of material as well as the period required for its total degradation.

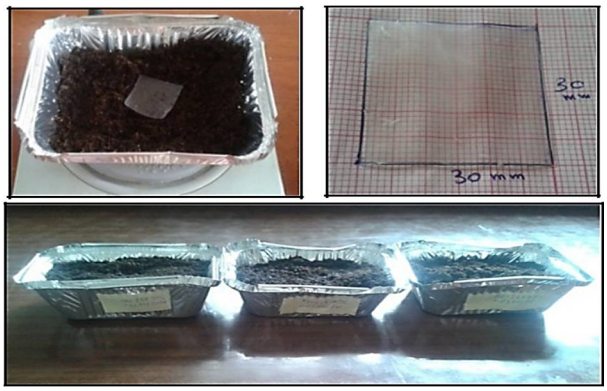

Figure 9. **Biodegradation experiment of synthesized biopolymer in soil**

Benchmarking of Images

The surface degradation of biocomposite samples was meticulously assessed through image analysis, providing valuable insights into their degradation process. Notably, the surface measurements captured in Fig. 10 and Fig. S1 (a-f) (*see supplementary material*) revealed significant changes over time, indicating ongoing degradation. It's essential to highlight that while surface degradation was quantified, variations in thickness were not considered in this analysis, emphasizing the need for comprehensive assessment methods.

Biodegradation experiments conducted on composite materials unveiled considerable variability in degradation rates, influenced by factors such as sample size, the type and quantity of incorporated sludge. Visual observations during the initial 10 days of exposure highlighted noticeable alterations in sample morphology and color, indicative of microbial activity instigating accelerated degradation kinetics. Subsequent incubation periods led to further deterioration, with samples losing structural integrity and eventually becoming indistinguishable from the surrounding soil after 30 days.

