Study of the influence of the almond variety in the properties of injected parts with biodegradable almond shell based masterbatches

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Abstract

This article is focused on the development of a series of biodegradable and eco-friendly masterbatches based on polylactic acid (PLA) filled with almond shell of different varieties to study of the influence of almond variety in the properties of injected biodegradable parts. These innovative masterbatches have 20 wt% of almond shell. These masterbatches have been added 4% to PLA to study mechanical properties of injected samples**.**

This study is part of a LIFE project (LIFE11 ENV/ES/513) aimed to create and to test at preindustrial level new coloured masterbatches based in biodegradable plastics and containing in its formulation a high percentage of almond shell, a natural waste material, which firstly will permit to cover technical requirements of two traditional industrial sectors: toy and furniture, although the results achieved could be extended to other industrial sectors.

Keywords

Almond shell, masterbatch, additivation, PLA, injection moulding, characterization

1. Introduction

A masterbatch consists of a polymeric matrix in which a high proportion (50-80%) of pigments, colorants, dispersing waxes and other additives and fillers are included. The masterbatch, in the form of pellets or granules, is added to the polymer, also in pellets, during the injection moulding process being a simple and economic way of additivation for the plastic transformers.

Currently, there are not masterbatches in the market based on biodegradable plastics, as these materials are poorly introduced in sectors different from the packaging sector [1]. This work shows the development of a series of biodegradable and eco-friendly masterbatches based on polylactic acid (PLA) filled with almond shell of different varieties. Current uses of almond by-products are for biomass generation, pellets or other form, where the most of it is applied, as a livestock feed, and fertilizers [2]. Punctually (and in a non significant percentage), it is being used for drug additives.

2. Materials and Experimental Procedure

2.1 Material

Two commercially available PLA materials were used in this study (supplied by Ercros, Barcelona, Spain), one for the masterbatch development, ErcrosBio PLL 600, and the other one for injection moulding of test samples, ErcrosBio LM 6230, which have a melt flow index (MFI) of 22 g/10 min and 9 g/10 min, respectively, and a density of 1.25 g/cm³ (data provided by Ercros).

Six types of almond varieties were selected for this study: Comuna, Largueta, Desmayo Rojo, Marcona, Guara and Mollar, all of them from Spain (
Figure 1). A mixture of all of them was also studied in order to compare the results with the separated varieties because this is the most usual format of providing this waste. Almond shell powders (ASP) of 1 mm were obtained by milling in two steps, using a Milling Shini model SG- 1621 (size particle less than 5 mm) and Milling ZM 200 (size particle less than 1mm). The obtained powders were sieved using a 0.5 mm diameter sieve. In order to minimize its moisture, the ASP was dried in an air circulating oven for 24 h at 80ºC before processing. The moisture content of the ASP was less than 2 wt %.

Figure 1. Almond shell varieties used: Comuna, DesmayoRojo, Largueta, Marcona and Guara (left). Mixed varieties, supplied in fragments (right)

Figure 2. Milled Almond Shell: Size Particles less than 5 mm (left). Size Particles less than 1 mm (right)

2.2 Experimental Procedure

2.2.1. Infrared spectroscopy (FTIR). The infrared spectra of the each almond variety were recorded on a NICOLET NEXUS 6700 Spectrophotometer. The spectrums were obtained at an angle of incidence of 45°, and the transmittance range of the scan was 400 to 4000 cm^{-1}.

2.2.2 Thermogravimetric analysis (TGA). TGA was carried out using a TA Instrument Q500 thermogravimetric analyser to study the thermal stability. Each type of almond variety was subjected to the following temperature program: from 30°C to 550°C under nitrogen atmosphere and from 550°C to 900°C under oxygen atmosphere, both of them at a rate of 10 °C/min and with a purge gas flow of 10 ml/min.

2.2.3. Scanning Electron Microcopy (SEM). The morphological structure and size of obtained ASP were analyzed using a Jeol JSM-840 SEM system. ASP samples were gold-coated before analysis and the energy of the electron beam was 20 kV.

