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Characterization of an Almond Shell Composite Based on PHBH

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***Abstract*—** The utilization of almond crop by-products to obtain Poly(3-hydroxybutyrat-co-3-hydroxyhexanoat) (PHBH)-based composites was carried out by using an extrusion process followed by an injection to obtain test samples. To improve the properties of the resulting composite, the incorporation of Oligomer Lactic Acid (OLA 8) as a coupling agent and plasticizer was additionally considered. A characterization process was carried out by the measurement of mechanical properties, thermal properties, surface morphology, and water absorption ability. The use of the almond residue allows obtaining composites based on PHBH with a higher environmental interest and lower cost.

***Keywords*—**Almond shell, PHBH, composite, polymer.

I. INTRODUCTION

ALMONDS are a nut consumed around the world. Aproximately 3 million tons are grown each year, among the total crop, the shell accounts up to 75% [1]. The main almond producers are countries such as USA, Spain, Syria, Italy, Iran and Morocco. In these countries, the reuse of the agricultural by-product has a special interest in order to obtain an added value [2]. The revalorization of wastes as fillers in a polymer has attracted interest in recent years. This implies that composite materials can be developed with lower cost, low density or ease of processing. In general, these wastes consist mainly of cellulose, hemicellulose and lignin [3].

The correct performance of composites depends on the adhesion between the polymer and the lignocellulosic particle. A good adhesion allows the correct transfer between the filler and the polymer. Due to the hydrophilic behavior of natural fillers, it is difficult to achieve adhesion of the particles to the polymeric chains. This is why it is necessary to incorporate additives or carry out treatments to improve the coupling by creating chemical interactions between the different parts [4].

The problems associated with polymers have led to a growing demand of biodegradable polymers. In this regard, polyhydraxyalkanoates (PHAs) are of particular interest as replacements for polymers of petrochemical origin because they are obtained by a fermentation process using microorganisms. One of the best known is poly(3-hydroxybutyrate) or PHB, which has very limited thermal stability, making it difficult to process [5]. Among the different PHA, PHBH presents a high interest because it presents a larger processing window due to its better thermal stability and higher flexibility compared to PHB.

This work proposes the use of almond shell wastes to obtain composites based on PHBH. In order to obtain them, it is proposed the use of different amounts of almond and a coupling agent to determine the mechanical, thermal and water absorption properties. To obtain, the composites it is proposed the use of a twin-screw corotating extruder mixing process followed by an injection process to obtain the test samples [6], [7].

II. MATERIALS AND METHODS

A. Materials

Almond shells are obtained from Jesol Materias Primas (Valencia, Spain) with a maximum particle size of 150 µm and average of 75 µm. PHA pellets were commercial grade called PH110 from ErcrosBio S.A. (Barcelona, Spain) with a density of 1.2 g/cm^3 and a melt flow index (MFI) of 1 (g/10 min) at 160 °C. As coupling agent/plasticizer, a commercial grade Glyplast OLA 8 from Condensia Química S.A. (Barcelona, Spain) was employed. At room temperature OLA8 is a liquid polyester with a viscosity of 22.5 mPa s (at 100 °C) and a maximum acid index of 1.5 mg KOH g^{-1}.

B. Test Sample Obtention

Almond shells and polymer pellets were dried for 6 h at 80 °C before mixing with an extrusion process. The correct amount of each material was premixed in a zipper bag according the proportions proposed in Table I and then introduced in a twin-screw corotating extruder from DUPRA S.L. (Alicante, Spain) to obtain a homogeneous mixing. Temperatures were set from the hopper to the extrusion die as 110 °C, 120 °C, 130 °C and 140 °C.

