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**Characterization and enzymatic degradation study of poly(ϵ -caprolactone)-based
biocomposites from almond agricultural by-products**

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Abstract

Reinforced poly(ϵ -caprolactone) (PCL)/almond skin (AS) biocomposites were prepared by extrusion and injection moulding at different AS contents (0, 10, 20, 30 wt%) in order to revalorize this agricultural residue. AS particles were characterized by field emission scanning electron microscopy (FESEM), attenuated total reflectance infrared spectroscopy (ATR-FTIR) and thermogravimetric analysis (TGA). Hemicelluloses were the first compound thermally degraded (263 ± 2 °C) followed by cellulose (330 ± 5 °C) and lignin (401 ± 3 °C) with a remaining residue of 20 % which was associated to the fibre content present in AS. Mechanical, morphological, thermal, and water absorption properties; and enzymatic degradation using *Pseudomonas lipase* were evaluated for the obtained biocomposites. A significant improvement in Young's modulus with a gain of 73 % at 30 wt% AS loading was obtained compared to neat PCL. An increase in Shore D hardness and decrease in elongation at break and impact energy were also observed with increasing AS content caused by the reinforcement effect. Lower DSC thermal enthalpies and higher crystallinity were obtained for the biocomposites. Some decrease in thermal stability and higher water absorption values were also found with AS addition. Finally, the presence of AS retarded the enzymatic degradation of PCL, showing neat PCL higher weight loss after 25 days of study followed by PCL with 10 wt% AS.

Keywords

Agricultural by-products, almond skin, poly(ϵ -caprolactone), reinforcement, enzymatic degradation.

1. Introduction

Over the last few years, the petroleum crisis has made biocomposites significantly important. The worldwide capacity of bio-based polymers is expected to increase from 2.33 million metric tons, Mt, (2013) to 3.45 Mt in 2020 [1]. Among biodegradable polymers, poly(ϵ -caprolactone), PCL, has emerged as an important candidate for polymer-based biocomposites in various applications due to its biodegradable character and ease of processing using conventional plastics machinery [2-3]. However, the relative high price (ranging 4.50-6.00 € per kg) of PCL and its poor mechanical properties have limited its large-scale production as a substitute of traditional polymers [3-4].

The hydrolytic degradation and biodegradation by microorganisms in the environment of PCL have been extensively investigated, being them very slow due to the polymer hydrophobicity and crystallinity. Highly crystalline PCL was reported to totally degrade in 4 days, observing a decrease in crystallinity during degradation [5-6]. Three types of lipase were found to significantly accelerate the enzymatic degradation of PCL: *Rhizopus delemer*, *Rhizopus arrhizus*, and *Pseudomonas*. The result of this process is increasingly smaller molecules, which enter into cellular metabolic processes, generating energy and turning into water, carbon dioxide, biomass and other basic products of biotic decomposition. It is extremely important to know the exact rates of degradation and mineralization, not only in terms of use since certain properties of plastic materials must be guaranteed; but also in terms of the environmental impact of the decomposition products (e.g. fragments) [7].

Agricultural by-products are normally incinerated or dumped causing environmental problems such as air pollution, soil erosion and decreasing soil biological activity [8].

The incorporation of agricultural residues into polymer matrices is currently a trending

topic in research due to the relatively high strength, stiffness and low density of natural fibres present in these residues. Different studies can be found regarding the valorisation of agricultural residues, such as orange tree pruning fibres, bamboo, jute, flax, wood, among others; as reinforcement in composite materials due to their desirable properties: availability, recyclability, low-cost, environmental friendliness, no toxicity, lower pollution emissions and energy consumption for their production and disposal, biodegradability and mechanical performance [9-12]. Nut by-products, such as macadamia [13] and walnut shells [14] have been also used as reinforcing agents improving physical and mechanical properties of several polymer matrices. Regarding PCL, different composites were obtained by the incorporation of various natural fibres (wheat gluten, rice, wood) with a remarkable improvement in mechanical properties [15]. In this context, almonds are a very important crop throughout the world's temperate regions, being the worldwide almond production in 2012 about 1.9 Mt [16]. The research on almond reinforced composites from the literature is not very extensive. Pirayesh et al. studied the suitability of using different walnut/almond shell ratios (0, 10, 20, 30, 100 wt%) in wood-based composites manufacturing [8]. Almond shell particles were used as reinforcement in polypropylene by using particle contents up to 30 wt%; obtaining a clear improvement in mechanical and rheological properties [17]. Almond skin (AS) is industrially removed from the nut by hot water blanching, and it constitutes 4–8 % of the total shelled almond weight. Almond-processing industries are interested in the valorisation of AS by-products, which at present are mainly used in cattle feed and in gasification plants to produce energy [18]. This residue is considered to have one of the highest fibre contents of all edible nuts (around 12 %), among other interesting compounds such as flavonoids and phenolic acids with high antioxidant activity [18]. In a preliminary study, the evaluation of morphological, mechanical,

thermal, barrier properties and degradation in composting environment of PCL-based biocomposite films, obtained at laboratory scale, containing AS residue at contents up to 30 wt% were carried out [19]. Results showed that PCL-based composite films reinforced with AS residue at 10 wt% loading showed a high disintegration rate with a clear improvement in mechanical properties, corresponding to a gain in elastic modulus of 17 %, increasing the added-value potential of agricultural wastes and reducing the packaging cost. The aim of this study was the development and characterization of biocomposites based on PCL and AS by-products obtained by extrusion and injection moulding in order to revalorize this agricultural residue and to obtain reinforced biomaterials with added value. AS filler and the obtained PCL-based biocomposites at different AS contents (0, 10, 20, 30 wt%) were fully characterized by the use of different techniques to evaluate their main properties. Moreover, the influence of AS by-product addition on the biocomposites enzymatic degradation was evaluated in the presence of *Pseudomonas lipase*, which is capable of cleaving the ester bonds of PCL [3].