2.2.4 Moisture Content analysis. The moisture content of the ASP was obtained by using a Cobos FD-720 Moisture Analyzer. The test was performed at 80°C and the analysis finished when the weight value was equal or less than0.01% over two consecutive periods of 30 seconds.

2.2.5. Compression test. Compression strength of the almond shell of the selected varieties was determined using an Instron 6025 Universal testing machine with 5 kN power sensors.

2.2.1. Composite preparation: Masterbatches based on PLA and ASP were developed using melt mixing in a Brabender PlastographW 50 EHT PL. The amount needed from each compound was 20wt% ASP and 80 wt%

PLA. The parameters during the melt mixing were: mixing temperature=200°C, rotational speed= 50 rpm and mixing time= 25 minutes. The compound produced was cooled to room temperature and then milled to obtain homogeneous biodegradable masterbatches.

2.2.2. Injection Moulding. Testing samples were molded using a DEMAG Ergotech 110-430h/310V injection machine by adding a 4% of biodegradable almond shell-based masterbatches to PLA. The injection conditions used to prepare test samples are shown in table 1. Finally, specimens were conditioned at a temperature of 23 ºC and relative humidity of 50 % for at least 16 h before testing.

Table 1. Injection condition

Parameters	Injection moulding conditions
InjectionTemperature (°C)	40-180-190-200-200
MouldTemperature (°C)	30
Injection speed (mm/s)	70
Injection pressure (max)(bar)	165
Presión posterior (bar)	83
Cooling time (s)	35

2.2.3. Tensile strength and modulus. Tensile testing of the injection molded composite specimens was performed with an Instron 6025 universal testing machine with 5 kN power sensors. The tests were performed according to standard ISO 527, starting with a crosshead speed of 1 mm/min, accelerating to 5 mm/min when the strain exceeds the 0.25 mm limit. Recorded values include ultimate tensile strength (UTS), Young's modulus and strain at break. A total of 5 specimens from each material were tested.

2.2.4. Impact Strength. Impact testing was performed with a Resil 5.5 impact testing device (CEAST RESILIMPACTOR) with a 1 Joule hammer. Test samples were cut and tested according to standard ISO179 (Charpy un-notched). A total of 5 specimens from each material were tested.

2.2.5. Flexural. The flexural strength and the flexural modulus of elasticity were determined as the 3-point bend. Test speed was 2 mm/min. The flexural strength was calculated according to standard ISO75. Test was run with five specimens.

3. Results

FTIR spectrums of different variety of almond shell are shown in Figure 3. The spectrum of the almond shell shows the basic structure of all cellulose fibre i.e. strong broad OH stretching vibrations (3300-4000 cm^{-1}), due to inter and inter-molecular hydrogen banding of polymeric compounds (macromolecular associations) such as alcohols, phenols and carboxylic acids, as in pectin, cellulose groups on the adsorbent surface. The peaks at 2916 and 2852 cm^{-1} are attributed to the symmetric and asymmetric CH stretching vibration of aliphatic acids. The peaks around 1395 cm^{-1} are due to the symmetric bending of CH_3. The peak observed at 1630 cm^{-1} is the stretching vibration of bond due to non-ionic carboxyl acids or their esters. Broad peak at 1072 cm^{-1} may be due to stretching vibration of C-OH of alcoholic groups and carboxylic acids [3]. No important differences are appreciated between the almond shells from different almond variety.