TABLE I
COMPOSITIONS OF EACH ALMOND COMPOSITE CONSIDERED IN WEIGHT PROPORTION (WT%) AND AS PARTS PER HUNDRED RESIN OF THE COMPOSITE (PHR)

Code	PHBH (wt%)	Almond (wt%)	OLA (phr)
PHBH	100	-	-
PHBH 10 Almond	90	10	-
PHBH 20 Almond	80	20	-
PHBH 30 Almond	70	30	-
PHBH 30 Almond + OLA	70	30	10

Mixed materials were pelletized and then submitted to an injection molding process to obtain the samples employed in the experimental section. The injection molding process was carried out in a Sprinter 11 injection machine form Erinca S.L. (Barcelona, Spain) with a temperature profile from the hopper

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to the nozzle of 150 °C, 145 °C, 140 °C and 135 °C with an injection molding time of 1 s and 15 s of cooling. Additionally, tempered mold at 60 °C as recommended by the polymer provider was used.

C. Mechanical Properties Analysis

Tensile tests were performed according to ISO 527-2:2020 in a universal testing machine, model ELIB-50 from Ibertest (Madrid, Spain) equipped with a 5 kN load cell. The test conditions were set as 10 mm/min cross head speed. Impact behavior was measured by means a Charpy impact test. 1J pendulum from Metrotec S.A. (San Sebastian, Spain) was employed to break samples with "V" notch. All mechanical tests were performed 14 days after the injection molding process to ensure the correct recrystallization of the samples due to the characteristic ageing process of PHBH.

D. Surface Morphology Analysis

Fractured specimens from impact tests were observed by means of an emission scanning electron microscopy ZEISS ULTRA 55 from Oxford Instruments (Abingdon, Oxfordshire, UK) under an accelerating voltage of 2 kV. Samples were metallized with platinum to ensure the conductivity.

E. Thermal Properties Analysis

Differential scanning calorimetry (DSC) analysis was carried out in a TA Instruments Q2000 (New Castle, Delaware, USA) with an inert atmosphere of nitrogen. Dynamic cycle from 0 °C to 190 °C at a heat rate of 10 °C/min, then a cooling to −40 °C at -10 °C/min and finally from −40 °C up to 190 °C at 10 °C/min.

The degree of crystallinity (Xc) of each sample was assessed with (1) with the melt enthalpy (ΔH_m), cold crystallization enthalpy (ΔH_{cc}) and weigh fraction of PHBH (w) of each material. The fully crystalline enthalpy of PHBH (ΔH_m^0) is taken as 146 (J/g) [8].

$$X_c = \left[\frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^0 \times w}\right] \times 100 \tag{1}$$

Thermal gravimetric analysis (TGA) was carried out in a Mettler-Toledo TGA/SDTA 851 (Schwerzenbach, Switzerland). Alumina pans (70 µL) with the sample (6-7 mg) were subjected to a heating ramp from 30 to 700 °C at a constant heating rate of 20 °C/min under a nitrogen atmosphere.

F. Water Absorption Analysis

Rectangular samples of 80 x 10 x 4 mm^3 of each material were dried and then immersed in distilled water for 9 weeks at a controlled temperature of 23 °C. Each week, the samples were taken out from water to measure the weight (W_t) after removing the surface water. Water absorption was calculated with (2) where W_0 is the initial weight of the sample.

$$\Delta m_t(\%) = \left(\frac{W_t - W_0}{W_0}\right) \times 100 \tag{2}$$

III. RESULTS

A. Mechanical Properties

Fig. 1 shows the values of the mechanical characterization of the composites manufactured by the extrusion and injection process. The introduction of almond resulted in a higher stiffness due to the reinforcement effect offered by the particles inside the polymeric matrix. The value obtained for the neat polymer was 1064 MPa and with the incorporation of 30 wt% almond, an increment of 64% could be observed. The introduction of lignocellulosic particles usually gives rise to this phenomenon, an example of this is the work of Erdogan et al. who analyzed the effect of different types of fillers in composites based on polypropylene [9]. The incorporation of the coupling agent allowed to obtain a modulus similar to the neat polymer with only a difference of 9%. In spite of having incorporated the almond, the OLA improved the particle adhesion as could be seen in Fig. 2 (c), also a plasticizing effect was produced which increased the mobility of the polymeric chains [10]. Regarding the ductile properties such as elongation or impact strength, it can be seen that the introduction of the almond gave a reduction in both cases. PHBH developed an elongation of 8.2% and an energy of 4.3 kJ/m^2. The reduction for the composite with 30 wt% almond resulted in 57% reduction in elongation and 44% for the impact strength due to the presence of stress concentrators arising due to the presence of particles [11].

