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Research Article

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Effect of Fiber Surface-Treatments on the Properties of Poly (Lactic Acid)/Olive Husk Flour Biocomposites

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ABSTRACT

In Algeria, considerable quantities of olive husk are rejected as waste causing consequently inconvenience to environment. Therefore, our work is focused on the valorization of this waste by its incorporation in PLA matrix to obtain biocomposite materials with specific performances. The hydrophilic nature of natural fibers affects negatively its adhesion to hydrophobic polymeric matrix. To improve interfacial adhesion, chemical treatment of the fiber can stop the moisture absorption process clean the fiber surface, chemically modify the surface or increase surface roughness. Therefore, our paper reports the effects of three chemical surface modifications (alkali, silane and benzoylation) on the properties of biocomposites based on poly lactic acid (PLA) reinforced with olive husk flour (OHF) incorporated at 10, 20 and 30 wt.%. From the samples produced by extrusion-injection, the thermal and mechanical properties of biocomposites with both treated and untreated olive husk flour are reported and compared with the properties of the neat matrix. The results show that the mechanical and the thermal properties of the biocomposites with treated fiber are better than that of neat PLA and the biocomposites with untreated fiber.

Keywords: Poly lactic acid; Olive Husk; Chemical treatment; Mechanical properties; Thermal behavior

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INTRODUCTION

The evolution of fully biodegradable composite materials based on polylactide and natural fibers has been well researched in recent years [1,2]. In order to enhance mechanical and thermal properties of the matrix, some natural fibers that provide reinforcement, such as low density, high strength and stiffness, can be added at low cost, also improving environment friendliness and health/safety factors [3-6]. However, like many other natural fibers, using olive husk flour (OHF) has drawbacks such as a high hydrophily due to the presence of hydroxyl groups on the olive husk surface. Furthermore, the presence of non-cellulosic components (e.g., lignin and wax) may prevent husks from having a good interfacial adhesion with the neat polymer. Therefore, chemical treatments for husks are commonly investigated. The quality of the fiber-matrix interface is important when applying natural fibers as reinforcement for polymer matrices. In order to improve the compatibility between the hydrophobic thermoplastics and the hydrophilic cellulosic fibers, many chemical and physical surface treatments have been applied to obtain reinforced composites with high performance natural fibers. Therefore, studying potential improvement of the interface adhesion between natural fillers and bio degradable polymers is of essential importance. Various studies have been carried out to enhance the interfacial properties of the cellulose/PLA biocomposites through physical, chemical treatments of cellulose fiber and grafting reactions of PLA matrix [7].

Many researchers have investigated the modification of natural fibers and their subsequent characterization in composites. In addition, many chemical treatments have been performed to enhance the fiber/matrix interface. These include alkali [8], acetylation [9] and silane treatments [10].

Of these, alkali and silane treatments are the most widely used and effective methods. Considerable work has been done regarding how to use alkali and silane treatments to improve the mechanical properties of natural fibers and their composites [11,12]. Thi et al [13] studied the effects of alkali and silane surface treatments of husks reinforced poly (lactic acid) (PLA). The results indicate that when silane treatments are combined with an alkali pre-treatment, biocomposites have higher mechanical properties and better thermal stability than biocomposites that are only treated with silane treated. Alkali treatments clean the surface of rice husks and activate the hydroxyl groups. These active hydroxyl groups react with the silanes more easily than the hydroxyl groups on the surface of untreated husks. Masud et al. [14] investigated the effect of alkali and silane fiber surface-treatment on the properties of laminated PLA/kenaf fiber composites. They observed a significant improvement in the overall mechanical properties after the fiber surface treatments. Ming et al [15] highlighted the effects of the alkali treatments on the mechanical characteristics and interfacial adhesion of the abaca fiber/epoxy composites. They denoted that after 5 wt.% NaOH treatment, the crystallinity, tensile strength and Young's modulus of composites increased in comparison to untreated ones. Moreover, interfacial shear strength with an epoxy also improved. Orue et al. [16] examined the effect of different chemical treatments on sisal fiber bundles' tensile properties, as well as on the tensile properties of composites based on a poly (lactic acid) (PLA) matrix and sisal fibers. After treating the sisal fibers, the tensile strength values decreased compared to untreated fibers, especially when the combination of NaOH and a silane treatment was used. Moyeenuddin et al. [17] studied the effects of alkali and silane surface treatments on random short fiber and aligned long hemp fiber reinforced PLA composites. They found that alkali and silane fiber treatments improve tensile and impact properties which appears to be due to good fiber/matrix adhesion and increased matrix crystallinity.

