# Study of the biodegradation of composite materials reinforced with natural resources recovered from industrial areas.

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## Abstract

*The aim of our work is to contribute to the search for solutions to the problem linked to environmental pollution by plastic materials and lignocellulosic waste. Composites based on polyvinyl chloride/olive pomace flour (PVC/FGO) with 20% fiber content were prepared. The lack of compatibility between plant fibers and some polymers is due to the hydrophilic nature of plant fibers and the more hydrophobic nature of the matrix. This incompatibility causes poor dispersion of the fibers and the formation of a heterogeneous material whose overall mechanical properties are not satisfactory. In order to improve adhesion at the fiber/matrix interface, the fibers were modified by gamma irradiation. To complete this work, it is essential to carry out an in-depth study of the biodegradation of the materials produced. The PVC/FGO composites were subjected underground under environmental conditions. The changes induced by the exposure of composite materials to biodegradation were evaluated by optical microscopy and the measurement of mass loss.*

*Keywords: Composites, Natural Resources, Biodegradation*

## I.    Introduction

Plant-based fiber composites are currently experiencing strong growth due in particular to the growing interest in them from the automotive industry. These fibers present an excellent alternative to glass fibers from an environmental point of view due to their biodegradability and their much more neutral combustibility in terms of the release of harmful gases or solid residues [1]. However, plant fibers, although they have many qualities, have some major flaws when it comes to combining them with polymers [2]. Modification of the surface of the fibers is generally necessary in order to improve their adhesion with a polymeric matrix and to reduce the absorption of humidity. It has been shown that appropriate treatment applied to the fibers can result in compatibility with the polymer matrix, which improves the quality of the composites [3]. PVC/wood composites are widely used in the field of building materials, as they offer acceptable mechanical properties, good chemical and fire resistance, low water absorption and long service life [4]. In this context, the main objective of this thesis is the characterization of a composite material based on PVC reinforced with untreated olive pomace fibers and treated with gamma irradiation in order to improve the mechanical and thermal properties. Subsequently, we conducted an in-depth study of the biodegradation of the materials produced. Several characterization methods were used such as SEM, TGA, IR, to monitor the changes in the characteristics of this composite and its biodegradation over time.

## II.    Material and methods

PVC type 3000H manufactured by CIRES (USA) was used to prepare the formulations. The plasticizer added is dioctylpthalate (DOP). The heat stabilizer used, of industrial quality, is a mixture of calcium and zinc salts (Ca/Zn), and stearic acid as a lubricant. The natural filler used is olive pomace flour, a by-product of oil mills. The pomace was brought from the Tazmalt region (Beni Mellikeche) of the wilaya of Bejaia, Algeria [1].

### A.    Pretreatment of olive pomace

The olive pomace were washed with cold water then with hot water to remove the remains of the pulp, followed by drying at room temperature for 48 hours, drying is completed in an oven for 24 hours at 105°C. The grinding was carried out with traditional methods using a manual stone mill then with a coffee grinder. To have a homogeneous particle size, sieving was carried out using a controlab type sieve shaker "Automatic Sieve Shaker D411". The dimension of the flour is less than 100 μm. The olive pomace flour is washed with acetone for 24 hours using a soxhlet to eliminate any contamination or

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impurity. The recovered flour is steamed at a temperature of 100°C for 24 hours [1].

### B. Chemical composition of olive pomace

The chemical composition of olive pomace flour was determined at the laboratory of advanced polymer materials, University of Bejaia.

**Table 1** Chemical compositions of olive pomace flour [1].

| Composition | rate in % by mass |
|---|---|
| Cellulose | 40,56 |
| Hémicellulose | 18,10 |
| Lignin | 23,43 |
| MS | 92,10 |
| Th | 07,90 |
| MM | 03,61 |
| MG | 14,31 |

### C. Samples preparation

The PVC resin and the various additives are mixed in a beaker using a spatula until the mixture becomes homogeneous. 1 mm thick sheets of F0 (virgin PVC) and composites loaded with 20% untreated and treated pomace flour with γ radiation, were prepared using a LE SCUYER brand calender type M89. The temperature along the two-roll mixer is maintained at 160°C, for a residence time of 15 min. The sheets are then cut into the appropriate shape for the characterize [1].