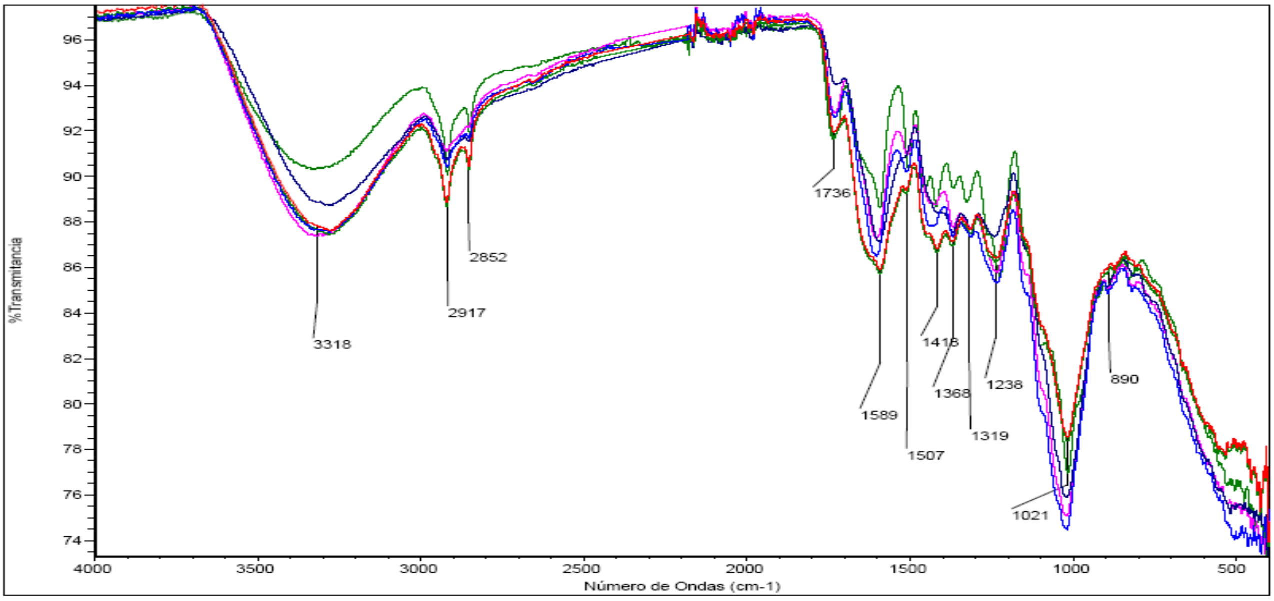


Figure 3. FTIR spectrums of almond shell: Guara variety (green), Comuna variety (blue), Desmayo rojo variety (pink), Largueta variety (red), mollar

The morphology of almond shells were studied by SEM. Figure 4 shows the view of almond shell. It also shows the agglomeration of many fine micro particles, which led to a rough surface and the presence of pores structure.