2. Materials and methods

2.1. Materials

Poly(ϵ -caprolactone) PCL-CAPA 6800 ($M_n = 80000$, density = 1.1 g cm^{-3}) was supplied in pellets by Perstorp Holding AB (Sweden).

AS industrial by-product was obtained by “Almendras Llopis” (Alicante, Spain) and it was pulverized to a fine powder with a high speed rotor mill (Ultra Centrifugal Mill ZM 200, RETSCH, Haan, Germany) equipped with a 1 mm sieve size. The AS fraction obtained was then dried in a laboratory oven at 40°C for 24 h. Morphological, structural, thermal and water absorption properties of AS were studied.

2.2. PCL/AS biocomposites preparation

PCL/AS biocomposite dog-bone bars (150 x 20 x 4 mm) were processed in a twin-screw extruder (DUPRA D30, Castalla, Alicante). Before processing, PCL was dried at 50 °C for 20 h to eliminate moisture. A 88-127 °C temperature profile, a screw speed of 80 rpm and a residence time of 2.5 min were used [20]. After mixing, tensile dog-bone bars (ISO 527-2/1A) [18] were prepared by using a Meteor 270/75 injection moulding machine (Mateu & Solé, Barcelona, Spain). The cooling time was 35–45 s, the maximum injection pressure was 14,000 psi, and the mould temperature was 45 °C [20]. Four different formulations were obtained by adding different AS contents to PCL (0, 10, 20, 30 wt%). The obtained biocomposites were designed as PCL, PCL10, PCL20 and PCL30; where the number corresponds to the percentage of AS filler added by weight.

2.3. AS and PCL/AS biocomposites characterization

Field emission scanning electron microscopy (FESEM). A Supra 25-Zeiss microscope (Jena, Germany) with energy of 5kV was used to examine the surface morphology of AS. Twenty five measurements were performed and subsequently plotted in a histogram to offer a visual impression of dimension distribution ($n \pm SD$, $n=25$).

Scanning electronic microscopy (SEM). A JEOL JSM-840 scanning electron microscope (Peabody, MA, USA) under an acceleration voltage of 15 kV was used. Fracture surfaces from impact tests of PCL/AS biocomposites were registered at magnification 500X in order to study the AS dispersion into the PCL matrix. Composite samples were coated with gold under vacuum using a SCD 004 Balzers sputter coater

(Bal Tec. AG, Furstentum, Lichtenstein) prior to scanning in order to increase their electrical conductivity.

Attenuated total reflectance infrared spectroscopy (ATR-FTIR). A Bruker Analytik IFS 66 FTIR spectrometer (Ettlingen, Germany) equipped with a DTGS KBr detector and Golden Gate single reflection diamond ATR accessory (incident angle of 45°) was used. AS powder (2.00 ± 0.01 mg) was directly placed on the ATR crystal area for measurements. Spectra were recorded in the absorbance mode from 4000-600 cm^{-1} , using 64 scans and 4 cm^{-1} resolution, and corrected against the background spectrum of air. Two spectra replicates were obtained for each sample.

Mechanical properties. Before testing, all biocomposite samples were equilibrated for 48 h at 23 °C and 50 % RH. Mechanical properties were determined at room temperature in terms of tensile, impact and shore D hardness tests. Tensile tests were carried out using an Ibertest ELIB 30 universal testing machine (S.A.E. Ibertest, Madrid, Spain) equipped with a 5 kN load cell. An initial grip separation of 100 mm and a crosshead speed of 50 mm min^{-1} were used. Tensile strength, elongation at break and elastic modulus were determined following the ISO 527 standard [21-22]. Five replicates were performed for each formulation and mean values were reported.

Impact tests were carried out with a Charpy type pendulum (6 J, Metrotec S.A., San Sebastián, Spain) following the ISO 179 standard [23]. Shore D hardness of biocomposites was determined using a JBA 673-D durometer (Instruments J.Bolt S.A., Barcelona, Spain), following the UNE-EN ISO 868:2003 standard [24]. Five different specimens (80 mm x 10 mm x 4 mm) were tested for the different standardized tests and average values of the corresponding property were calculated.

Thermal properties. Differential scanning calorimetry (DSC) tests of PCL/AS biocomposites were conducted, in triplicate, by using a TA DSC Q-2000 instrument

(New Castle, DE, USA) under N₂ atmosphere (50 mL min⁻¹). Composite samples (3 mg) were introduced in aluminium pans (40 µL) and were submitted to the following thermal program: -80 °C to 160 °C (3 min hold), cooling to -80 °C (3 min hold) and heating to 160 °C, all steps at 10 °C min⁻¹. Crystallization and melting parameters were determined from the second heating scan. The degree of crystallinity (χ_c) at room temperature was calculated as:

$$\chi_c = \frac{\Delta H_m}{w * \Delta H_m^0} * 100 \quad (1)$$

where ΔH_m is the experimental melting enthalpy of the sample, w is the PCL weight fraction in the biocomposite and ΔH_m^0 is the melting enthalpy of 100 % crystalline PCL (136 J g⁻¹) [2].