As mentioned earlier, silane treatment is one of the most applied methods for improving the interfacial adhesion between the fiber and matrix [18]. Fact, silane is hydrolyzed, forming reactive silanols, which are then adsorbed and condensed on the fiber surface (sol-gel process). Thus, the hydrogen bonds formed between the adsorbed silanols and the hydroxyl groups of natural fibers improve the mechanical performances of the resulting polymer/fiber composites [19]. Yuan et al. [20] used silanized flax fibers as reinforcement in PLA biodegradable composites. They emphasized that increases in from 30 to 50% and silane treatment from 1 to 5% result in an increase the tensile strength and modulus. On the other hand, the flexural strength and modulus first increased and then decreased with increasing flax rate. Panayiotis et al [21] noted that the surface treatment with maleic anhydride resulted in the highest Young's modulus increment, whereas silanization and plasticization improved both tensile and flexural properties of the composites with modified flax fibers. Tao et al. [22] have treated ramie fiber with alkali and silane (3-aminopropyltriethoxy silane and γ-glycidoxypropyltrimethoxy silane) reinforced poly (lactic acid) (PLA) composites. They found that the tensile, flexural and impact strength of the composites were significantly improved.

The present paper describes the preparation of olive husk flour reinforced polylactide green biocomposites by extrusion. The selection of PLA is based on the fact that it is the most widely commercialized and readily available bio-based thermoplastic polyester derived from renewable resources such as corn, beet, and sugar. For comparison, OHF/PLA composites with untreated, alkali-treated, silane-treated and benzoylation-treated olive husk flour are fabricated and their mechanical and thermo-mechanical properties are assessed.

MATERIALS AND METHODS

Materials

Polymer used in our work was PLA of Grade 7001D, melt flow index of 6 g/10 min (210 °C/ 2.16 kg), density of 1.24 g/cm3, glass transition temperature and a melting point of 60 and 154 °C respectively. It was supplied by Nature Works LLC.

Olive husk flour (OHF) used as reinforcement fiber was supplied by local olive manufacturers from the south region of Algeria after the end of the olive oil extraction process. OHF was washed with hot water in order to eliminate the oil residue, crushed and sieved. The average diameter used is <100μm.

Chemical modifications of OHF surface

Alkali treatment:

The fibers were treated with 5% NaOH for one hour and washed many times with distilled water containing 1% acetic acid to neutralize excess sodium hydroxide. Finally they were washed with distilled water until pH neutral, dried at the ambient air temperature for 12 h and then in an oven at 80°C for 6 h.

Silane treatment:
1 wt.% of silane (weight percentage compared to the husks) was dissolved in water/ethanol mixture (30:70 w/w). The pH of the solution was adjusted to 4 with acetic acid and stirred continuously for 30 min. Next, the husks were soaked in solution for 3 h, washed by tap water and dried on oven at 60 °C for 24 h.

Benzoyl chloride treatment:
The fibers treated with alkali were suspended in 10% sodium hydroxide and then stirred with 50 ml of benzoyl chloride for 1 hour, filtered and dried. Then they were placed in ethanol for 1 hour to remove the benzoyl chloride unreacted. Finally, the fibers were washed with distilled water and dried in an oven at 70 °C for 24 h.

Processing conditions
Composites samples of PLA and OHF treated and untreated at different rates (10, 20 and 30%) were compounded by melt mixing using extrusion type 5&15 micro compounder DSM Xxplore method followed by injection molding. Screw temperature was set at 180 °C, screw speed was maintained at 50 rpm and residence time was fixed at 8 min.

Characterization
Mechanical testing:
Measurement of mechanical properties of the specimens was performed using a brand traction machine "Instron 5565". The strain rate was kept constant at 10 mm/min. The machine was connected to a computer that performs all necessary calculations and plots the stress/strain curves.

Dynamic mechanical analysis (DMA):
The storage modulus, loss modulus, and loss factor (tan delta) of the composite specimens were measured as a function of temperature (20°C-100°C) using a TA Instruments RSA-3 tension compression at a frequency of 1 Hz and a heating constant rate of 4°C/min.