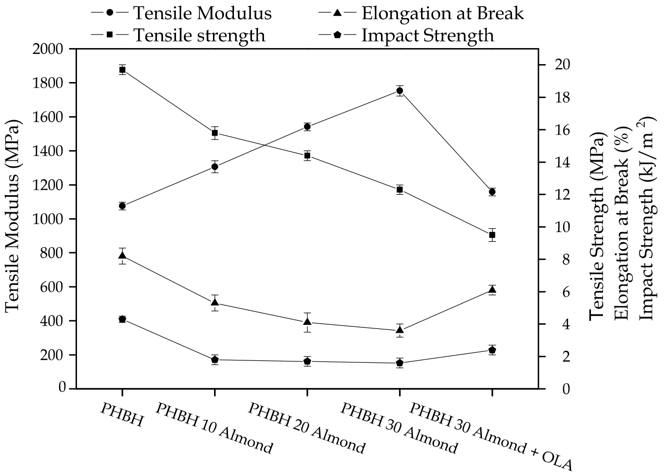

Fig. 1 Summary of the main mechanical properties of the Almond PHBH composites

For the composite with OLA, in spite of having incorporated the coupling agent with plasticizing capacity, the values obtained were higher, but in any case, the values were lower than the PHBH values. As for the tensile stress, due to these same stress concentrators the resulting stresses were lower than those obtained for the unmodified composite.

B. Surface Morphology

II. On the surface of the PHBH neat break can be seen in Fig. 2 (a), it shows the presence of dispersed flakes, attributed to the presence of boron nitride that incorporates the polymer with the aim of improving the crystallization capacity of the polymer due to the capacity of nucleating agent [12]. The incorporation of almond shell particles had a noticeable effect on the fracture morphology because it was possible to observe the particles of almond shell. The uncompatibilized composite showed a small gap between the polymer and the lignocellulosic type particle. This phenomenon is common when fillers with hydrophilic behavior that limits the chemical interaction are incorporated [13]. The presence of the polyester resulted in a no-gap presence between the particle and the polymer and therefore a better load transfer between the different parts was achieved, which improved the resulting mechanical properties.