### D. Gamma irradiation of samples

The charge was irradiated at the nuclear research center in Algiers (CRNA) using the gamma radiation source. These gamma rays are obtained from the decay of Co60. Several formulations have been prepared, varying the dose of gamma irradiation [1]. An unfilled PVC formulation denoted F0.

A PVC formulation filled with 20% untreated olive pomace rated F20.
A formulation of PVC filled with 20% olive pomace treated with gamma irradiation at doses of 10; 25; 50; 60 and 70KGy rated F20CH10KGy, F20CH25KGy, F20CH50KGy, F20CH60KGy and F20CH70KGy respectively.
Olive pomace flour treated with gamma radiation at doses of 10; 25; 50; 60 and 70KGy, denoted by: F, F10 KGy, F25 KGy, F50 KGy, F60 KGy and F70 KGy respectively.

**Table 2** Mass composition of PVC/ olive pomace formulations [1]

| Formulation / Products | F0 | F20 | F |
|---|---|---|---|
| | | F20CH10KGy | F10KGy |
| | | F20CH25KGy | F25KGy |
| | | F20CH50KGy | F50KGy |
| | | F20CH60KGy | F60KGy |
| | | F20CH70KGy | F70KGy |
| PVC | 100 | 80 | 0 |
| DOP | 30 | 30 | 0 |
| Ca/Zn | 2 | 2 | 0 |
| Stearic acid | 06 | 0.6 | 0 |
| Olive pomace flour | | 0.3 | 20 | 100 |
| PVC | | 100 | 80 | 0 |

### E. Sample characterization by Scanning Electron Microscopy (SEM)

Scanning electron microscopy was used to characterize the surface condition of the filler. The equipment used is a Philips model scanning electron microscope at the macromolecular materials laboratory (LMM) of INSA Lyon. [1].

### F. Sample characterization by Thermogravimetric Analysis (ATG/DTG)

Thermogravimetric analysis (TGA) is based on the determination of the mass loss that a sample undergoes during its heating. These mass losses are recorded as a function of temperature in an appropriate interval. This method allows us to graphically determine the decomposition temperature of the sample. Measurements of the thermal stability and the rate of decomposition of the various samples are carried out using a SETERAM TGT-DTA type thermogravimetric device controlled by a microcomputer. A mass of 10 to 15 g of a sample is introduced into an aluminum crucible and the loss in mass of the sample as a function of temperature is recorded with a heating rate of 10°C/min in a temperature range ranging from 25°C to 700°C [1].

### III. Study of the biodegradation of prepared composite materials

The PVC/FGO composites that were subjected underground under environmental conditions, were evaluated by optical microscopy, the measurement of mass loss and Fourier transform infrared spectroscopy.

### A. Surface characterization of composites by optical microscopy

The observation by optical microscopy of the untreated and treated samples allows us to visualize the surface condition of different composites under the effect of irradiation and after their exposure to climatic conditions. Observations are made using a euromex optical microscope with 100x magnification.

### B. Mass loss

After immersing the films to be studied underground for an extended period, samples are regularly taken. The operating mode consists in weighing the samples before their immersions in the basement (m0).

In each collection, the samples are removed from the soil and wiped off any surface soil that covers them, using a clean, dry

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cloth. Each specimen was weighed again (mass mi). The mass loss m (%) is calculated by the following equation:

$$\mathbf{m\ (\%)} = ((mi-m0)/m0) \times 100 \qquad \textbf{Eq. (1)}$$

Where:
**m (%):** The mass loss m (%)
**m0:** The mass, in grams, of the initial specimen and before immersion;
**mi:** The mass, in grams, of the specimen after immersion.

### IV. Results and discussion

#### A. Study of the morphology of olive pomace flour by the scanning electron microscope (SEM)

Fig. 1 shows a scanning electron micrograph (SEM) of untreated Fig. 1.a, and treated olive pomace flour at 70 kGy Fig.1.b. It is observed that the untreated filler tends to agglomerate, furthermore, after the irradiation of the olive pomace flour, the size of the particles are reduced and are well dispersed [1]. A similar result was found by Bhowmick A-K., for clay treated by electron beam irradiation [2].
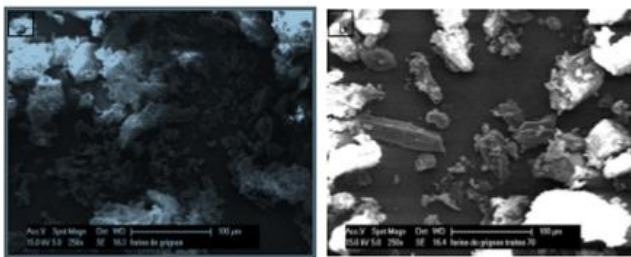


