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DEVELOPMENT OF BIODEGRADABLE COMPOSITE MATERIALS BASED ON POLYLACTIC-ACID (PLA) AND OLIVE KERNELS/ALFA FIBERS REINFORCEMENTS

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This study focuses on the development and characterization of Poly-lactic acid (PLA) based composites and vegetal reinforcements: (i) olive kernels particles (OK); (ii) Alfa short fibers and (iii) OK + Alfa mixtures. The interest of developing these materials from PLA powder and vegetable reinforcements in pulverulent form is twofold: to obtain environmentally friendly biodegradable materials and to make the most of the many advantages of elaboration by hot compression of these powders.

Scanning Electron Microscopy (SEM) examinations show a good dispersion of reinforcements in PLA matrix and a relatively continuous interface between components. By X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) characterizations, increases in the inter-reticular distances of PLA and a formation of new chemical bonds in the elaborated composites have been highlighted. From Differential Scanning Calorimetry (DSC) analyzes, decreases of the transformation temperatures of the PLA were noticed. Thereby, it has been demonstrated that chemical compounds from the used reinforcements decompose at high temperature and the released atoms diffuse into the PLA thus modifying its structure and transformation temperatures.

Keywords: olive kernels particles, Alfa short fibers, biodegradable composites, poly-lactic acid

1. Introduction

In the current context in which sustainable development is at the heart of economic development strategies, the priority of researchers and industrialists is to replace fossil-based materials with fully biodegradable ones environmentally friendly [**1-4**]. In this perspective, several studies focus on the development of fully biodegradable materials and, therefore, environmentally friendly. Among these works, several, in increasing number, concern biodegradable polymeric matrix composites and vegetal reinforcements [**5-14**]. These latter are mainly cellulosic tissues obtained from stems, leaves, seeds such as flax, Alfa, hemp and olive kernels [**5**, **6**, **8**, **15-19**].

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In addition to their biodegradability, these reinforcements offer many other advantages such as abundance, low cost, low densities and good mechanical properties [**15, 16-26**].

In the region of Kabylie (Algeria) where the olive tree is very widespread, the exploitation of vegetable wastes from olive growing appears as a very interesting prospect. In fact, except few applications in biology and agronomy [**27-28**], wastes from olive growing are not widely used. To valorize these wastes, it is possible to use them as reinforcements in composite materials based on biodegradable polymer matrices [**19, 22, 29-30**]. Other vegetal reinforcements having good mechanical properties, namely Alfa fibers, can be used in composite materials and make it possible to improve the characteristics of these materials [**31-32**].

Among the most used biodegradable matrices is poly-lactic acid (PLA). PLA is a kind of biodegradable thermoplastic polymer derived from vegetal renewable resources as corn, potato or sugar which offers good properties such as high strength and degradability. However, PLA has disadvantages of poor toughness, poor thermal stability, low crystallization kinetics and high cost [**33-35**].

Several works have been dedicated to the study of biodegradable composites based on PLA matrix and Olive Kernels or Alfa reinforcements. The production methods used up to now are mainly based on internal mixing and extrusion. Indeed, Khemakhem et al. [**29, 30**] developed different biocomposites based on PLA and Olive Solid Wastes (OSW or Olive Kernels) using a co-rotating twin-screw extruder with rotation speed of screw 40 rpm under 190°C. Their results highlighted that the inclusion of OSW under high temperatures resulted in the degradation of the matrix leading to a reduction of the viscoelastic properties and molar masses. It was suggested that PLA can react, via its hydroxyl groups, with other organic compounds and create the covalent bonds. They report the presence of an agent that interacts with PLA and OSW and improves the interface between them [**29, 30**].

Among the other reinforcements that can be used, Alfa short fibers can improve the mechanical properties of the composite, especially if it is mixed with OK particles. In fact, it will be possible to combine the shape effect and mechanical properties of these reinforcements [**36, 37**]. Therefore, the development of such materials by hot compression allows, among other advantages, to minimize the loss of raw materials and to promote the interaction matrix (PLA) / reinforcements (OK particles-Alfa fibers) and possibility of producing mechanical parts, of various shapes, in very few operations and the saving of materials. These biodegradable PLA/natural reinforcements composites will find potential applications in the manufacture of wide ranges of household objects, tools, spare parts for machines and equipment with short and medium service life. The aim of this study is to develop fully biodegradable materials using poly-lactic acid as matrix and olive kernels (OK) powder, Alfa short fibers and their mixture as reinforcements. Thus, three materials have been hot-compacted at 180°C under 10 MPa. In order to understand the interaction between the components of the developed composites, microstructural characterizations using X-ray diffraction (XRD) and Scanning electron microscopy (SEM) was carried out in parallel with Differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR) analysis.