Thermogravimetric analysis (TGA) of AS and PCL/AS biocomposites were performed in a TGA/SDTA 851 Mettler Toledo (Schwarzenbach, Switzerland) thermal analyser. Samples (4 mg) were heated from 30 to 700 °C at 10 °C min⁻¹ under N₂ atmosphere (50 mL min⁻¹). Analyses were performed in triplicate. The following parameters were extracted from TG/DTG curves: initial degradation temperature (T_{ini}), calculated at 5 % of weight loss and temperature of maximum decomposition rate (T_{max}). For AS, the final programmed temperature was 1000 °C in order to determine also the residue content (wt%) estimated at the end of the temperature program.

Water Uptake. Water absorption of AS and PCL/AS biocomposites was determined, in triplicate, according to UNE-EN ISO 62:2008 standard [25]. AS (0.04 ± 0.01 g) and biocomposite (8 cm length x 1 cm width x 4 mm thick) samples were dried in a vacuum oven at 23 °C for 4 h, cooled in a desiccator, and then immediately weighed to the nearest 0.001 g. Then, samples were immersed in distilled water and maintained at 23 °C and 50 % RH. Samples were taken out at different times, wiped out properly and then reweighed. Water absorption (WA) was calculated as follows:

$$WA = \frac{W_t - W_0}{W_t} * 100 \quad (2)$$

where W_0 was the sample weight prior to water adsorption experiment and W_t was the final mass at the pre-determined time t .

2.4. Enzymatic degradation of PCL/AS biocomposites

The enzymatic degradation of biocomposites was carried out in 5 mL phosphate buffer saline solution (0.05 M, pH = 7, 37.0 ± 0.5 °C) in the presence of 1.0 mg *Pseudomonas lipase* and 0.02 % of sodium azide as anti-mildew and antibacterial agent to avoid bacterial proliferation [26-27]. The buffer-enzymatic solution was changed every 24 h to maintain the enzymatic activity. Specimens (10 x 4 x 1 mm) were placed in tubes filled with the degradation medium, in triplicate. A PCL control was also analysed by using only buffer solution without the presence of the enzyme. Samples were taken out of the solution at predetermined time intervals (0, 1, 2, 3, 7, 13, 17, 25 days), then washed with distilled water to remove the lipase, gently wiped with paper, and vacuum-dried at room temperature to constant weight. The degradation process was followed by determining the water adsorption and mass loss of the materials. Changes in the surface structure of degraded samples were evaluated from FESEM images. For this purpose, Cryo-surface sections of degraded biocomposites were gold-sputtered before scanning. Finally, thermal parameters by DSC and TGA were also determined by using experimental conditions previously described.

2.5. Statistical analysis

Statistical analysis of experimental data was performed with SPSS commercial software (Version 15.0, Chicago, IL). A one-way analysis of variance (ANOVA) was carried out.

Differences between means were assessed on the basis of confidence intervals using the Tukey test at a confidence level of 95 % ($p < 0.05$).

3. Results and discussion

3.1. Morphological study of AS by FESEM

AS powder, ASP, (Fig. 1b) was obtained from AS industrial by-product (Fig. 1a) after milling and sieving. The morphological characterization of ASP particles was studied by FESEM. Fig. 1c shows the FESEM micrograph obtained for ASP surface at 300 X. A heterogeneous fibrous microstructure was observed with different morphologies and dimensions, due to the organization of different compounds present into the matrix. According to the literature, AS contains 21.90 ± 1.12 % cellulose, 12.19 ± 0.60 % hemicellulose, 10.01 ± 0.63 % lignin, 3.33 ± 0.15 % pectin and 0.225 ± 0.017 % gums and mucilages, among other compounds [28-29].

Fig. 1.

The distribution of ASP diameters are shown in Fig. 2. Dimensions ranging from 26 to 65 μm in width, with an average of 43 ± 12 μm , were observed with a Gaussian frequency distribution. On the other hand, dimensions ranging from 73 to 157 μm in length, with an average of 107 ± 31 μm , were obtained probably due to the heterogeneous structure of the ASP. These dimensions are in agreement with previous works regarding the use of natural residues as reinforcing agents in polymer composites, such as okra fibres, with a diameter distribution ranging from 40 to 180 μm and average diameter of 88 μm [28]; and curaua fibres with diameters ranging from 20 to 130 μm and average value of 60 μm [30].

Fig 2.

3.2. Structural characterization of ASP by ATR-FTIR

Fig. 3 shows the ATR-FTIR spectrum obtained for ASP. Similar bands were reported for almond shell samples [17] and different natural fibres [31], corresponding to specific functional groups characteristic of lignocellulosic raw materials. Table 1 shows the average of the main significant bands identified which were related to characteristic components present in the sample, according to the reported information of different authors [28,30,32].

Fig 3.

Table 1.

