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Study of Biocomposites Based of Poly(Lactic Acid) and Olive Husk Flour

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Abstract**—**In this work, the composites were prepared with poly(lactic acid) (PLA) and olive husk flour (OHF) with different percentages (10, 20 and 30%) using extrusion method followed by injection molding. The morphological, mechanical properties and thermal behavior of composites were investigated. Tensile strength and elongation at break of composites showed a decreasing trend with increasing fiber content. On the other hand, Young modulus and storage modulus were increased. The addition of OHF resulted in a decrease in thermal stability of composites. The presence of OHF led to an increase in percentage of crystallinity (Xc) of PLA matrix.

Keywords**—**Biopolymers, composites, mechanical properties, poly(lactic acid).

I. Introduction

DURING the last 150 years, plastics were a means of innovation, and contributed to the progress and development of society. The expansion of polymer type leads to growth of their application in several fields of industry [1]. The main three markets of plastics are packaging, automotive, and building and construction. Most of these materials are not biodegradable and as waste ended up in the environment and which has a multiplier effect on ecologic system. So, the challenge has the goal to have zero plastics to landfill. Therefore, the possible alternative is to use of biodegradable polymers which can provide a positive role in environment i.e., PLA [2] PLA, having good process ability, received great interest [3], [4]. This biopolymer is linear aliphatic thermoplastic polyester. It is obtained from lactic acid (2-hydroxy propionic acid) using ring opening polymerization resulting in a cyclic dimer [5], [6]. However, the high price of PLA represents the main restriction to wide application. One of convenient approaches to optimize the cost and enhance the PLA properties is the incorporation of various fibers as reinforcement for the development of totally biocomposite materials. The addition of natural fibers is a positive environmental benefit with reduction of waste and raw material utilization [7]. Several studies have been conducted in this sense. Indeed, Lee et al. [8] investigated the properties of PLA reinforced with bamboo fibers, their results showed the increase in the Young modulus with increase fiber content whereas the tensile strength decrease. These results were in agreement with those obtained by Vila et al. [9]; their study showed that the tensile strength of PLA was not affected in the presence of eucalyptus wood and rice husk, but the Young modulus increased by 57% for PLA/wood and 45% for PLA/ rice husk composites.

The studies of authors quoted above showed that the adding of natural fiber can improve the Young modulus of PLA. This is due to fiber stiffness. This rigidity of composites can be increased with increasing fiber content.

In this paper, we investigate the effect of OHF content on morphology, mechanical and thermal properties of PLA composites.

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II. Experimental

A. Materials

The PLA used was supplied in the form of pellets by Nature Works under trade name 7001D.

The properties of PLA matrix were summarized in Table I. OHF used in this study as reinforcement was obtained from a local olive manufacturer in Bejaia (Algeria). The average diameter used is <100 µm.

TABLE I
THERMAL PROPERTIES OF PLA AND COMPOSITES AT DIFFERENT FIBER LOADING

Formulation	T5%	T50% (°C)	Char residue (%)
PLA	310	355	2.8
PLA/10%OHF	300	347	4.2
PLA/20%OHF	279	339	5.1
PLA/30%OHF	279	344	7.2

B. Composites Processing

Composite samples of PLA and OHF with different percentages (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 is set at 180 °C, screw speed was maintained at 50 rpm, and residence time was fixed at 8 min.

C. Techniques

1.Mechanical Properties of Composites

The tensile strengths of the composites were measured using "Instron 5569" testing machine with a crosshead rate maintained at 1 mm min^{-1}. Five measurements were conducted and average for the final result was considered. The dimensions of the calibrated part have a width of 4 mm and a length of 45 mm.

2.Thermogravimetric Analysis (TGA)

TGA measurement was carried out using TA Instrument Q-500 in inert atmosphere at a heating rate of 10 °C min^{-1}. The samples were scanned in the temperature range starting from 20 to 700 °C.

3.Scanning Electron Microscopy (SEM)

The morphology of composites was obtained by using a Hitachi S-2700 electron microscope. The samples were cryogenically fractured in liquid nitrogen. The micrographs were taken at a magnification of x100.