Differential scanning calorimetry (DSC):
Thermal characterization using DSC was performed using a DSC7 Perkin Elmer apparatus. A heat/cool/heat procedure was applied over a temperature range from 40 to 250 °C at 10 °C/min under nitrogen atmosphere (N_2).
The glass transition temperature (Tg), crystallization temperature (Tc), melting temperature (Tm), and melting degree of crystallinity of PLA and its biocomposites were calculated as expressed by the following equation:

$$x(\%) = \frac{\Delta Hm}{\Delta H°m} \times \frac{100}{\varphi}$$

Where ΔH_m represents the heat of fusion (J/g), $\Delta H°_m$ represents the theoretical heat of fusion of 100% crystalline PLA (93.1 J/g) and Φ represents the weight fraction of PLA in the biocomposites.

Thermo-gravimetric analysis (TGA):
Thermal analysis of untreated and treated olive husk flour, pure PLA, and composites were analyzed using TA instrument Q500 with a heating rate of 10 °C/min. The samples were heated from 20 °C to 700 °C to determine the complete thermal degradation of bio-composites. All tests were carried out in nitrogen atmosphere using a flowing rate of 50 ml/min.

Scanning electron microscope (SEM):
The measurements were performed on samples to fractured surface and metallized by a layer of gold on a scanning electron microscope JEOL 840-A.

RESULTS AND DISCUSSIONS

Mechanical properties
Tensile test:
The effects of various chemical treatments on tensile strength, Young's modulus and elongation at break values of untreated and treated bicomposites were given in Figure 1. With the addition of olive husk flour, the Young's modulus was increased with the increase in fiber content from 3101 MPa for the neat PLA to 3816 MPa for untreated composite with a fiber content of 30%. This is due to the rigidity of the olive husk flour itself (Figure 1a). While the ultimate tensile strength (Figure 1b), the elongation at break (Figure 1c) was decreased obviously, this

was mainly attributed to the bad dispersion of olive husk flour and poor interfacial interaction between the filler and matrix. [23,24]