3.3. Thermal stability of ASP by TGA

Fig. 4 shows the TGA curves obtained for ASP at $10\text{ }^{\circ}\text{C min}^{-1}$ after drying at $40\text{ }^{\circ}\text{C}$ for 24 h. As it can be seen, an initial step related to water loss was not visible after ASP drying since no degradation was observed around $100\text{ }^{\circ}\text{C}$ [28]. Three different decomposition stages were observed in the temperature range of $200\text{--}600\text{ }^{\circ}\text{C}$, which were attributed to the thermal degradation of different compounds present in the sample. A similar DTG profile was observed by Essabir et al. when studying the thermal stability of almond shell particles used as reinforcement in polypropylene matrices [17]. The first peak observed at $263 \pm 2\text{ }^{\circ}\text{C}$ was attributed to the thermal depolymerisation of hemicelluloses and pectin, and the glycosidic linkages of cellulose. The main degradation step (peak II) with T_{max} at $330 \pm 5\text{ }^{\circ}\text{C}$ was related to the degradation of cellulose. Finally, the third peak was related to the oxidative degradation of lignin at $401 \pm 3\text{ }^{\circ}\text{C}$. In addition, a remaining non-volatile residue was observed at $1000\text{ }^{\circ}\text{C}$ (around 20 %) which was associated to the fibre content present in the tegument; which is composed of polysaccharides such as pectin and arabinose, and microfibrils of

cellulose [18], that are not thermally degraded. Also, the degradation of lignin occurs slowly in the temperature range due to its complex structure of aromatic rings with various branches organized in a three-dimensional structure, which serves as the matrix materials along with hemicellulose to embed cellulose fibres [33-34]. These results are in agreement with those reported in the literature for okra [28], curaua [30] and arundo [32] natural fibres.

Fig 4.

3.4. Water absorption of ASP

Water absorption (WA) values obtained for ASP increased with time obtaining values of 182 ± 22 , 246 ± 50 , 270 ± 25 and 272 ± 26 % at 24, 30, 36 and 60 h, respectively; at controlled conditions of humidity and temperature (50 % RH at 23 °C). After 36 h, ASP absorbed the water present in the medium at a constant rate, being this absorption rate higher around the first 30 h. Hemicellulose is mainly responsible for moisture absorption; but cellulose and lignin also contribute to this process. The obtained results are in agreement with those reported for lignocellulosic curaua fibres by Spinacé et al. obtaining a highest water absorption rate for the first 25 h [30]. According to these authors, moisture swells the cell wall and the fibre swells until the cell wall is saturated with water. Beyond this point, moisture exists as free water in the void spaces of the fibre.

3.5. Mechanical characterization of PCL/AS biocomposites

The results obtained for tensile, impact and hardness tests for the studied PCL/AS biocomposites are shown in Table 2. Regarding tensile properties, a significant improvement in Young's modulus was observed with the addition of AS particles and

increasing loading. In fact, the highest modulus value was observed at 30 wt% AS loading (462 ± 30 MPa) compared to neat PCL (267 ± 12 MPa). The increase in Young's modulus can be attributed to a good ASP/matrix adhesion allowing a high homogeneity [26]. Also, this fact could be a result of the AS residue exerting a resistance against the plastic deformation of the PCL matrix, which in turn restricts polymer chain elongation with an increase in the rigidity of the material because the mobility in the amorphous region becomes increasingly restrained, as the filler is stiffer than the thermoplastic [10, 27, 35].

No significant differences were observed in tensile strength values among the studied samples. Some authors have observed a decrease in tensile strength for different biocomposites which was attributed to weak interfacial adhesion between the filler and the plastic matrix [35], and to the agglomeration of filler particles [36]. Regarding elongation at break, neat PCL and PCL10 samples did not break during tensile testing. On the other hand, a significant reduction (about 97 %) in elongation at break was observed for PCL 30 compared to PCL 20. These results are in good agreement with those obtained when studying green PP composites obtained by twin screw extrusion using turmeric spent as reinforcing filler [37]. In the present study, the obtained PCL-based biocomposites clearly showed an increase in tensile modulus and a reduced elongation at break which are typical results for the reinforcement of the polymer matrix [38].

In addition to tensile mechanical behaviour, the Charpy impact energy and the Shore D hardness of the studied biocomposites were also determined (Table 1). The ability of composites to absorb energy in impact conditions is directly related to the presence of a continuous matrix which allows deformations and subsequently, energy absorption. Full embedment of filler reinforcements is required for optimum performance versus impact

[39]. The energy absorption during impact tests can be directly related to the deformation capacity of the sample. In this sense, the impact energy of the biocomposites decreased with increasing AS content. As it can be seen in Table 2, PCL did not break during Charpy testing, whereas PCL10 showed the highest energy value, followed by PCL20 and PCL30 (decreasing by 60 % compared to PCL10). The incorporation of the ASP into the composite creates regions of stress concentration, due to the high aspect ratio of AS particles, that require less energy to initiate a crack in the composite [2,35]. In general, as higher modulus was obtained less energy during impact testing was shown. Also, the harder the material (Shore D hardness), the lower energy will be able to absorb the polymer in an impact event (Table 2). Then, the AS residue reduces the polymer chain mobility and therefore its ability to absorb energy during fracture propagation [36]. The obtained results are in accordance with previous works in which different natural fibres such as wood [15], *Luffa cylindrica* cellulose nanocrystals [40] or chitosan [41] have been used as a reinforcement using PCL as matrix.

Table 2.