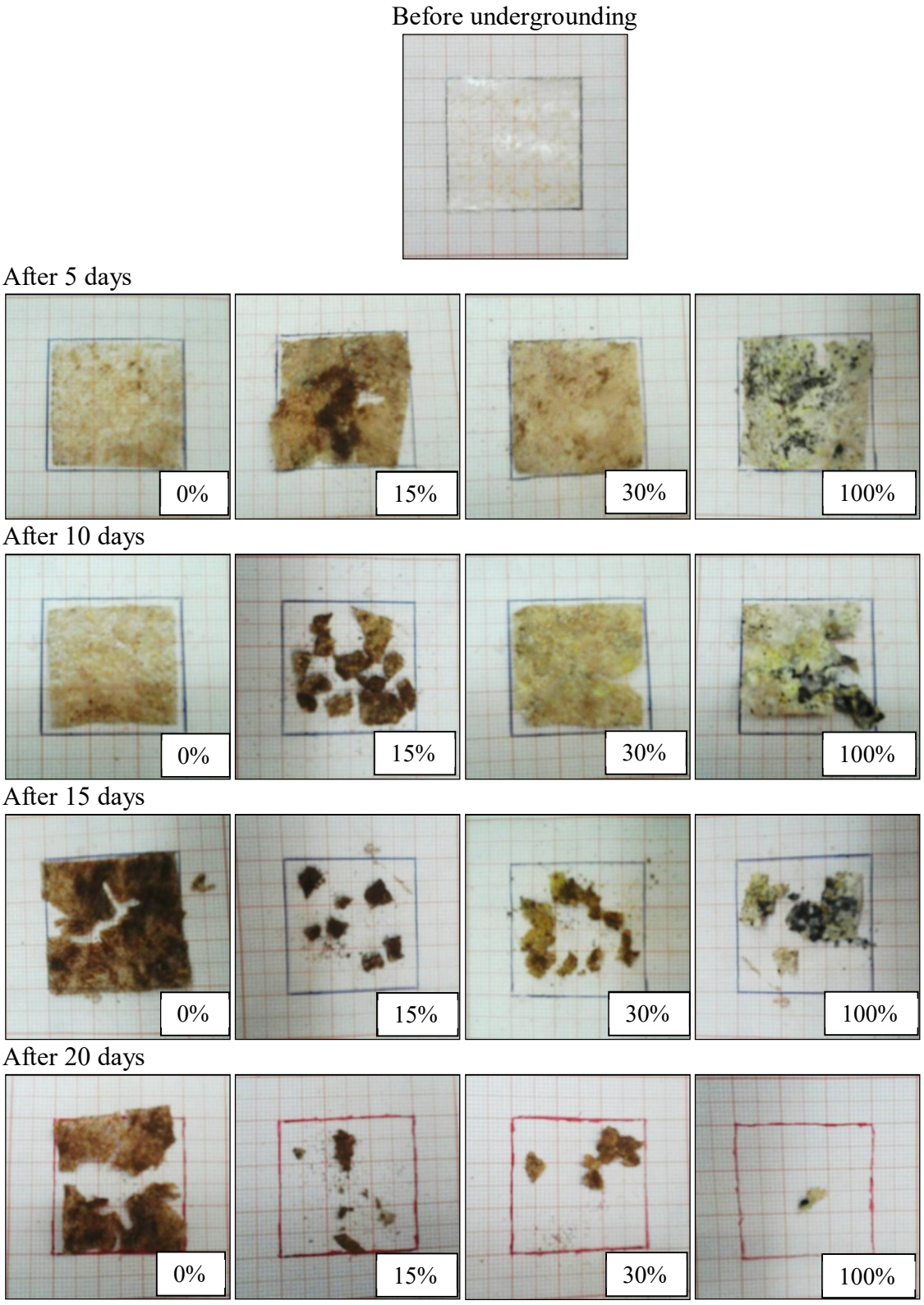

Figure 10. **Biodegradation of starch/fiber composite films (untreated fibers: 6% and 500 µm)**

Comparative analysis between different experimental setups elucidated the impact of sludge content on degradation kinetics. Samples containing higher sludge concentrations exhibited faster degradation rates, while those composed with 0% sludge (soil only) demonstrated minimal degradation. Furthermore, examination of untreated and treated fibers revealed differential degradation rates, with untreated fibers undergoing rapid degradation compared to their treated counterparts. Notably, variations in fiber size significantly influenced degradation dynamics, with larger fibers exhibiting prolonged degradation timelines [61].

Moreover, the influence of additional fiber mass on degradation kinetics was evident, with higher fiber content correlating with slower degradation rates. Notably, optimal degradation outcomes were observed with lower fiber content, emphasizing the importance of carefully balancing material composition for enhanced biodegradability. These findings underscore the intricate interplay between material composition, fiber characteristics, and environmental factors in governing the biodegradation of biocomposite materials. Such insights are invaluable for the development of sustainable and environmentally friendly composite materials [62, 63].

Conclusion

Woodwork waste “sawdust” has been recovered and successfully used as reinforcement in polymers. The physicochemical analysis of sawdust reveals that it consists mainly of 98.83% organic matter, of which cellulose is the major constituent, representing 43.54% of the overall composition of the waste. The treatment with sodium hydroxide solution results in the reduction of hydrophilicity of the fibers, thus increasing the compatibility between polymer and fiber. As shown on the infrared spectra, this decrease is attributed to the decrease in hydroxyl groups (-OH) and to the solubilization of lignin at the surface of fibers.

Different formulations of starch/fiber composites were developed. It was found that composites with 3, 6, and 10% of treated fibers absorb more moisture than untreated fibers. By increasing fiber content up to 12%, the composites with treated fibers absorb less than untreated fibers. This is due to the decrease in the hydroxyl groups of the fibers. As for the effect of fiber treatment time, beyond 24 h of treatment, composites with treated fibers absorb more than untreated ones.

The biodegradation of the composite films in sludge alone is better compared to those containing 15 and 30% of sludge. For samples with 0% sludge (soil only), the biodegradation takes place very slowly. The biodegradation process was widely affected by alkaline treatment, in which the composites biodegrade more rapidly with untreated fibers than with treated fibers. The decrease in fiber content promotes the kinetics of the degradation process, as well as the decrease in fiber size, where the best degradation results were obtained with 500 µm fibers.

The assessment of surface degradation through image analysis offers valuable insights into the biodegradation process of composite materials, though it's limited to surface-level changes. Variability in degradation rates across experiments underscores the influence of factors such as sample size and sludge composition. Visual observations suggest microbial activity accelerates degradation kinetics, while comparisons between untreated and treated fibers highlight the importance of fiber characteristics in degradation dynamics. Additionally, the correlation between fiber content and degradation rates emphasizes the

need to optimize material composition for enhanced biodegradability. These findings contribute to understanding the complex interplay of factors governing biodegradation and inform the development of sustainable composite materials.

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Conflict of Interest

All the authors declare that there is no conflict of interest regarding research work presented in this paper.

Data Availibilty Statement

The related supplementary data can be obtained from PJAEC or corresponding author on request.

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