2. Experimental

2.1. Processing of raw materials into powders and short fibers

The used PLA, grade A, is supplied by Real filament in the pellets form (3 to 5 mm in diameter). The PLA powder was obtained by grinding cut tips of a coil of this polymer used in 3D printing. The used grinder-chopper is equipped with propellers rotating at 1500 rpm. During the blades rotation, the tips are subjected to important shearing forces that lead to their fragmentation for the production of the PLA powder. The later is sieved to select size particles lower than 200 µm.

The olive kernels (OK) powder is obtained by grinding the kernel aggregates recovered from a two-phase industrial oil mill in Tizi-Ouzou region. These granulates were separated from the pulp by sieving. After cleaning with hot water they undergo drying at 105 °C during 24 hours [**22**].

Alfa plants were collected in the Algerian highlands region, dried in the sun and stored away from the moisture. The stems were cut and processed into short fibers using a grinder-chopper.

2.2. Samples preparation

The PLA-OK, PLA-Alfa and PLA-OK-Alfa samples were prepared from a mixtures of PLA-50%OK, PLA-50% Alfa and PLA-33% Alfa-33%OK (% vol) ; which correspond, approximately, to PLA-48.97%OK, PLA-40% Alfa and PLA-24.61% Alfa-36.92% OK (% wt). After homogenization in a Turbulat during 15 minutes, these mixtures were hot-compacted at 180 °C under 10 MPa during 10 mn. Samples were characterized by Scanning electron microscopy (SEM, using a Philips XL30) and X-ray diffraction (XRD, using a Panalytical X'Pert diffractometer; λ = 1.5406 Å, equipped with X'Celerator detector, step per time 0.02°/s). The structural transformations in our materials were highlighted by Fourier Transform Infrared Spectroscopy (FTIR, using a Jasco spectrometer, DeltaX Resolution 0.964233) and Differential scanning calorimetry (DSC, using a NETZSCH 200 F3). For FTIR Spectroscopy, the analyzed samples are in the form particles smaller than 120 µm. For DSC, the analyzes were carried out in the temperature range 50-400 °C with a heating rate of 4 °C/mn.

3. Results and discussion

3.1. SEM observations of raw materials

Fig. 1 shows the SEM micrographs of raw materials. In Fig. 1.a., we note that the PLA particles are of micrometric sizes and have polyhedral shapes with rounded edges. The rounded shape of the particles edges can be explained by an increase in the temperature during grinding leading to a softening of the material and deformations in these areas. Fig. 1.b. shows that Olive Kernels powder is constituted by agglomerates of small particles. The SEM image of Alfa short fibers is shown in Fig. 1.c. We observe that Alfa fibers are of micrometric stems shape.