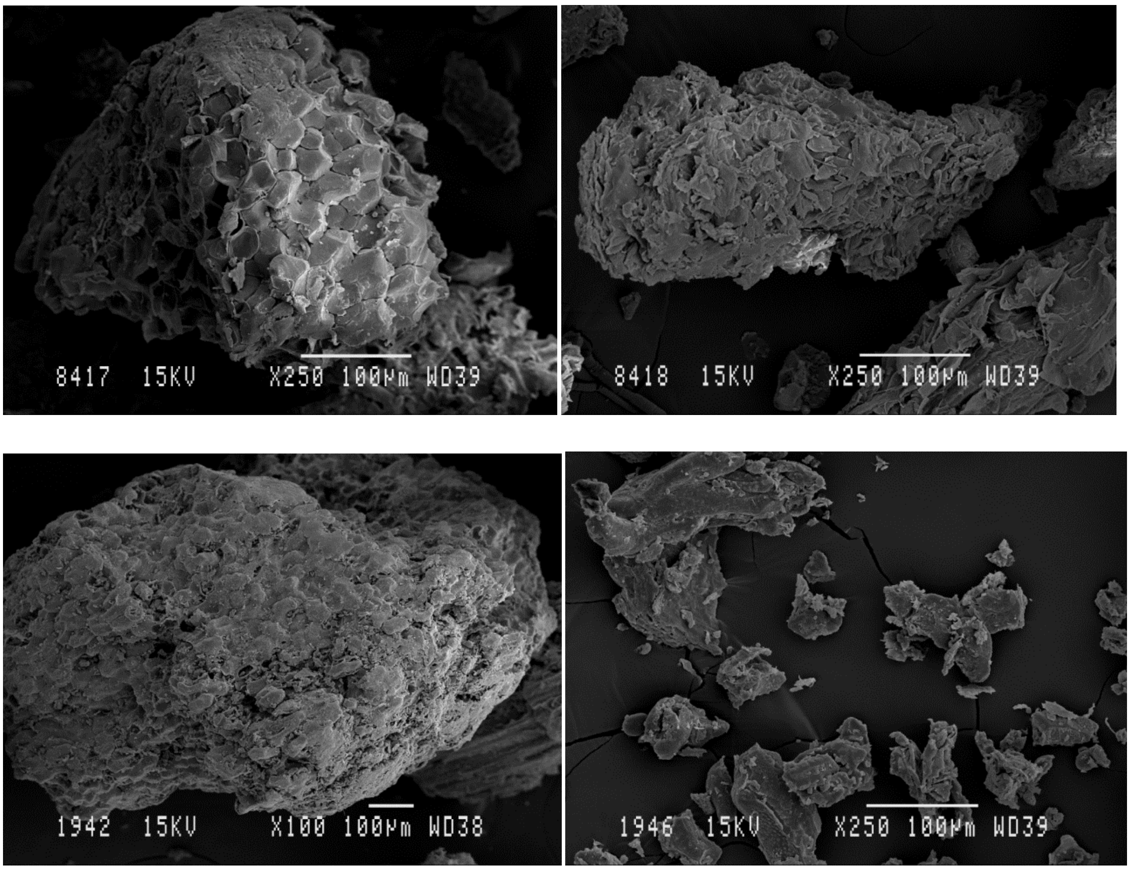


Figure 4. SEM micrograps of almond shell: Comuna variety (top left), Desmayo Rojo variety (to right), Largueta (botton left) and mixture of all (botton right)

The thermal stability of natural fibre is a very important parameter in the production of natural fibre polymer composites. The thermal decomposition of almond shell occurs in several stages depending on its main components, hemicelluloses, cellulose and lignin. The first stage of descomposition was the evaporation of moisture where the temperature ranged from 30°C to 180-200°C. As the fibre was heated, the weight of the material decreased via a release of the bound water and volatile extractives. This phenomenon is common for plant fibres and makes the fibre more flexible. White et al (2011) [4] found similar mass loss during evaporation of moisture when they studied different agricultural plant fibres. The lowest mass loss (around 6%) was observed for Mollar almond shell at this stage. Between 180-220° C (Onset) decomposing almond shell is initiated, so that this temperature will be the maximum temperature that can be obtained by extruding composites. The second weight loss is a complex jump up to 550 -580° C, depending on the variety, where most of the almond shell (60-70%) in an inert atmosphere is lost. By switching to an oxidizing atmosphere latest weight loss between 23-30% is produced, leaving a residue of 1-2%.

This is consistent with studies of several authors who have studied degradation of lignocellulosic fibers in inert atmosphere, and indicate that they are degraded in the range of 225-600 ° C due to the decomposition of its three major constituents (cellulose, hemicellulose and lignin). The cellulose which is the major component of natural fibers decomposes between 325-400 ° C and is characterized by low residual mass end. Hemicellulose is decomposed at lower temperatures (225 - 325 ° C), because it is easier to hydrolyze than cellulose. Lignin was the most difficult component to decompose compared to other components, where the decomposition occurred slowly under whole temperature range up to 700°C. According to some author [5], although the descomposition of lignin could start as early as 160°C, it decomposed slowly and extended its temperature as high as 900°C