4.Dynamical-Mechanical Analysis (DMA)

DMA was conducted in a tension mode using Rheometrics TA instrument DMA Q 800. Temperature scans were run from 0 °C to 100 °C at a heating rate of 4 °C/min. The data were run at 1Hz.

III. Results and Discussion

A. Mechanical Properties

Fig. 1 illustrates the tensile strength of PLA and its composites. As we can see, the tensile strength of composites decreases linearly with fiber content up to 30%. This observation was caused probably: This trend was caused probably by poor adhesion between PLA matrix and OHF fiber. This result was in good agreement with the previous literature [10], [11] Koutsomitopoulou et al. [12] investigated the composites contained OHF dispersed into PLA matrix. The results show a decrease in tensile strength with fiber volume fraction due to the poor interfacial bonding between OHF and PLA. Indeed, this is the main disadvantage of lignocellolose fiber added in to polymer matrix as reinforcement. According to Islam et al. [13], the interfacial adhesion between fiber and matrix is critical factor in determining the mechanical properties of composites. Increases in fiber volume fraction increase the interfacial area which therefore leads to a weak interaction. Fig. 2 shows the Young modulus of composites at different fiber loading. It is clear that the presence of OHF fiber increaseS significantly the young modulus with increasing fiber content. OHF improved the stiffness of the composites compared to the PLA matrix. According to Sujaritjun et al. [14], this result was due to the better mechanical properties of fiber which are related to the composites of natural fiber. Furthermore, elongation at break of composites reinforced decrease in comparison with PLA. This result was due to high stiffness of composites in the presence of fiber. Tawakkal et al. [15] suggest that the high stiffness of the composite leads to the decrease in flexibility.

B. Thermogravimetric Analysis (TGA)

Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves for PLA and composites reinforced with 10%, 20% and 30% as function of temperature were given in Fig. 3. The onset decomposition temperature was characterized by the temperature at which 5% weight loss (T5%) occurred as given in Table I. TG result shows that the onset decomposition temperature of PLA was 310 °C and the temperature assigned to the maximum rate of thermal decomposition was 380 °C. A total of 97.2% of weight loss was recorded in PLA decomposition. From DTG curve of PLA, there was a single peak at 361 °C with maximum degradation rate of 2.5 %/min. However, the thermal stability of composites decreases with increasing OHF fiber content firstly due to thermal degradation of hemicelluloses, cellulose and lignin and then depolymerization of PLA. Similar result in thermal behavior is already reported in literature [16], [17]. The weight percentage of char residue of PLA was lower than composites. According to the literature [2], [18], this increasing of char residue means that the thermal stability was improved. The char residue can limit the exothermicity of the pyrolysis reactions, decreases the production of volatile gases and inhibit the thermal conduction of composites.