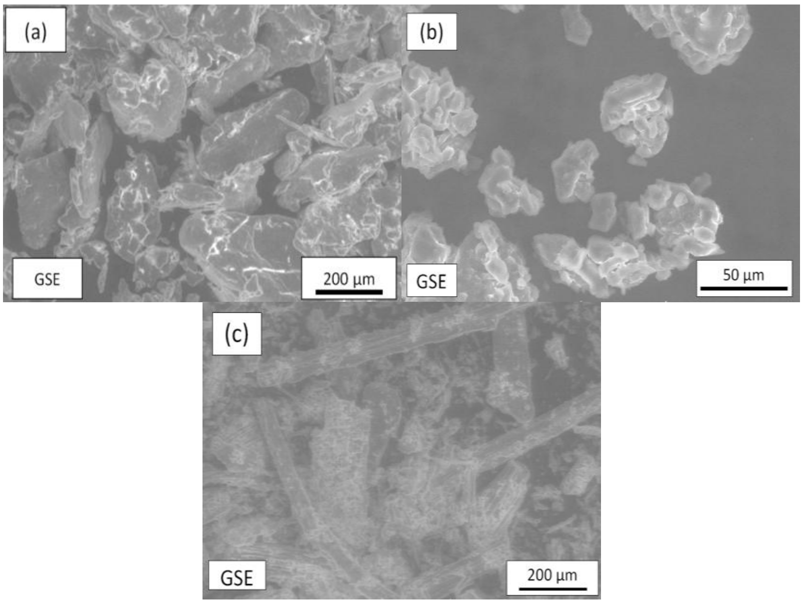

Fig.1: SEM micrographs of raw materials: (a) PLA particles, (b) Olive kernels particles and (c) Alfa short fibers

3.2. Study of PLA-OK, PLA-Alfa and PLA-OK- Alfa composites

Fig. 2 shows the XRD patterns of PLA alone, PLA-Alfa, PLA-OK and PLA-OK-Alfa composites. In the XRD data of the PLA alone, we observe the characteristic peaks of L-Lactide-poly(ethylene glycol) with a general formula $[(C3H4O2) - (C2H4O) - (C3H4O2)]_n$ (JCPDS n°49-2174). For the composite samples, we notice a decrease of the intensities of the PLA peaks. For these samples, a hump appears also for the fifth diffraction peak of PLA. By superimposing and enlarging the significant diffraction peaks of the PLA (Fig. 3), we observe a shift of these peaks towards the small angles. Calculations of inter-reticular distances of PLA for the different cases give the results grouped in table1.

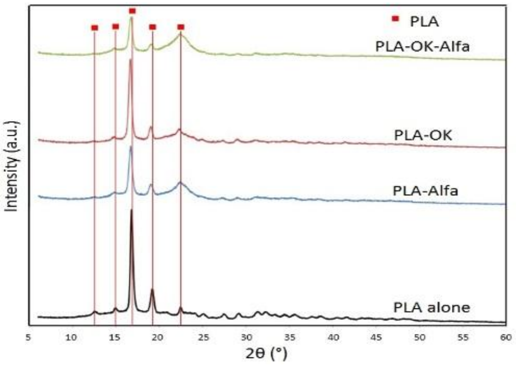

Fig.2: XRD patterns of PLA alone and PLA-alfa, PLA-OK and PLA-OK-alfa samples.

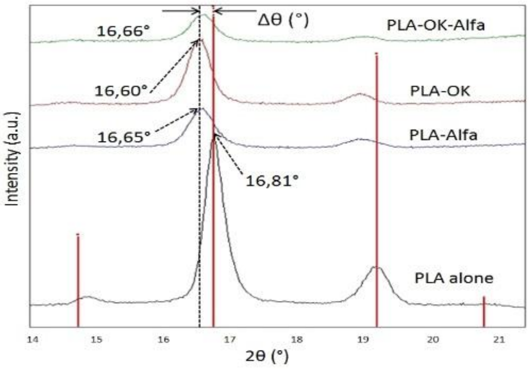

Fig.3: Enlargement of the significant diffraction peaks of PLA in the studied samples.

Table 1

Inter-reticular distances and average crystallographic parameter of PLA for the different samples (given in Å)

Sample	$d_{(hkl)}$	$d_{(h'k'l')}$	$d_{(h''k''l'')}$	$d_{(h''''k''''l'''')}$	Average parameter
PLA alone	5.92849	5.27524	4.61959	3.95621	0,49307
PLA-alfa	5.99038	5.31997	4.68207	3.99252	0.49946
PLA-OK	6.01655	5.33643	4.67890	3.99252	0.50601
PLA-alfa-OK	6.02181	5.31997	4.66000	3.97982	0.51049

These results show an increase of the inter-reticular distances of PLA in all cases. This is due to the insertion of atoms in PLA structure by interaction between compounds contained in the vegetal reinforcements and the PLA. Indeed, during the hot compaction process, PLA and reinforcements particles have been subjected to temperature and pressure that favor the interfacial reactions, which produce the dissociation of molecules derived from reinforcements followed by diffusion of the released atoms in PLA macromolecules.