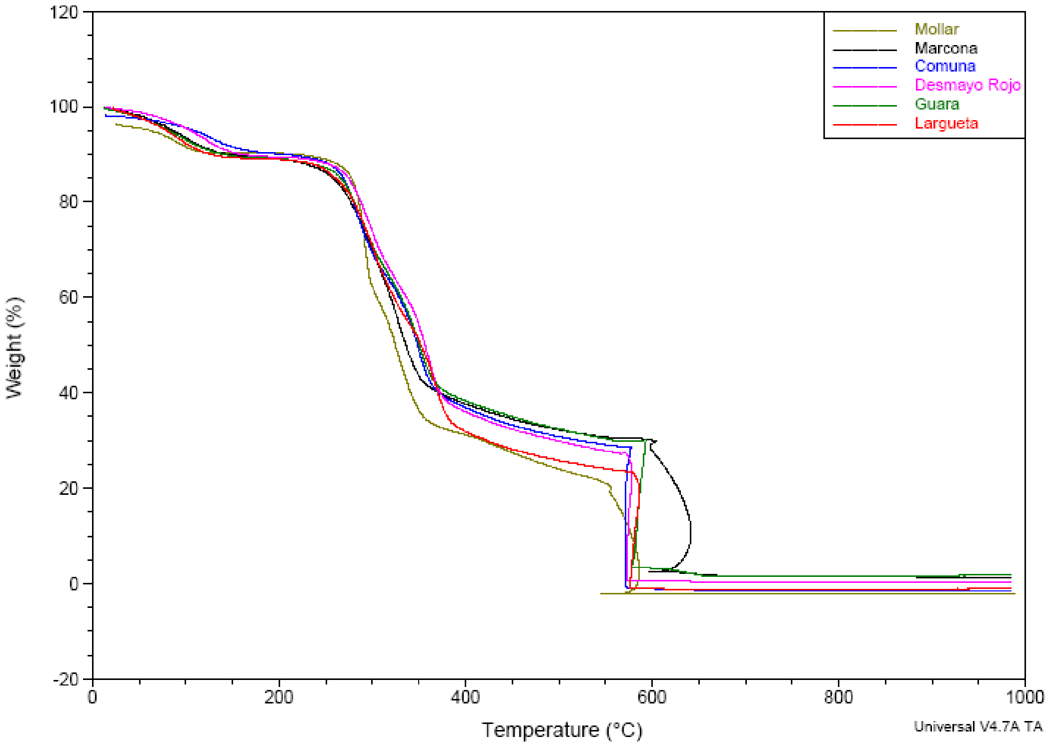


Figure 5. Thermogravimetric curve (TGA) of almond shell

Table 2. Range of temperature and % loss weight

Types of almond shell varieties	Range of Temperature °C	% Loss Weight	Range of Temperature °C	% Loss Weight	Range of Temperature °C	% Loss Weight	% Residue
Largueta	30-206	10	206-567	65	567-650	25	0
Guara	30-194	11	194-579	59	580-650	28	2
Desmayo Rojo	30-211	10	211-562	62	562-650	27	1
Comuna	30-218	8	217-565	61	565-650	30	1
Marcona	30-181	10	181-582	59	582-650	29	2
Mollar	30-200	6	200-549	69	549-650	23	2

The moisture content of almond shell is around 10-13%. The moisture content can drastically affect during the processing and in some mechanical characteristics, such as compression, tensile/flexural properties [6-9] and impact strength. So that, it is important to dried the (ASP) in an air circulating oven ºC before processing. Table 3 includes the initial moisture content of ASP.

Table 3. % Moisture Content

Types of almond shell varieties	***% Moisture Content***
Comuna	12.15±0.21
Largueta	13.40±0.46
Desmayo Rojo	11.44±0.10
Marcona	11.54±0.23
Guara	11.31±0.47
Mollar	10.21±0.24

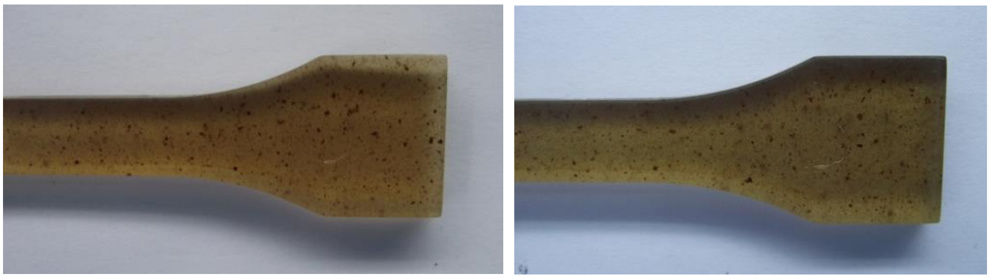
Three of the almond shell types (Desmayo Rojo, Largueta and Guara) presented compression resistance higher than 700 N whereas the Mollar variety is the least resistant, 296 N (Table 4). This could influence the final properties of the materials in which they are included.