**Figure 1.** SEM micrograph of olive pomace flour : a) F, b) F70 kGy.

#### B. Effect of gamma irradiation on the thermal stability of olive pomace flour

To study the thermostability of olive pomace flour after treatment by gamma irradiation, we used thermogravimetry which consists in monitoring the evaluation of the loss of mass as a function of temperature. Fig.2.a and Fig.2.b represent the thermograms giving the variation of the mass loss (TG) and mass loss rate (DTG) as a function of the temperature of olive pomace flour before and after treatment at irradiation doses of 10 and 70 kGy [1].
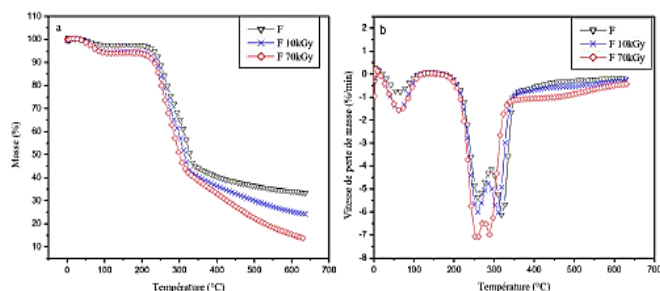


**Figure 2.** The thermograms: a) TG of untreated and treated F, b) DTG of untreated and treated F.

According to fig. 2.a, the thermograms of the mass loss (TG) of the treated and untreated olive pomace flour show the appearance of a mass loss around 65 and 68 °C, attributed to water evaporation [3]. After this temperature, the two flours are thermally stable up to 216°C, where the temperature at which the untreated or treated flour begins to decompose is recorded and this informs us that the irradiation has no effect on the temperature at which olive pomace flour begins to decompose.

In the temperature range between 216 ° C and 335 ° C, a significant loss of mass was observed and which is attributed to the degradation of hemicellulose, it is of the order of 50%, 51.7% and 50.6% for F, F10kGy and F70kGy respectively. Hemicellulose is the least stable constituent, it begins to decompose at 225°C and degrades at 325°C [4].

After 335°C, a second phenomenon of less significant mass loss was observed, it is due to the degradation of cellulose and lignin [5]. 13%, 19% and 28.35% are recorded for F, F10kGy and F70kGy respectively. Lignin begins to decompose before cellulose (200°C compared to 375 for cellulose), but its rate of decomposition is slower than cellulose and it is the last component to completely degrade [4].
The residue rate tends to decrease for irradiated flour, it goes from 33% for F to 24 and 13% for F10kGy and F70kGy respectively.

As indicated in the literature, the carbonization yield is proportional to the degradation of cellulose and increases if the structure degrades and becomes less crystalline [6]. In our case, the amount of carbon content tends to decrease, emphasizing that the starting material subjected to thermal analysis becomes more resistant to the increase in absorbed dose.

The three phases of mass loss discussed previously, manifested as peaks in mass loss rate (DGT) thermograms Fig 2.b. These peaks correspond to the maximum mass loss rate values.

The first peak located between 60 and 66°C corresponds to water evaporation. It is noted that the water evaporation rate is higher for the irradiated flour compared to the non-irradiated flour. 0.77, 1.54 and 1.56%/min are recorded at temperatures of 66, 64 and 62°C for F, F10kGy and F70kGy respectively.
The second peak located between 258 and 262 °C corresponds to the decomposition of hemicellulose and to the glycedic bonds of cellulose [7]. 5%, 6% and 7%/min are noted at temperatures of 259, 260 and 261°C for F, F10kGy and F70kGy respectively.

The third peak, which is between 260 and 320°C, is attributed to the decomposition of cellulose and lignin [8]. 6.12%, 6% and 7%/min are recorded at temperatures of 318, 311 and 288.5°C for F, F10kGy and F70kGy respectively.