Fig. 4 shows SEM micrographs of PLA-OK and PLA-Alfa samples. In Fig. 4.a, we distinguish an OK particle embedded in PLA matrix. This particle, with typical wood structure forms a continuous interface with PLA matrix. Fig. 4.b, shows short Alfa fibers in PLA matrix with a relatively continuous interface. However, we observe some furrows in this interface, due to shearing forces undergone by the sample during mechanical polishing. Fig. 4.c is an enlarged SEM backscattered electron image of Alfa fiber microstructure (framed in Fig. 4.b). This image shows two zones: (i) a transversal section and (ii) a longitudinal one. In transversal section, we note the presence of micro-fibers constituted by relatively heavy elements. In the second zone, we observe a typical structure of cellulosic tissues. For the PLA-OK-Alfa sample, similar results are obtained.

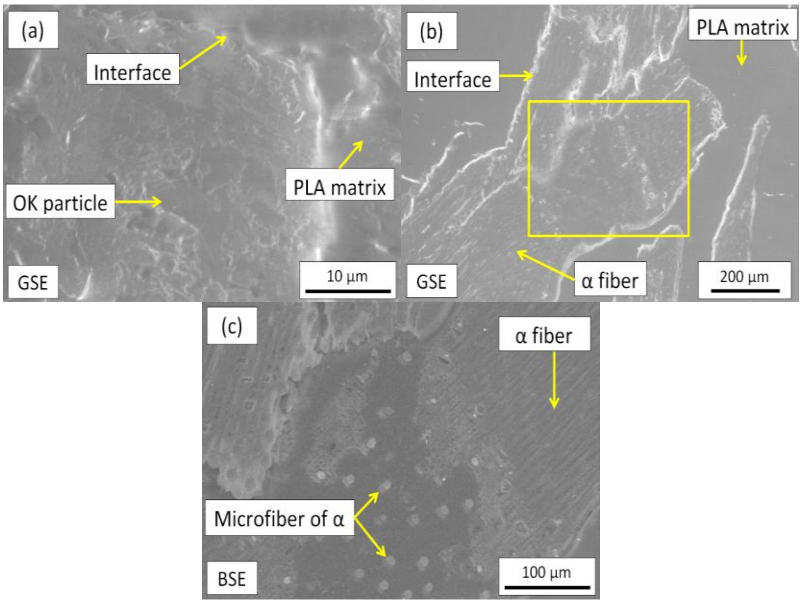

Fig.4: SEM cross-sectional view of: (a) PLA-OK sample; (b) PLA-Alfa sample and (c) enlarged SEM backscattered image of Alfa fiber microstructure (framed in b).

The FTIR spectra of PLA alone and the composite samples are presented in Fig. 5. We note a breaking of C-H bonds of the PLA due to the high temperature interaction between the PLA and the reinforcements (zone 1). In the case of PLA-Alfa composite, we observe a widening of the peaks from 2910 to 2850 cm^{-1} due to the presence of Alfa that produces peaks at these same wave numbers according to Paiva et al. [**32**]. Otherwise, the asymmetric elongations of double and triple bonds in PLA are not observed in the case of the composites (zone 2). Moreover, C=C, C=O and C=N double bonds of wave numbers between 1555 and 1690 cm^{-1} are mainly present in OK-based composites (zone 3). For these last ones, peaks corresponding to angular deformations of single bonds C-C and C-H (for lower wave numbers: 520-670 cm^{-1}) are also observed (zone 4). These peaks reflect the formation of C-C and C-H bonds between macromolecules of PLA and OK compounds.