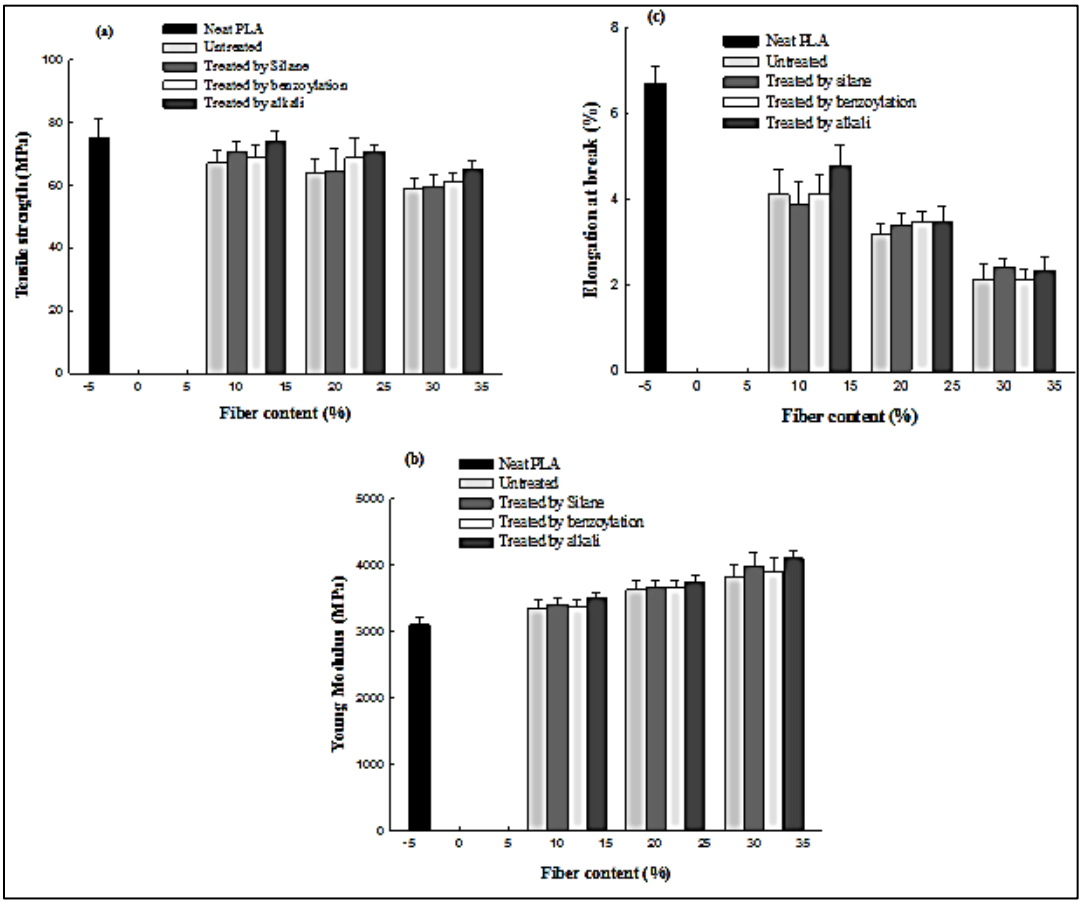

Figure 1: Tensile strength (a), Young Modulus (b) and Elongation at break (c) of OHF/PLA

It was observed that chemical treatment improved the tensile strength of all composites and the improvement followed the order: alkali treated > silane treated > benzoylated > untreated. Indeed the maximum improvement in tensile strength was observed for alkali treated fiber. This result can be attributed to the improved adhesion between the fiber and the matrix after chemical modification of the fiber. According to Agrawal et al. [25], the chemical treatment has an effect on the mechanical behavior of natural fibers, especially on fiber stiffness.

Dynamic mechanical properties (DMA):

The temperature curves of storage modulus and loss factor is shown in Figure 2. It is obvious that the storage modulus of the composites is higher than the PLA matrix, due to the reinforcement effect imparted by the olive husk [26,27]. As seen in Figure 2, the composite with alkali-treated fiber had higher storage modulus than that of the untreated composite. This suggests that the adhesion between the PLA matrix and the olive husk flour was better with NaOH treated olive husk flour rather than the untreated olive husk flour. It is believed that the removal of lignin is a key step in producing high modulus composites. Besides, many authors are in substantial agreement on this result [28].

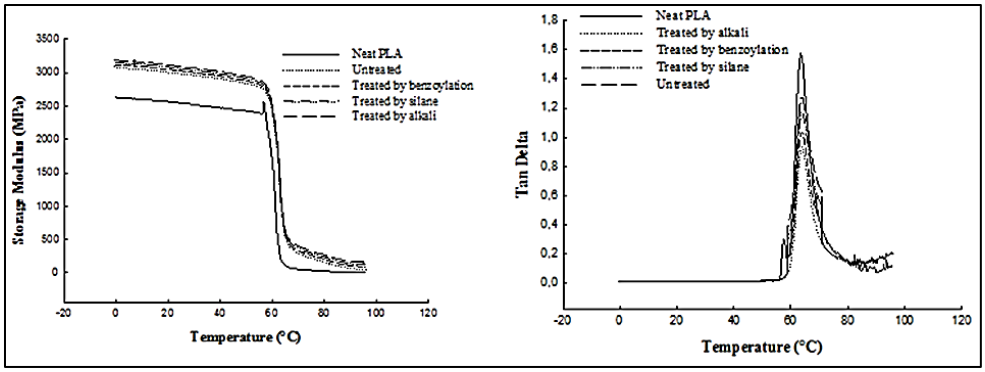

Figure 2: Temperature dependence of storage modulus and tangent delta of PLA and PLA based biocomposites

Surface-treated fiber reinforced composites indicate the longer plateau on the storage modulus than that of neat PLA where the softening temperature is increased from about 48 °C for neat PLA to 57 °C with olive husk flour, which implies an increase in thermal stability of the neat PLA matrix with the addition of treated fibers and it is further increased if the composite is crystallized [27,29]. DMA results show important variations in main relaxation temperature, which can be linked both, to interactions resulting in a decrease of chain mobility and to a regular reinforcing effect. These results are consistent with the static mechanical behavior, which vary according to the fiber content and the treated or untreated fiber.

Figure 2 shows also the loss factor (Tan delta) of the PLA and its composites as a function of temperature, where the ratio of storage modulus and loss modulus gives the tangent of the phase angle delta, a measure of energy dissipation. Loss factor in the transition region measures the imperfections in the elasticity of a polymer, with the possibility of additional losses occurring at the matrix-fiber interface [29,30].