3.6. Morphological characterization of PCL/AS biocomposites

An analysis of the fractured surfaces from impact tests can be useful to support previous results obtained from Charpy impact energy and overall mechanical performance of the studied biocomposites; as well as to deeply study the interaction between ASP and PCL matrix (Fig. 5). As it has been previously discussed, the obtained formulations reinforced with AS particles showed increased resistance. This fact could be related to an increase in density, being interactions considerably stronger as AS content increased. In this sense, for PCL with 30 wt% AS loading (fig. 5d) some gaps and agglomerates between the reinforcement phase and the matrix could be detected. As a result, as the

AS portion in the composite increased, the capability of the polymer to form a continuous phase decreased. This may create regions in the composite where less energy is required to initiate a crack, in accordance with the results obtained from impact tests [42]. However, a good adhesion between AS and PCL matrix was achieved even at high AS loadings which results in a positive effect on tensile properties; as it was observed from Young's modulus results which increased with the AS content present in the matrix. As previous authors underlined, this fact could be directly related to interface phenomena among AS/matrix with a positive effect on maximum flexural stress making the pieces stronger [27]. This fact could be attributed to the high hydrophilicity of the AS and also to the incremented ASP exposed surface area that promotes the formation of hydrogen bonds between the individual hydrophilic residue [2].

Fig. 5.

3.7. Thermal characterization of PCL/AS biocomposites

The DSC results obtained for the studied biocomposites are shown in Table 3. Similar DSC curves were obtained for all the tested samples (data not shown). A significant decrease in melting and crystallization enthalpy values (ΔH_m and ΔH_c , respectively) was obtained with increasing AS content. The addition of ASP decreased the crystallization enthalpy due to the presence of a lower PCL quantity in the biocomposites, resulting in a lower capacity to organize into a crystalline structure. As a consequence, a lower heat is necessary to melt the polymer matrix, which allows a reduction in the melting enthalpy as the ASP content increased. Similar results were obtained by Ayrimis and Kaymakci when studying wood flour filled polypropylene composites. These authors indicated that this behaviour could be due to filler absorbing more heat energy in

melting of the composites as the ΔH_m of the filler is much lower than that of the neat polymer [35].

The melting enthalpy of the sample is directly related to the degree of crystallinity (χ_c) and inversely proportional to the PCL weight fraction in the biocomposite, as it is shown in equation 1. As a result, the crystallinity of the biocomposites significantly increased with the addition of the ASP content. The degree of crystallinity (X_c) of a material is an indicator of its stiffness, and the higher its crystallinity is, the higher its stiffness [10]. X_c is generally affected by the dispersion, the loading level, and the surface chemistry of the filler [35]. Crystallinity also influences the mechanical properties of thermoplastics. In this sense, the observed improvement in the tensile modulus of AS filled PCL composites can be attributed to the obtained increase in crystallinity. Different works related with the characterization of biocomposites can be found which are based on this premise [35]. Also, it is accepted that cellulosic fillers can act as nucleating sites for the crystallization of the polymer or restrict the mobility of the polymer chains [43].

On the other hand, no significant differences were obtained for crystallization and melting temperatures (T_c and T_m , respectively) among the studied samples. Regarding glass transition temperature (T_g) values, a slightly increase was observed with the addition of the AS filler. This shows that the presence of the residue could restrict the segmental motion of the polymer chains through the establishment of hydrogen bonding forces [43]. Similar observations were reported for PCL reinforced with cellulose nanocrystals [40].

Table 3.

TGA was performed to evaluate the thermal stability of the obtained biocomposites. Only one degradation step was observed for the neat polymer and the biocomposites

(data not shown). Some decrease in thermal stability was observed for biocomposites with the addition of the AS filler regarding T_{ini} and T_{max} values (Table 3). This behaviour was more evident for T_{ini} values where a significant decrease was observed with increasing AS content compared to neat PCL. In this sense, a reduction of 26 % in T_{ini} was shown at 30 wt% AS loading. The reduction of the overall thermal stability of the resulting material with the addition of AS particles to the polymer matrix could be explained by the high shear and frictional forces experienced by the composites during the extrusion process, which produce a split in the polymer chain resulting in a decrease in thermal stability of the composite [17]. It is interesting to note that the T_{ini} values obtained for the biocomposites were higher than that obtained for the ASP (174 ± 3 °C). So, we can assume that the thermal stability of the AS filler was maintained in these formulations with no apparent degradation of the AS residue. Finally, as it was expected, the final inorganic residue obtained at 1000 °C at the end of the thermal program increased with AS content. This behaviour was related to the high content of non-volatile residue present in AS as it was previously mentioned [18].

3.8. Water uptake of PCL/AS biocomposites

Water absorption (WA) behaviour of PCL/AS biocomposites as a function of immersion time is shown in Fig. 6. As ASP loading increased higher WA values were obtained, particularly for 30 wt% after long-term water immersion. According to different authors, this fact may be related to the hydrophilic character of the ASP [44] and the formation of microvoids in the residue–matrix interface, as it was observed in SEM images, that enhances the water absorption through the matrix [45]. Finally, for biocomposites with higher AS content, more AS particles are supposed to be on the surface or located at the edge of the sample; being these AS particles more accessible

for moisture uptake [35]. The obtained results are in good agreement with a previous study in which cellulose and hydrolysed cellulose fillers from cotton were incorporated into PCL [2].

Fig. 6.