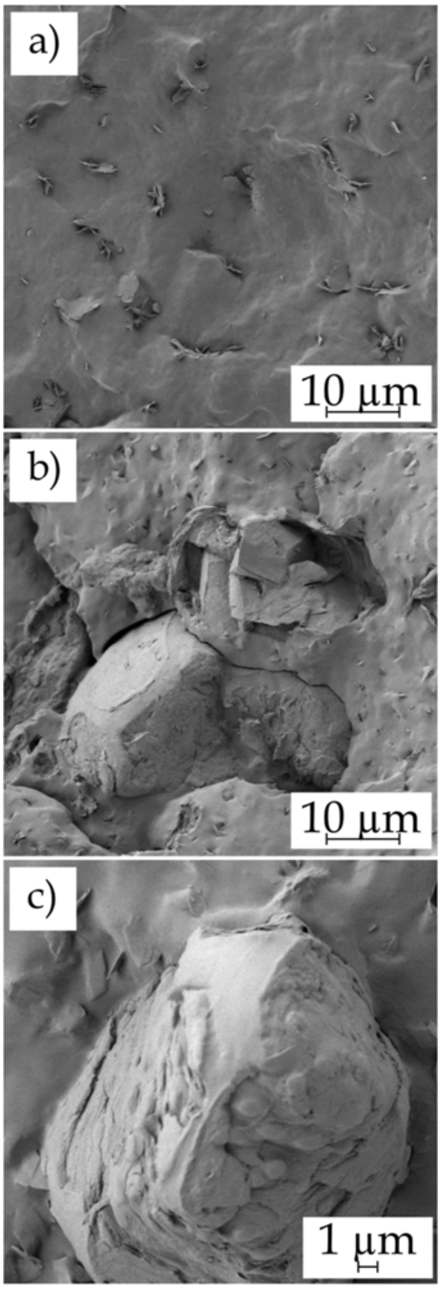

Fig. 2 Surface morphology of the Almond PHBH composites: (a) PHBH (x1000), (b) PHBH 30 Almond (x1000) and (c) PHBH 30 Almond + OLA (x2500)

C. Thermal Properties

Fig. 3 shows the most representative thermograms of this work. The first point to highlight is the glass transition temperature, for which PHBH is close to 0 °C for both PHBH and the composite with 30 wt% almond shell loading. On the other hand, due to the plasticization phenomenon that takes place when OLA is incorporated, there was a reduction in the glass transition temperature of approximately -10 °C due to the higher movement capacity of the polymeric chains [13].

Regarding the crystallization process that takes place during heating between 40 °C and 70 °C, it could be seen how the incorporation of the residue resulted in the enthalpy of crystallization being reduced. This same phenomenon also took place in the work of Essabir et al., in which when high amounts of charge were incorporated. This was because of the fillers acting as a nucleating agent allowing the chains to crystallize on their own [14]. In this sense, the degree of crystallinity of the PHBH sample was only 4.8%, while with the incorporation of the almond shell this parameter adopted values of 17.2%. On the other hand, when considering the introduction of OLA, the degree of crystallinity adopted values of 14.6% and the enthalpy of crystallization decreased because the presence of OLA hindered the nucleating agent effect seen with the almond.

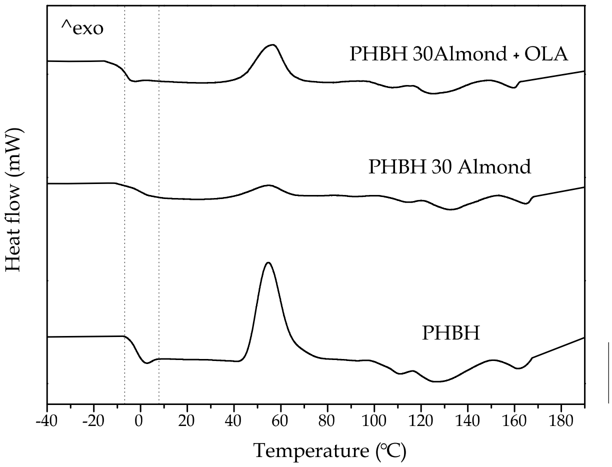

Fig. 3 DSC curves of the Almond PHBH composites

The thermal degradation of the composites was analyzed by thermogravimetry analysis in Fig. 4. PHBH has a characteristic degradation process that occurs in a single step with a highest degradation rate at 309 °C and a residual mass of 1.5%. The introduction of the filler resulted in a reduction of the highest degradation rate temperature of 280 °C, this difference arises due to the introduction of the lignocellulosic type particles which results in the resulting curve adopting two degradation steps. The almond shell has a composition of approximately 38% cellulose, 29% hemicellulose and 30% lignin which resulted in the degradation temperature of the composite being reduced [15].

The introduction of OLA improved the thermal stability, this was mainly due to the improvement of the chemical interaction produced by the coupling agent [16].