Table 4. Compression strength

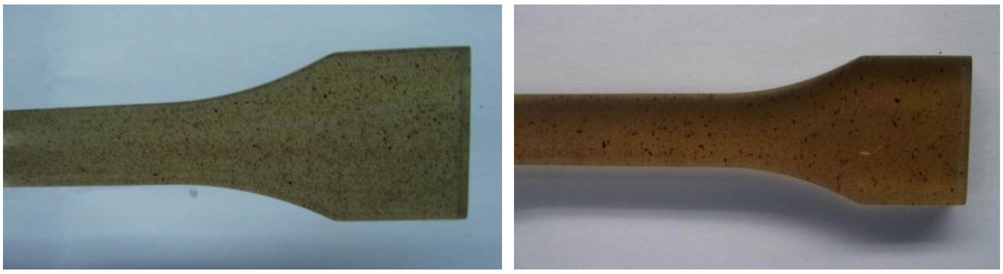
Types of almond shell varieties	***Compression Strength (MPa)***
Comuna	---
Largueta	725±99
Desmayo Rojo	790±98
Marcona	503±49
Guara	712±77
Mollar	296±43
Mix all of them	---

Fibres play an important role in determining the mechanical properties of natural fibres filled thermoplastic composites. So that, it has been studied the mechanical properties: tensile, flexural and impact strength and finally shore hardness.

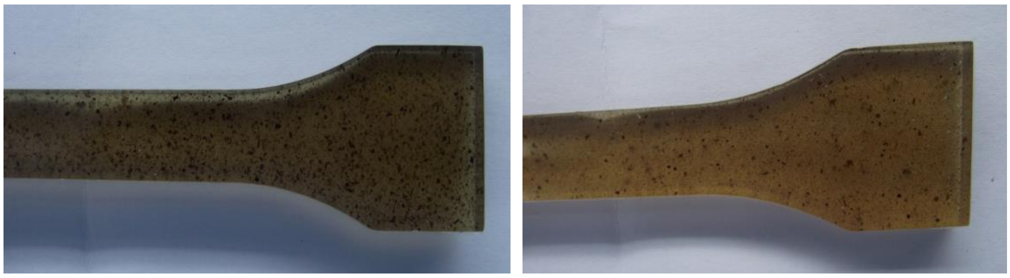
Figure 3 shows the injected samples obtained by introducing 4%wt of the different variety almond shell-PLA masterbatches.



a) b)



c) d)



e) f)

Figure 6. Injected samples of PLA with 4%wt almond shell masterbatch: a) Marcona variety, b) Largueta, c) Comuna, d) Desmayo Rojo, e) Mollar, f) Guara.

The tensile strength and modulus of injected samples of PLA with 4% of biodegradable almond shell-based masterbatch are shown in Figure 7 and Figure 8, respectively. In previous studies, the addition of the fibres increases the tensile modulus. However, in this case the final content de almond shell into a polymer matrix is low, so that it is not possible to observe this effect. The tensile strength of composites is related to interfacial strength and thus if there is weak strength in interface, the tensile strength of composites will be low.