As seen in Figure 2, the fibers contribution to the damping is extremely low compared to that of the PLA matrix. This suggests that the combined attenuation of olive husk flour reinforced composites would be mainly caused by the molecular motion of PLA and the interaction at the fiber/matrix interface.

PLA crystallinity in composites

In Figure 3, it is apparent that the crystallinity of PLA in composites increased with increased fiber content which could be due to the increased availability of nucleation sites leading to the formation of increased transcrystallinity [31-33].

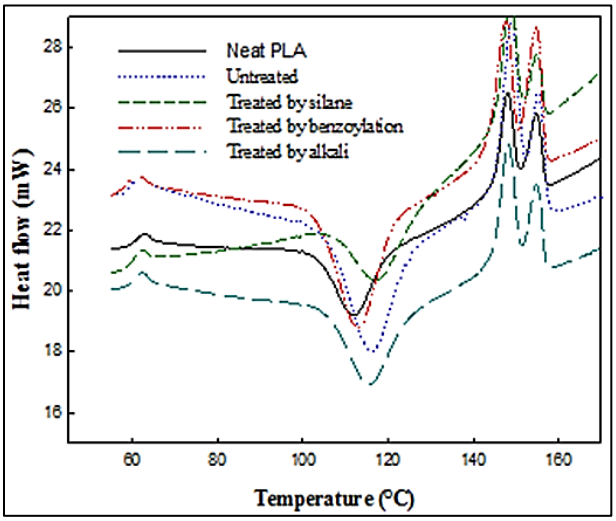

Figure 3: DSC curves of neat PLA and PLA-based biocomposites

PLA shows double melting peaks. It can be due to the fact that the less perfect crystals have enough time to melt and reorder into crystals with higher structural perfection, and melt again at higher temperature. The biocomposites exhibit constant in Tg compared with that of neat PLA (Table 1). The results obtained are in agreement with the results of DMA.

Table 1: Typical thermal property of various OHF/PLA biocomposites

	ΔH_{cc} J/g	ΔH_m J/g	X %	T_g °C	T_c °C	T_m °C
Neat PLA	19,5	22,5	26,8	60	112	149
Untreated	24	23	27,4	60	117	149
PLA/Alkali	24	25,7	30,7	59	115	149
PLA/Bezoylation	30	26	31	60	113	148
PLA/Silane	19	25	29,8	59	117	147

It is apparent that the crystallinity of PLA in the PLA/Alkali treated fiber, PLA/benzoylated fiber and PLA/Silane treated fiber composites increased compared with that of neat PLA and PLA/ untreated fiber composites. This result can be explained by the fact that impurities (i.e. wax and pectin) were removed from the fibers after treatment [34], which in turn increased the number of nucleating sites of the fibers. Incorporating natural fibers in the PLA matrix can be responsible for modifications in its crystallization by playing the role of nucleating agents. As shown by Wang et al. [35] sisal fibers have a nucleating ability to transcrystallize the PLA matrix.

Thermogravimetric analysis

The thermal stability of neat PLA and PLA based composites was investigated with thermal analysis, and the results are shown in Figure 4.