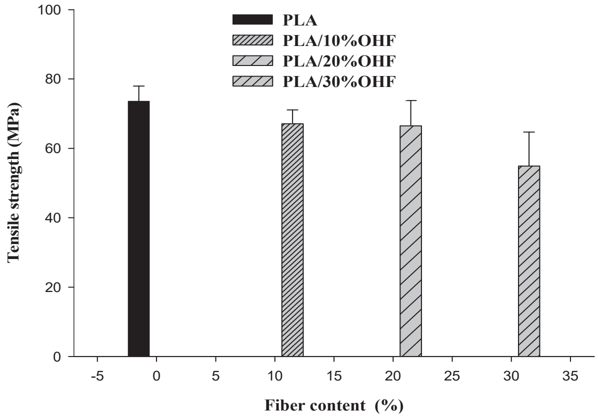


Fig. 1 Tensile Strength of PLA and composites at different fiber loading

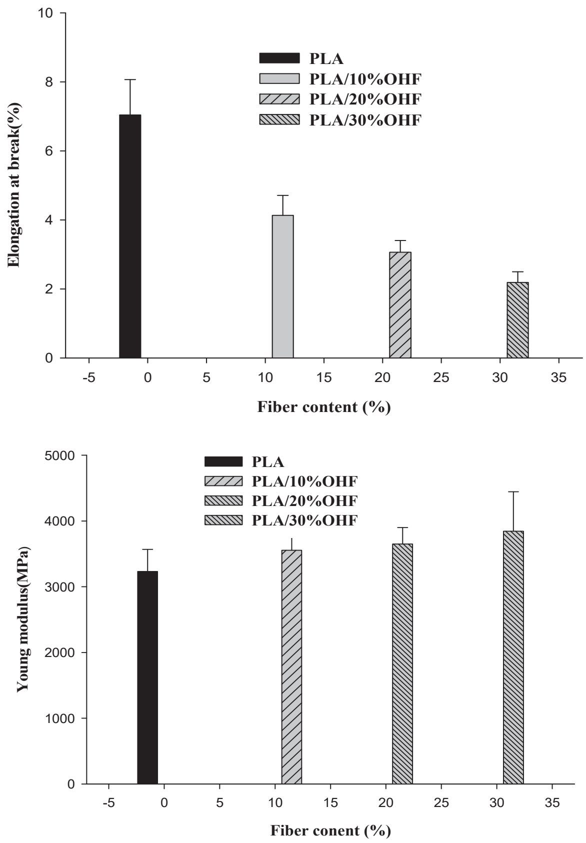


Fig. 2 Young modulus and elongation at break of composites at different fiber loading

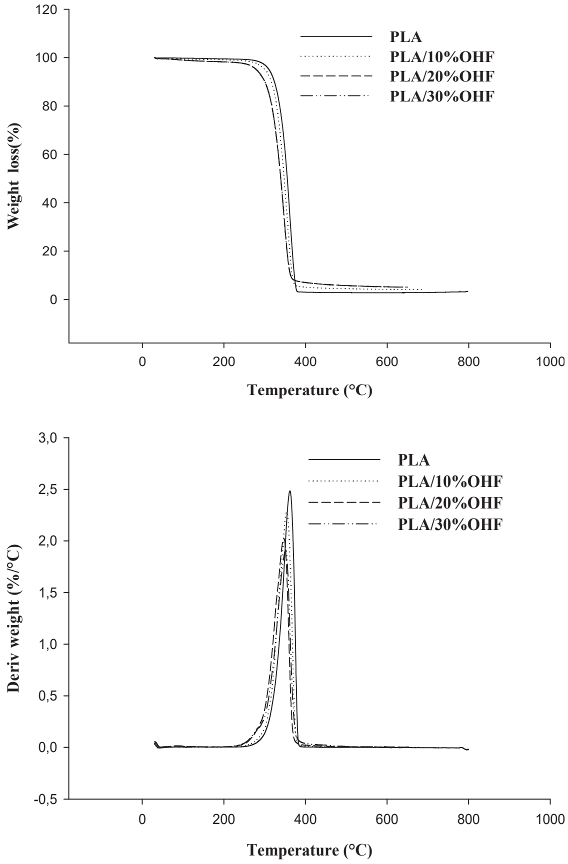


Fig. 3 Thermographs of PLA and composites at different fiber loading

C. *Scanning Electron Microscopy*

Fig. 4 shows the morphology of PLA/OHF composites. The surface structure exhibited some voids and cavities due to the fiber pull-out in the composites. This can be explained by the decrease in tensile strength of composites which caused ineffective stress transfer between fiber and matrix. The micrographs show also more voids with increasing fiber content. At low fiber content, OHF is well dispersed; however, agglomeration of fiber was seen at high fiber content.