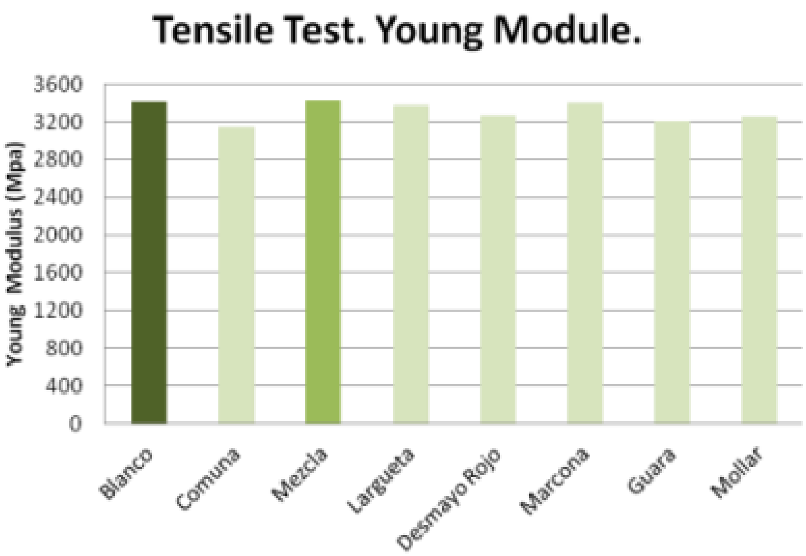


Figure 7. Young Modulus of as-received (Blanco) PLA material and compounds with different almond shell varieties.

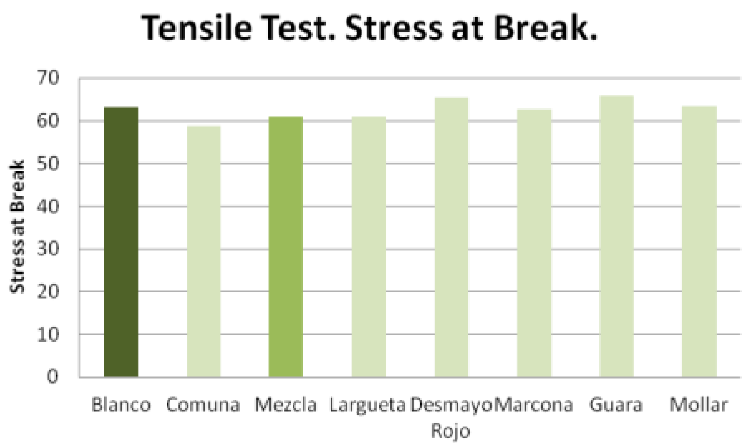


Figure 8. Tensile strength of as-received PLA material ("blanco") and compounds with different almond shell varieties.

The incorporation of fibres usually increases the stiffness of the resultant material. The Figure 9 shows the flexural modulus. A mixture of all of variety studied gives a slightly higher reference value of PLA without masterbatches.

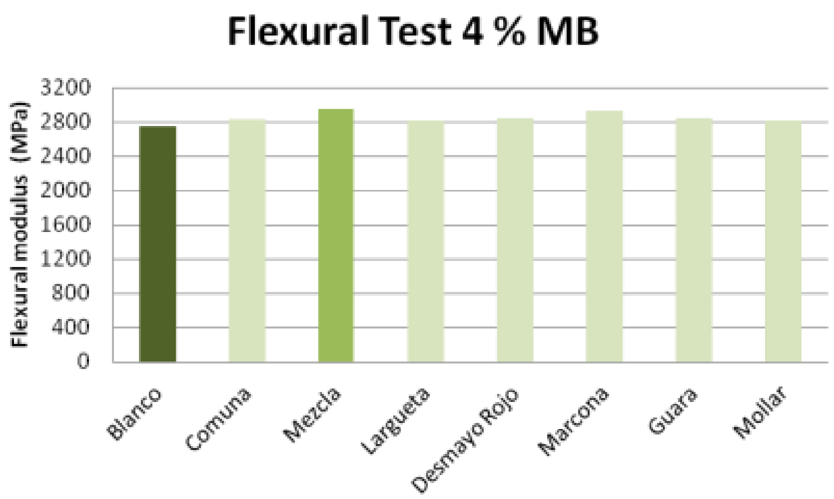


Figure 9. Flexural Modulus of as-received PLA material ("Blanco") and compounds with different almond shell varieties.

The shore D hardness values are shown in Figure 10. There is no remarkable influence of the introduction of 4% of biodegradable almond shell-based masterbatch to PLA.