It is noted that gamma irradiation at low doses, namely 10 and 70 kGy, slightly increases the rate of degradation of olive

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pomace flour and it can also be concluded that cellulose and lignin are less sensitive to gamma irradiation than hemicellulose.

### C. Study of the biodegradation of irradiated composite materials by optical microscope

As it is important to know the morphology of the olive pomace flour used as filler in the PVC matrix, we used optical microscope imaging. Fig. 5 represents the images of F0 obtained by the optical microscope at different immersion times.
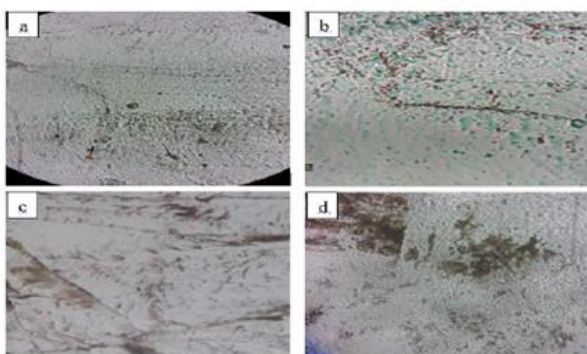


**Figure 3.** Morphology of F0 obtained by optical microscopy: a) before subsoil immersion, b) after 15 days of immersion, c) after 45 days of immersion, d) after 75 days of immersion.

According to this figure, we notice a change in the aspect of the different images obtained for the PVC, according to immersion time, this change and probably due to the possibility of migration or reaction of its additives with the medium where they are introduced.

Fig.4 represents the images of F20 obtained by the optical microscope at different immersion times.
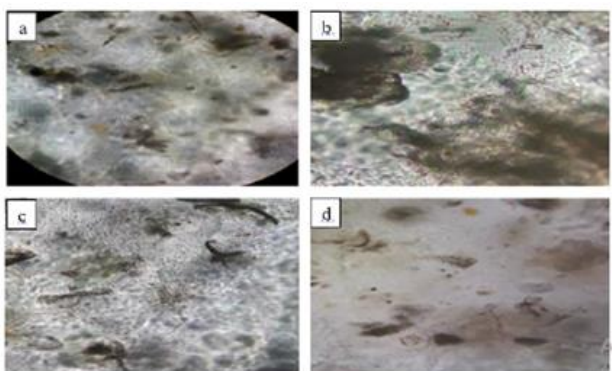


**Figure 4.** Morphology of F20 obtained by optical microscopy: a) before immersion basement, b) after 15 days of immersion, c) after 45 days of immersion, d) after 75 days of immersion.
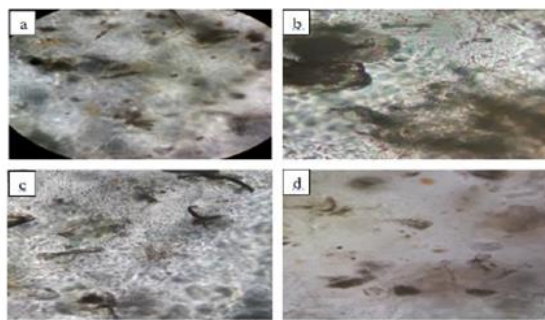


**Figure 5.** Morphology of F20 obtained by optical microscopy: a) before immersion

During the comparison, between the two fig.4, and 5 which are, accustomed to F0 and F20 successively, we notice for F0 that it has a single regular layer, and does not contains only additives, while for F20, we note that, it is made up of two layers which are the reinforcement and the matrix, this multilayer is due to the incompatibility between the two phases, where the structure appears in the form of conglomerates of olive pomace flour partially dispersed in the PVC matrix.

By comparing the images of F20 at different immersion times, we notice the increase in the size of the agglomerates. This increase is due to the swelling of the particles of the filler after the absorption of water due to rainfall precipitation during this period.