D. *Dynamical-Mechanical Analysis (DMA)*

Fig. 5 presents the variation of storage modulus (E') of PLA and different composites as function of temperature. For both cases, the storage modulus decreased with increasing temperature due to the increase polymer chain mobility.18 Storage modulus of composites is higher that of PLA matrix. It is also clear that E' increases with the fiber content due to the increase of stiffness of composites. This increment confirms the results obtained in mechanical test. This result is similar with one obtained by Yu et al. [19]. The DMA results also showed that the glass transition temperature (Tg) of the composite was slightly shifted to lower values with an increase in fiber loading. This result is in agreement with one obtained from Cheng et al. [20]. According to the authors, the damping in the transition region measures the imperfection in the elasticity and energy used to deform a material indicating that energy dissipation of composites was less than that of PLA.

IV. Conclusion

In this study, PLA and PLA/OHF composites were prepared using extrusion processing followed by injection molding. The results show that the Young modulus of composites increase with increasing fiber content while the elongation at break and tensile strength was reduced compared to PLA matrix. It was found that storage modulus of composites was higher than PLA; this could be to the stiffness of OHF fiber. TGA data showed a decrease in the onset temperature of composites but the char residue was improved due to the enhancement in the thermal behavior of composites. These results demonstrated that OHF could be used as alternative biodegradable reinforcement with cost reduction and extend the application of PLA for stiffer products. However, further investigations can be made using the PLA and OHF as reinforcement with introduction of coupling agent or using chemical treatment for promoting better interfacial bonding between fiber and PLA matrix in order to ameliorate the composites properties.

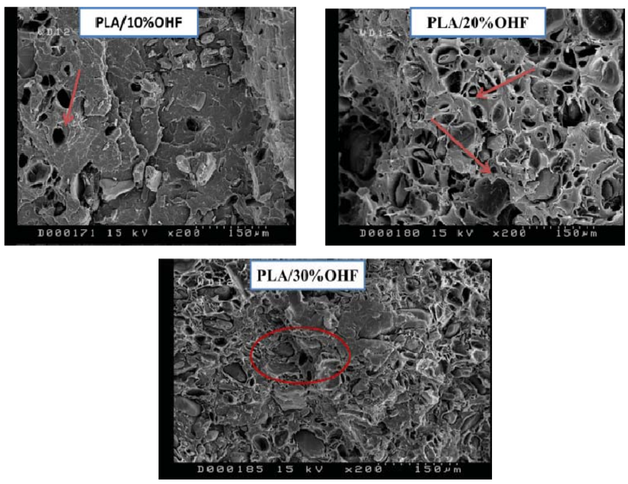
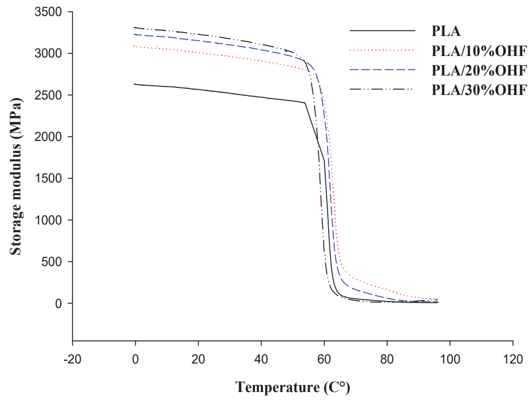
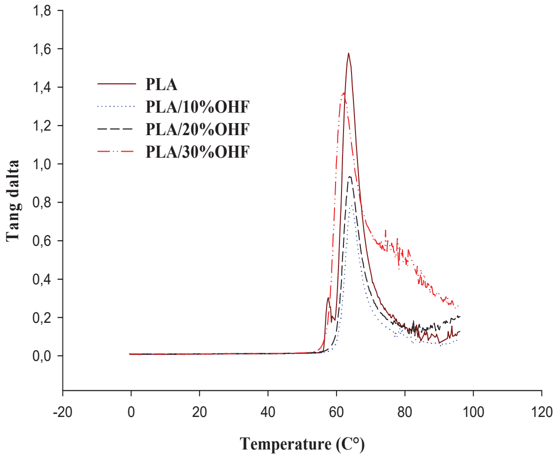


Fig. 4 Cross-section morphology of composites at different fiber loading



(a)



(b)

Fig. 5 Variation of storage modulus (E') and Tan δ of PLA and composites as function of temperature

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