3.9. Enzymatic degradation of PCL/AS biocomposites

The biodegradation of aliphatic polyesters in the presence of enzymes is a topic of growing interest for the potential application of the materials in future. In these tests, enzymatic activity is optimized to a particular microorganism and, frequently, they present more elevated degradation rate than the ones observed in natural conditions. This is considered as an advantage to the study of basic mechanism of polymer biodegradation [46]. The surface erosion and the bulk degradation of polymer samples depend on the relation between the rate of water/enzyme diffusion into the polymer, the rate of chain cleavage by water ions/enzymes, and the rate of transportation of scission products out of the solid [47]. The enzymatic degradation of plastics by hydrolysis is a two-step process: first, the enzyme binds to the polymer substrate then subsequently catalyses a hydrolytic cleavage. Polymers are degraded into low molecular weight oligomers, dimers and monomers and finally mineralized to CO₂ and H₂O. PCL can be degraded by lipases and esterases. The degradation rate of PCL is dependent on its morphology, molecular weight and degree of crystallinity, since enzymes mainly attack the amorphous domains of a polymer [47-48].

The mass loss of a material due to the enzymatic degradation process may serve as a measure of the degradation degree. Figure 7a shows the weight loss profiles of neat PCL and biocomposites as a function of time during enzymatic degradation with *Pseudomonas lipase*. As it was expected, a linear increase of weight loss with

degradation time was observed for all samples. As it can be seen from Fig. 7a, at the first stage, the rate of enzymatic degradation was slow for all samples, because there was an incubation period for the enzyme. However, a higher degradation rate was observed for samples with higher content of PCL, suggesting that AS did not significantly enzymatic degrade under these test conditions. As a result, the enzymatic degradation of PCL was retarded in the presence of AS. In fact, a significant higher weight loss was found for neat PCL ($62 \pm 8 \%$) compared to the biocomposites (around 50 %) after 25 days of degradation. A similar weight loss for PCL was obtained by Liu et al. in the presence of this enzyme, confirming that the hydrolysis of PCL is catalysed by *Pseudomonas lipase* which can degrade both amorphous and crystalline PCL [6]. On the other hand, the PCL blank sample placed in the buffer solution without the presence of the enzyme did not show significant changes in weight loss, suggesting that no significant hydrolytic degradation occurs over the studied time range used for the enzymatic degradation study. As a result, the addition of ASP provides a strategy to alter the degradation profile of PCL-based composites.

The rate of hydrolytic degradation of ester linkages is affected by different factors; such as water absorption (WA). In general, actions which increase the penetration of water accelerate the rate of hydrolysis. Two other important factors are the polymer's glass transition temperature (T_g) and crystallinity, both of which reflect the ability of water to access the polymer chains [49]. In this work, higher WA values were obtained with increasing AS content (Fig. 7b), showing a similar trend to that obtained for non-degraded samples. According to Kodama, *Pseudomonas lipase* is able to break esters linkages in hydrophobic substrates, as it is the case of PCL. Also, it was described that PCL did not absorb water [45]. In fact, an insignificant amount of water was absorbed for neat PCL despite its weight loss in this work. In this sense, WA largely depends on

the hygroscopic components present in the biocomposite material; so, if the polymeric matrix is hydrophobic, as PCL, it may act as a semi-permeable membrane [50].

Fig. 7.

DSC thermal parameters obtained for samples at different degradation times are shown in Table 4 and Fig. 8. As it can be seen, in general, no significant differences were obtained for crystallization and melting parameters, including T_g and X_c values, with degradation time for neat PCL; suggesting that thermal properties did not affect enzymatic hydrolysis rate of PCL in the biocomposites as they did not altered during the process. Regarding biocomposites, higher crystallization and melting enthalpies (Table 4), and T_g and X_c values (Fig. 8a and 8b, respectively) were obtained during hydrolysis at 25 days compared to neat PCL. A high T_g corresponds to relatively limited molecular motion and low free volume within the polymer network, meaning that less space is available for water molecules to penetrate. Similarly, a high degree of crystallinity limits hydration through the ordered packing of polymer chains [49]. Also, it is a well-known phenomenon that the amorphous regions are more susceptible to hydrolysis, leading to increasing crystallinity during degradation of semi-crystalline polyesters. The shorter chains formed during degradation also have higher mobility, allowing for reorientation of the crystalline phase, which increases crystallinity. The obtained DSC results are in good agreement with previous weight loss profiles where a lower rate of hydrolysis was observed for biocomposites compared to neat PCL which showed a higher weight loss at 25 days of study.

Fig. 8.

TGA results (Table 4) showed that the enzymatic degradation did not affect the thermal stability of neat PCL since no significant differences were observed in T_{max} and T_{ini} during degradation time. Regarding biocomposites, a general decrease in T_{ini} values

were observed for each formulation with degradation time; being more significant for PCL with 20 and 30 wt% of AS after 25 days of degradation.

Table 4.

Finally, the surface morphology of neat PCL and PCL/AS biocomposites before and after enzymatic degradation for different times was studied by FESEM. The obtained results are shown in Fig. 9. As it can be seen, the surface of neat PCL was very smooth before degradation compared with that of biocomposites. After 7 days of degradation, a clear surface erosion with the appearance of different holes on neat PCL and all biocomposites was observed by the function of lipase, in particular at higher AS loadings. In this sense, higher AS particles were observed in biocomposites with increasing time, being more noticeable for PCL20 and PCL30 samples. This fact could be explained by the chain mobility and water absorption observed with time which enhances the polymer erosion.