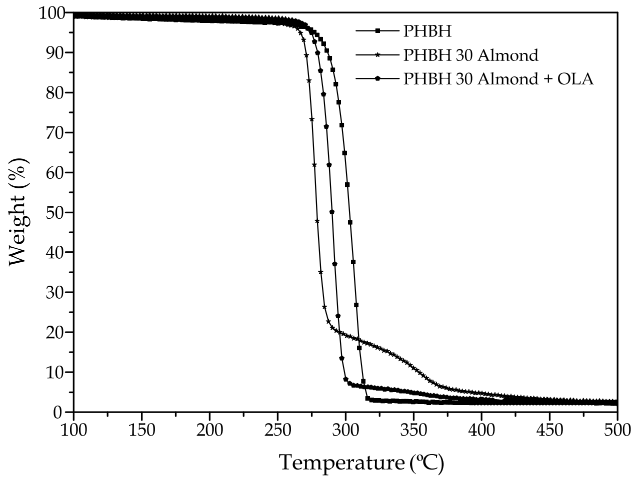

Fig. 4 TGA curves of the Almond PHBH composites

D.Water Uptake

During the water immersion period the samples progressively increased in mass as can be seen in Fig. 5. PHBH had a limited absorption capacity with values not exceeding 0.5% over 9 weeks. The introduction of the filler had a significant increase in water absorption capacity. In this sense it can be seen that there is no saturation of the water absorption capacity in 9 weeks in composites with 20% and 30% almond shell.

In the specific case of the 30 wt% almond compound after 9 weeks, the 7% water absorption was exceeded. This difference arises mainly due to a higher hydrophilic behavior [17].

The incorporation of the coupling agent made it possible to reduce the water absorption capacity. The main reason for this is the reduction of -OH bonds available on the surface of the lignocellulosic particle and which therefore reduces the water absorption capacity of the filler [18].

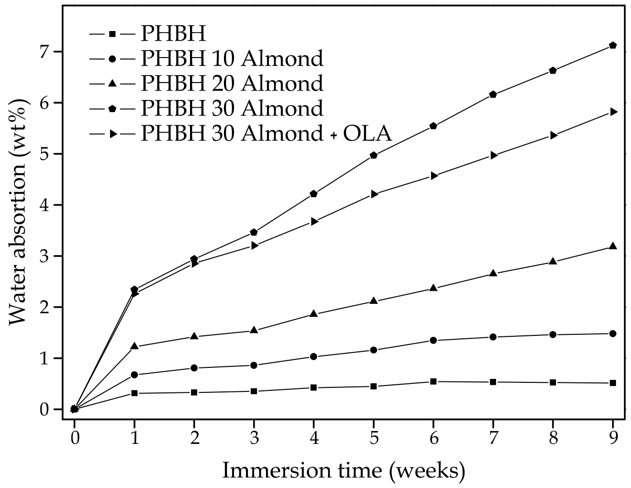

Fig. 5 Water uptake of the Almond PHBH composites over 9 weeks

IV. CONCLUSION

Shell almond composites based on PHBH were successfully prepared by the employment of an extrusion process and an injection molding process to obtain test samples. The mechanical properties measured showed that the introduction of almond particles inside the polymer matrix allowed to increase the tensile modulus, nonetheless the ductile properties like elongation at break or the impact strength were reduced. Additionally composite with 30 wt% with the introduction of OLA achieved a tensile modulus that was almost equal to the neat PHBH by the plasticization achieved in the polymer matrix; other phenomenon observed with OLA was the improvement of the compatibility of the filler by the reduction of the gap observed in surface morphology analysis. Regarding the thermal behavior of the composites, the presence of the almond shell resulted in an increase in the degree of crystallinity due to the nucleating agent effect. The effect of OLA from the thermal point of view allowed a reduction of the glass transition temperature due to the plasticizing effect. The degradation behavior of the almond hull resulted in a lower degradation temperature of the sample due to its lignocellulosic composition. The compatibilization process improved this behavior. Water absorption increased significantly with the amount of load considered due to the hydrophilic behavior of the kernel. The incorporation of OLA allowed to reduce the absorption phenomenon due to the reduction of the amount of free OH bonds.

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