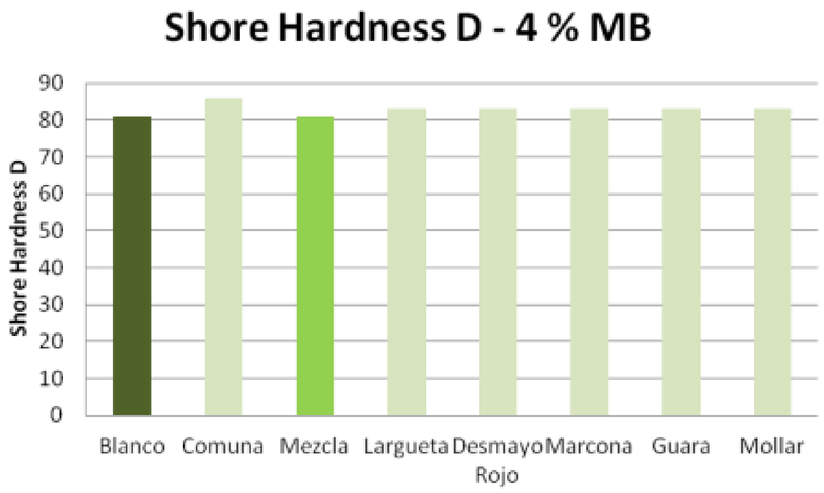


Figure 10. Shore Hardness of as-received PLA material ("Blanco") and compounds with different almond shell varieties.

Impact properties are the most affected ones by the addition of 4% of biodegradable almond shell-based masterbatch to PLA. This effect of impact strength for injected notched samples is shown in Figure 11. The addition of masterbatches reduces the impact strength, although the masterbatches obtained with mixed and Comuna varieties had better impact performance than the others.

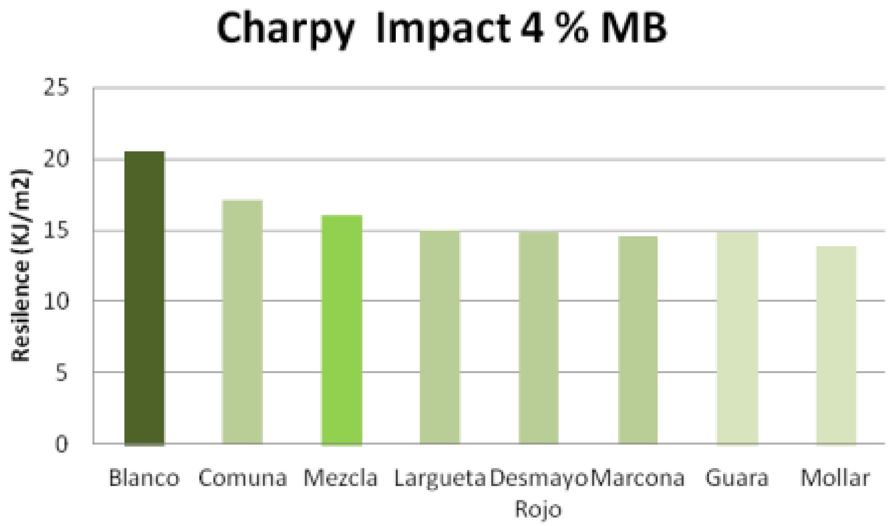


Figure 11. Impact Strength of as-received PLA material ("Blanco") and compounds with different almond shell varieties.

4. Conclusions

This study showed that thermal descomposition of almond shell occurs in several stages depending on its main components, hemicelluloses, cellulose and lignin and does not depend on the almond variety. The infrarred spectra of the different varities do not differ significatively.

Tensile and flexural strength and Shore hardness do not present significant differences between the diverse varieties, the mixture or the as-received PLA.

From these results it was concluded that the most recommended option is to work with the mixture of almond shell varieties as it presents slightly better mechanical properties than the other almond shell types separately. Moreover this is deployed in the supply chain as mixture of them, then it is easier and cheaper to acquire.

5. Acknowledgements

European Commission through LIFE+ programme, project LIFE11ENV/ES/513 MASTALMOND. (http://www.lifemastalmond.eu/)

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