Fig. 9.

Enzymatic degradation has been reported to occur only on the surface of a solid substrate by surface erosion and weight loss, because enzymes cannot penetrate a solid polymeric substrate. Enzymes degrade selectively amorphous regions or less ordered that allow them to diffuse through substrate and, subsequently, crystalline regions are eventually degraded. In this process, molar weight and molar weight distribution of non-degraded solid substrate do not change during enzymatic degradation because only the polymer on the surface of substrate is degraded and products of low molar weight from degradation are removed of substrate by solubilisation on the surrounding aqueous medium [45].

4. Conclusions

Biodegradable composites based on poly(ϵ -caprolactone) (PCL) and almond skin (AS) by-product were successfully produced by an extrusion followed by injection-moulding method. The addition of AS particles to PCL resulted in biocomposites with improved mechanical properties compared to neat PCL, showing a reinforcement effect. The best general performance was obtained for PCL10 showing an improved value for Young's modulus compared to neat PCL, but maintaining tensile strength and elongation at break values. Moreover, PCL10 showed higher hardness compared to the neat matrix, but without a remarkable increase in brittleness as it was observed for the rest of biocomposites with higher AS loading (PCL20 and PCL30). The enzymatic degradation of PCL by *Pseudomonas lipase* was retarded in the presence of the AS filler, suggesting that AS particles did not significantly enzymatic degrade under the test conditions used. This effect could also be explained in terms of the increase in crystallinity obtained for the biocomposites during hydrolysis at 25 days compared to neat PCL. In conclusion, the biocomposite containing 10 wt% of AS loading showed the best performance regarding the studied properties; since better mechanical behaviour and lower differences regarding thermal and water absorption properties were obtained compared to neat PCL. As a result, this reinforced formulation will be more competitive than pure PCL materials in the marketplace, increasing also the added-value potential of almond agricultural wastes.

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Figure captions

Fig. 1. a) AS industrial by-product; b) AS powder obtained after milling and sieving; c) FESEM micrograph of AS powder at 300X.

Fig 2. Distributions of ASP width and length diameters ($n = 25 \pm \text{SD}$).

Fig 3. ATR-FTIR spectrum obtained for ASP.

Fig 4. Thermogravimetric profile (—) and DTG curve (—) of ASP at $10\text{ }^{\circ}\text{C min}^{-1}$ in nitrogen atmosphere (50 mL min^{-1}).

Fig. 5. SEM images (500 X) of fractured biocomposites from Charpy impact tests: (a) PCL; (b) PCL10; (c) PCL20; (d) PCL30.

Fig. 6. Water absorption curves obtained for PCL (—●—), PCL10 (—■—), PCL20 (—▲—) and PCL30 (—■—) biocomposites as a function of immersion time ($n = 3$; $23\text{ }^{\circ}\text{C}$, $50\text{ \% RH}$). Different letters over the same time indicate statistically significant different values ($p < 0.05$).

Fig. 7. Weight loss (a) and water absorption (b) profiles of neat PCL (—●—), PCL10 (—■—), PCL20 (—▲—) and PCL30 (—■—) biocomposites as a function of time during enzymatic degradation with *Pseudomonas lipase* at $37\text{ }^{\circ}\text{C}$. Different letters over the same time indicate statistically significant different values ($p < 0.05$).

Fig. 8. Glass transition temperature (T_g) (a) and crystallinity degree (X_c) (b) values of neat PCL (—●—), PCL10 (—■—), PCL20 (—▲—) and PCL30 (—■—) biocomposites as a function of time during enzymatic degradation with *Pseudomonas lipase* at $37\text{ }^{\circ}\text{C}$. Different letters over the same time indicate statistically significant different values ($p < 0.05$).

Fig. 9. FESEM images of neat PCL and PCL/AS biocomposites surface before and after enzymatic degradation for different times (5 kx).

Tables

Table 1. Main significant FTIR bands identified for ASP sample.

Table 2. Mechanical properties of neat PCL and PCL/AS biocomposites. Mean $\pm$ SD, n = 5. Different superscripts within the same row indicate statistically significant different values ($p < 0.05$).

Table 3. Thermal properties of neat PCL and PCL/AS biocomposites obtained by DSC and TGA. Mean $\pm$ SD, n = 3. Different superscripts within the same row indicate statistically significant different values ($p < 0.05$).

Table 4. DSC and TGA parameters obtained for biocomposite samples at 0, 7, 17 and 25 days of enzymatic degradation. Different superscripts within the same column indicate statistically significant different values ($p < 0.05$) for each formulation.

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Table 1.

Frequency (cm ⁻¹)	Structural group	ASP component
3329	O-H stretching vibration and hydrogen bond of hydroxyl groups	Cellulose, hemicellulose, and lignin
2924	C-H stretching vibrations from CH and CH ₂	Cellulose
2852	C-H stretching vibrations from CH and CH ₂	Hemicellulose
1747	C=O stretching vibration of carboxylic acid linkages or ester group	Lignin and hemicellulose
1649	C=O stretching vibration	Hemicellulose
1620	O-H hydroxyl groups stretching vibration	Remaining water
1450	CH ₂ symmetric bending	Cellulose
1369	C-H and C-O bending vibration of aromatic ring in polysaccharides	Polysaccharides
1244	C-O stretching vibration of acetyl group	Lignin and hemicellulose
1138; 1093	C-O-C stretching vibration of pyranose ring	Polysaccharides
1028	C-O stretching modes of hydroxyl and ether groups	Cellulose

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Table 2.