After 45 and 75 days, the images of the composites show the progressive reduction in the size of the agglomerates over time, due to the subtraction of the water previously absorbed, under the effect of the climatic heat.
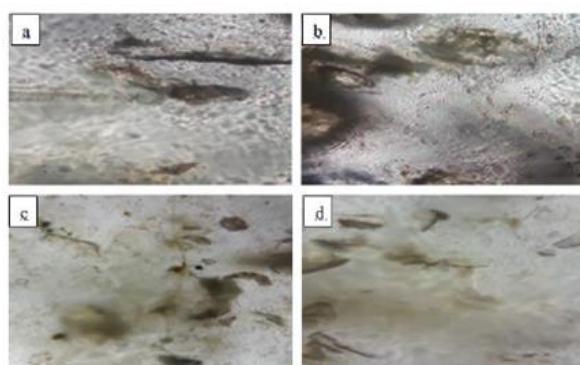


**Figure 6.** Morphology of F20CH10KGy obtained by optical microscopy: a) before subsoil immersion, b) after 15 days of immersion, c) after 45 days of immersion, d) after 75 days of immersion.
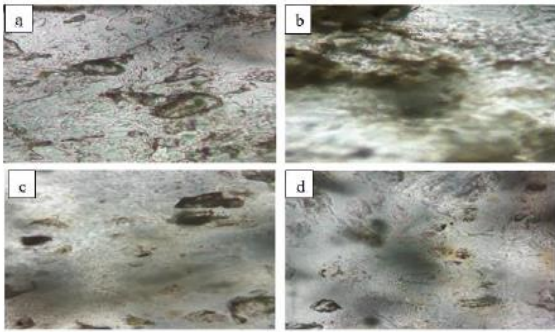
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**Figure 7.** Morphology of F20CH25KGy obtained by optical microscopy: a) before subsoil immersion, b) After 15 days of immersion, c) After 45 days of immersion, d) After 75 days of immersion.
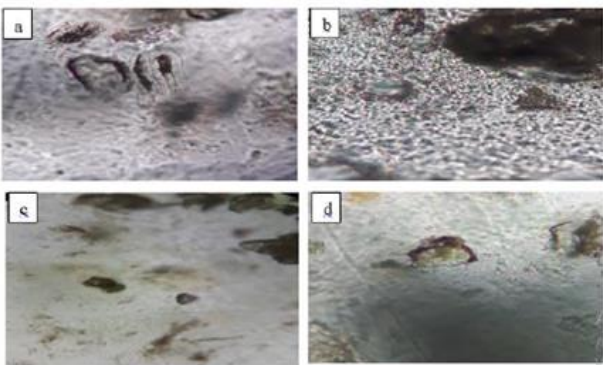


**Figure 8.** Morphology of F20CH50KGy obtained by optical microscopy: a) before subsoil immersion, b) after 15 days of immersion, c) after 45 days of immersion, d) after 75 days of immersion.
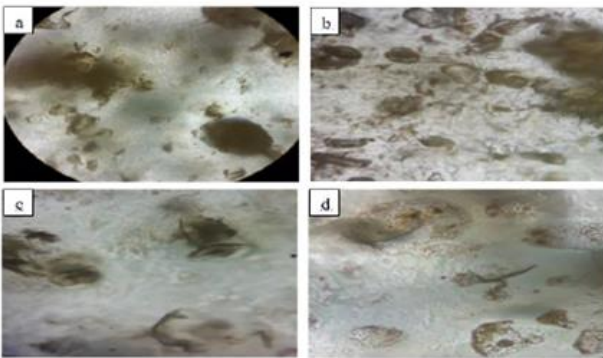


**Figure 9.** Morphology of F20CH60KGy obtained by optical microscopy: a) before subsoil immersion, b) after 15 days of immersion, c) after 45 days of immersion, d) after 75 days of immersion



**Figure 10.** Morphology of F20CH70KGy obtained by optical microscopy: a) before subsoil immersion, b) after 15 days of immersion, c) after 45 days of immersion, d) after 75 days of immersion.
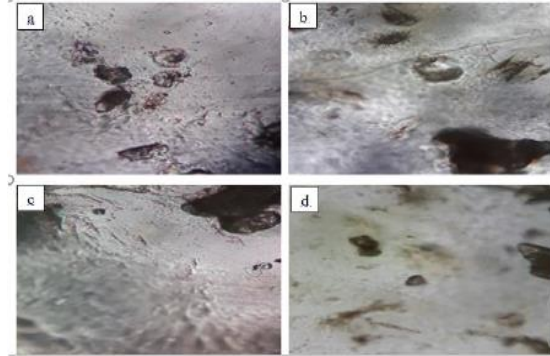
By analyzing the fig. from 6 to 10, we notice a change in the size of the olive pomace flour agglomerates after 15 days of immersion of the samples in the basement thanks to the absorption of humidity.