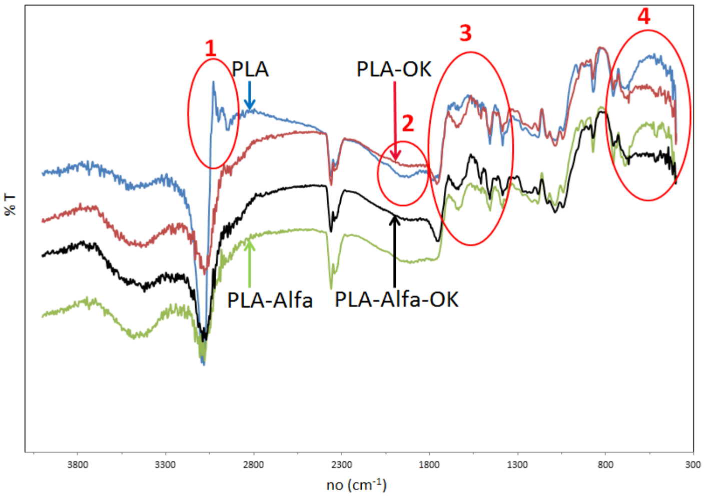

Fig.5: IR spectra of PLA alone and composite samples

In order to understand the behavior of PLA during heating and the influence of the addition of reinforcements on the structural transformations of the elaborated materials, DSC analyzes were performed from ambient temperature to 400°C under N_2/50%/air atmosphere. Fig. 6 shows the obtained DSC curves. We observe a peak at 176.1 °C (minima value) corresponding to the total melting of the PLA. At 307°C, the curve shows the beginning of a significant endothermic peak from the onset of PLA evaporation that ends at 355.3°C.

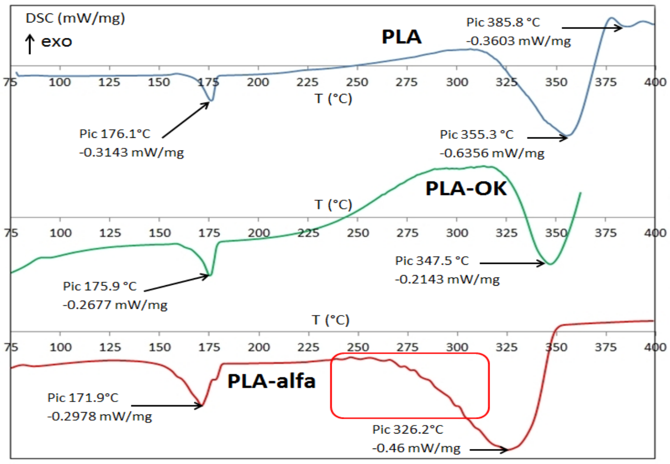

Fig.6: DSC curves of PLA alone, PLA-OK and PLA-alfa composites

A second endothermic peak appears at 385.8°C and corresponds to the evaporation of residual substances produced by PLA transformations.

In the case of PLA-OK sample, a slight inflection of the curve occurs at 90°C as an exothermic peak; which probably corresponds to the combustion of fatty substances contained in the OK. We note a shift of the two characteristic peaks of PLA transformations towards low temperatures. This decrease of the transformation temperatures (from 176.1 to 175.9 °C and from 355.3 to 347.5 °C) can be explained by the initiation of the transformation mechanisms at the PLA-OK interfaces consisting of PLA enriched by atoms coming from the chemical compounds contained in the OK particles. Furthermore, the curve is increasing between 225 and 287 °C; which is attributed to exothermic reactions due to the presence of fatty substances contained in OK.

For the PLA-Alfa composite, these shifts are more important than the PLA-OK ones. Note that the rise in the curve at the first endothermic peak is broken at around 175°C. Unlike the PLA-OK case, the curve shows a decreasing trend from 240 ° C. This reflects absorption of heat by Alfa fibers during the melting of PLA. Moreover, the curve shows fluctuations between 240 and 315°C (see the framed area). This is explained by the heterogeneous structure of Alfa fibers and consequently their non-monotonic heating behavior.

4. Conclusions

Three fully biodegradable composites have been developed from Poly-lactic Acid (PLA), Olive Kernels particles (OK) and Alfa short fibers using hot-compaction process. The results of XRD analyzes revealed an increase of inter-reticular distances of PLA due to the insertion of atoms released from compounds contained in the vegetal reinforcements in PLA structure at high temperature. SEM observations have highlighted a relatively continuous interface PLA-vegetal reinforcements and the typical morphology of OK particles and Alfa short fibers. By DSC analyzes, we noticed a decrease of the two temperatures of PLA transformations. These results have explained by the initiation of the transformation mechanisms at the PLA-OK interfaces consisting of PLA enriched by atoms coming from the chemical compounds contained in the OK particles. These results are in good agreement with FTIR ones which show formation of some chemical bonds in PLA and reinforcements.

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