Mechanical property	PCL	PCL10	PCL20	PCL30
Young's modulus (MPa)	267 ± 12^a	367 ± 22^b	392 ± 18^c	462 ± 30^d
Tensile strength (MPa)	15 ± 1^a	14 ± 1^a	14 ± 2^a	13 ± 1^a
Elongation at break (%)	Didn't break ^a	Didn't break ^a	454 ± 37^b	11 ± 2^c
Charpy impact energy (J)	Didn't break ^a	0.73 ± 0.03^b	0.42 ± 0.01^c	0.28 ± 0.02^d
Shore D hardness	54 ± 1^a	57 ± 1^{ab}	59 ± 1^b	60 ± 1^b

Table 3.

Thermal property	PCL	PCL10	PCL20	PCL30
ΔH_m (J g ⁻¹)	59 ± 1 ^a	58 ± 1 ^a	55 ± 1 ^b	49 ± 3 ^c
T _m (° C)	55 ± 1 ^a	55 ± 1 ^a	54 ± 1 ^a	53 ± 1 ^a
ΔH_c (J g ⁻¹)	57 ± 1 ^a	53 ± 1 ^b	50 ± 1 ^c	42 ± 1 ^d
T _C (° C)	31 ± 1 ^a	31 ± 1 ^a	31 ± 1 ^a	32 ± 1 ^a
T _g (° C)	-61 ± 1 ^a	-57 ± 2 ^b	-57 ± 1 ^b	-56 ± 1 ^b
Cristallinity degree (%)	43 ± 1 ^a	48 ± 2 ^b	51 ± 2 ^b	51 ± 3 ^b
T _{max} (°C)	416 ± 1 ^a	413 ± 1 ^b	410 ± 1 ^b	410 ± 1 ^b
T _{ini} (°C)	378 ± 5 ^a	364 ± 2 ^b	328 ± 4 ^c	279 ± 14 ^d
Residue (%)	4 ± 1 ^a	5 ± 1 ^a	7 ± 1 ^a	22 ± 4 ^b

Table 4.

Sample	ΔH_c (J g⁻¹)	T_c (°C)	ΔH_m (J g⁻¹)	T_m (°C)	T_{ini} (°C)	T_{max} (°C)
PCL (0)	65 ± 4 ^a	30 ± 1 ^a	78 ± 9 ^a	55 ± 2 ^a	378 ± 5 ^a	416 ± 1 ^a
PCL (7)	68 ± 1 ^a	29 ± 2 ^a	67 ± 2 ^b	56 ± 1 ^a	350 ± 13 ^a	415 ± 1 ^a
PCL (17)	65 ± 6 ^a	28 ± 1 ^a	77 ± 8 ^{ab}	60 ± 1 ^b	382 ± 3 ^a	413 ± 2 ^a
PCL (25)	61 ± 1 ^a	31 ± 1 ^a	77 ± 2 ^a	55 ± 1 ^a	385 ± 1 ^a	414 ± 2 ^a
PCL10 (0)	65 ± 12 ^a	29 ± 2 ^a	80 ± 6 ^a	55 ± 1 ^a	364 ± 2 ^a	413 ± 1 ^a
PCL10 (7)	69 ± 1 ^{ab}	29 ± 2 ^a	78 ± 9 ^a	57 ± 1 ^a	294 ± 11 ^b	412 ± 1 ^a
PCL10 (17)	67 ± 2 ^{ab}	31 ± 1 ^a	76 ± 1 ^a	56 ± 1 ^a	339 ± 10 ^c	419 ± 5 ^a
PCL10 (25)	75 ± 4 ^b	31 ± 1 ^a	78 ± 8 ^a	56 ± 1 ^a	367 ± 1 ^a	415 ± 2 ^a
PCL20 (0)	65 ± 2 ^a	30 ± 1 ^a	78 ± 3 ^a	55 ± 1 ^a	328 ± 4 ^a	410 ± 1 ^a
PCL20 (7)	61 ± 4 ^a	30 ± 4 ^a	56 ± 1 ^a	56 ± 1 ^a	311 ± 9 ^b	409 ± 1 ^a
PCL20 (17)	66 ± 2 ^a	31 ± 1 ^a	79 ± 2 ^a	55 ± 2 ^a	296 ± 12 ^c	410 ± 2 ^a
PCL20 (25)	134 ± 1 ^b	31 ± 1 ^a	150 ± 11 ^b	55 ± 1 ^a	306 ± 1 ^b	411 ± 1 ^a
PCL30 (0)	56 ± 1 ^a	30 ± 9 ^a	68 ± 1 ^a	55 ± 1 ^a	279 ± 4 ^a	410 ± 1 ^a
PCL30 (7)	60 ± 1 ^a	30 ± 2 ^a	53 ± 1 ^a	56 ± 1 ^a	273 ± 4 ^a	410 ± 2 ^a
PCL30 (17)	59 ± 1 ^a	31 ± 4 ^a	64 ± 1 ^a	54 ± 1 ^a	284 ± 5 ^a	407 ± 2 ^a
PCL30 (25)	123 ± 1 ^b	32 ± 2 ^a	136 ± 1 ^b	55 ± 1 ^a	269 ± 1 ^b	410 ± 1 ^a

TOC Graphic