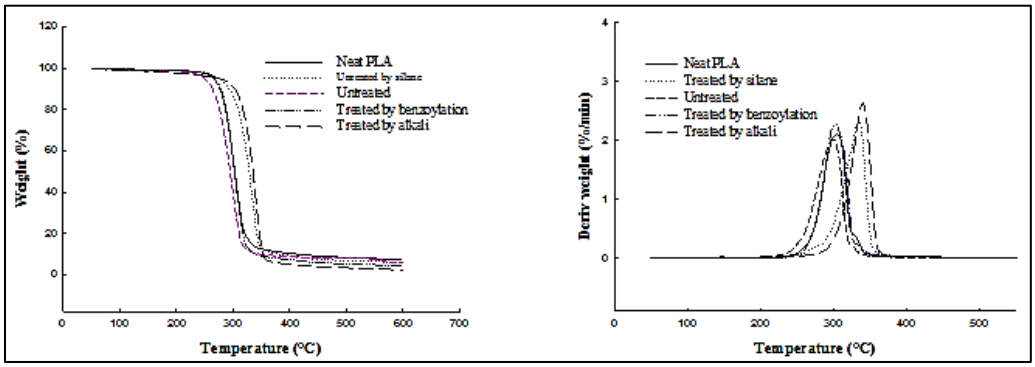

Figure 4: Thermogravimetric curves of neat PLA and PLA-based biocomposites

Thermal degradation of PLA shows completely in a single stage and occurs at 328 °C. From Figure 4, the biocomposites with untreated fiber show lower degradation temperature than that of PLA; this might be due to the incorporation of olive husk flour in PLA matrix. Thermal degradation temperature of the biocomposite with surface treatment is increased compared to the composite without surface treatment. The chemical bond between PLA matrix and olive husk flour could enhance the interfacial adhesion, consequently, the thermal degradation temperature increases. And even, this might be due to the increase in the crystallinity of composites as it was found in DSC analysis.

However, the thermal behavior of the biocomposites based on alkali treated fiber is better than those prepared with silane treated fiber. The result indicated that the stability of the interface bond between alkali treated olive husk flour and PLA is stronger than that of the interface bond between silane treated and benzoylated olive husk flour and PLA.

Morphology of the samples

The morphologies of the fractured surfaces of biocomposites with untreated fiber and treated fiber were investigated by scanning electron microscope.

Figure 5 shows that for the composites prepared using untreated fibers, visible gaps can be seen between fiber and PLA matrix, suggesting poor interfacial adhesion. This presumably arises because of the incompatibility between fibers and PLA matrix, as well as the presence of the impurities on the olive husk flour surface. However, the surface morphologies of treated composites are different (Figure 5).

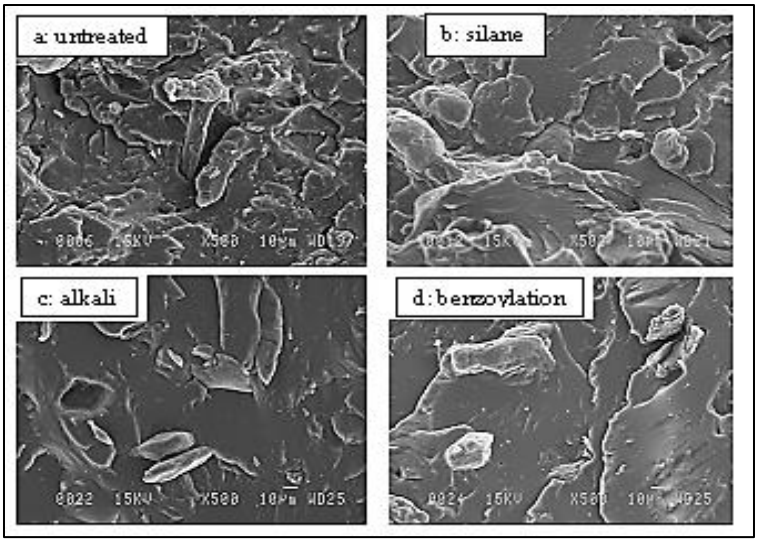

Figure 5: Fracture surfaces of (a) Untreated (b) treated by silane (c) treated by alkali (c) treated by benzoylation/PLA biocomposites

The treated fibers are coated by layers of matrix material that considerably reduce the gaps between them. It is also observed that the layers of material are pulled out together with the fiber during impact fracture, which further substantiates adhesion between the fiber and the matrix. The SEM analysis indicates that the matrix-fiber is better defined with treated OHF. Thus, one can understand the improvement of the mechanical properties for composites after treatment. SEM micrographs of the treated composites indicated clearly that surface-treatment boosted adhesion between olive husk flour and PLA matrix and shows that olive husk flour is well surrounded by the PLA matrix.

CONCLUSIONS

This manuscript points out the effect of alkali, benzoylation and silane treatments on the properties of PLA/olive husk flour biocomposites prepared by the extrusion. The results of this study showed that surface treatment improves the compatibility between the PLA matrix and olive husk flour. The mechanical properties and the thermo-mechanical properties of the composites with treated fiber are better than that of neat PLA and the composites with untreated fiber. These improvements are due to the enhanced interfacial adhesion between the PLA matrix and olive husk flour. According to the results of the mechanical properties and the thermomechanical properties tests, alkali is an effective surface treatment agent. The thermal behavior of PLA and PLA-based composites is also analyzed using DSC. The result confirms that the improvement in the thermal properties is because of the improved adhesion between both faces. The morphologies of fracture surface of the composites indicate the enhancement of fiber-matrix interface adhesion.

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