After 45 days of immersion of the samples underground, the figures indicate that the sizes of these agglomerates have decreased and that their compaction is less.

The same observation was recorded after 75 days, where it is found that the olive pomace flour particles have become fully spaced and less dense. This dispersion is further improved by increasing the dose of the irradiation. It can be seen that the treatment by gamma irradiation leads to good dispersion of the filler and better adhesion with the matrix.

In addition, the decrease in agglomerates can be attributed, to the decomposition of particles of olive pomace flour under the influence of certain environmental factors such as PH, microorganisms and other factors, which leads to the biodegradation of composite materials.

**D. Study of the biodegradation of irradiated composite materials by optical microscope the measure of the Mass loss**

**Fig. 11** represents the variation in mass loss of F0 and F20 as a function of immersion time.

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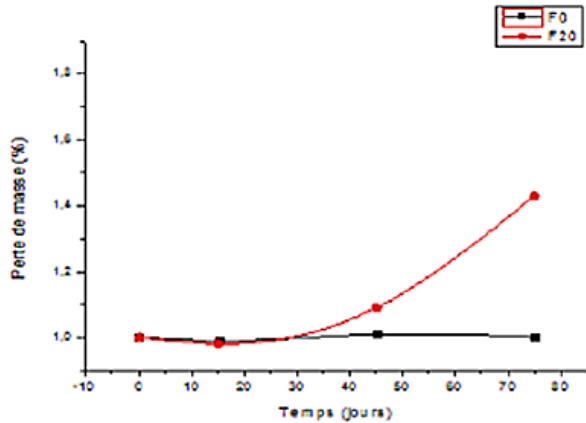*Nadira BELLILI et al.  Vol2 N°2, 2023, pp. 09-15*

**Figure 11.**  The variation of mass loss of F0 and F20 as a function of immersion time.

From this curve, we clearly see the absence of mass loss of F0, which is evident for polymeric materials that have a long life. We note the increase in mass loss of F20, by increasing the immersion time.

This mass loss is mainly due to the biodegradation of the filler presented in the PVC matrix. Figure.15 represents the variation in mass loss of F20, F20CH10KGy, F20CH25KGy, F20CH50KGy, F20CH60KGy and F20CH70KGy as a function of immersion time.
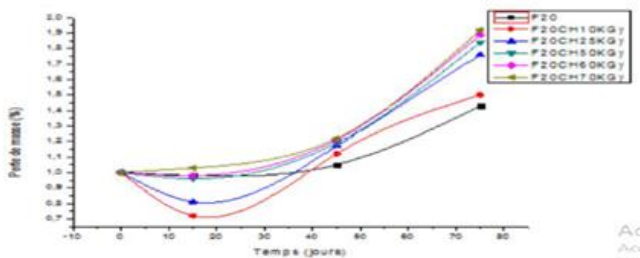


**Figure 12.** Curve represents the variation in mass loss of F20, F20CH10KGy, F20CH25KGy, F20CH50KGy, F20CH60KGy and F20CH70KGy

In this figure, we notice that the mass increased during the first 15 days for all the samples. We explained this increase by the amount of water absorbed by the hydrophilic reinforcement, which led to the swelling of its particles.

The composites reinforced by the irradiated filler show a greater mass loss compared to the composites loaded with the non-irradiated olive pomace flour. This mass loss became more important by increasing the radiation dose. It can be concluded that the treatment with gamma irradiation contributed to the biodegradation of composites.

## V.  Conclusion

The study carried out in this work aimed at the influence of natural fibers on the characteristics of PVC-based composites and olive pomace flour. The problem of the absence of adhesion between the PVC matrix and the olive pomace flour reinforcement has been treated and improved by low-dose gamma irradiation. The filler remained thermally stable and its particle size was reduced and well dispersed.

 The study of the biodegradability of the composites developed has allowed us to conclude that the addition of vegetable fibers in a thermoplastic matrix is an effective solution to obtain a biodegradable composite material which decomposes naturally when it is in contact with various environmental factors.

This conclusion is confirmed by the photos taken by the optical microscope, where the reduction in the size of the agglomerates was observed with a dispersion of the FGO. The decomposition of composites is evidenced by their loss of mass.

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