Tensile, Thermal and Morphological Characterization of Cocoa Bean Shells (CBS)/Polycaprolactone-Based Composites

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ABSTRACT: In this work, cocoa bean shells (CBS), which were ground, then sieved to less than 150 μm and dried in a vacuum oven, have been introduced in a polycaprolactone (PCL) matrix in three different amounts, 10, 20 and 30% wt. The obtained composites were tested under tensile loading, which indicated an enhanced rigidity with a slight decrease of strength with respect to the neat polymer and a reduced elongation, particularly evident for composites with 30 wt% CBS, where final collapse took place for strains only slightly exceeding the yielding point. Differential scanning calorimetry (DSC) indicated a rather negligible variation of melting temperature with respect to pure PCL, whilst thermogravimetric analysis (TGA) for CBS showed evident peaks for degradation of hemicellulose, pectin, then most clearly for cellulose at 313 °C and a final residue of 33.3% at 900 °C. Scanning electron microscopy images taken on the 30% wt. composite offered evidence of brittle fracture with appearance of irregular structures, related to the pull-out and fibrillation of cocoa shells.

KEYWORDS: Cocoa bean shells, polycaprolactone, composites

1 INTRODUCTION

The food processing industrial sector is a large and rapidly growing industry and plays an important role in economic development across the world [1]. Industrial production activities, however, have impacts on the natural environment through the entire cycle of raw materials exploration and extraction, transformation into products, and use and disposal of products by the final consumers. When considering the scope of food processing, the main (direct) impacts are water and energy consumption, causes of severe environmental deterioration in the world, in addition to waste generation, since most industrial activities necessarily generate wastes and/or byproducts. Within food processing, the largest producers of waste come from sectors such as milk, cocoa, brewing/distillation, and meat processing [2]. In the specific case of cocoa waste, it should be considered that most cocoa beans are used in the production of cocoa products, such as cocoa butter, cocoa powder, chocolate and chocolate-related products [3]. However, cocoa beans constitute only 10% of the fresh weight of the cocoa fruit: this means that only about 10% by weight of the cocoa fruit is commercialized, while 90% by weight (mainly cocoa pulp and cocoa pod husk) is discarded as cocoa waste [4]. Once the cocoa dried bean has been obtained, the coproducts that remain are composed mainly by three fractions: (i) cocoa pod husk, (ii) cocoa bean shells and (iii) cocoa mucilage. In most cases, these coproducts are underexploited and considered an undesirable "waste" of the cocoa/chocolate industry. Normally, they are left to rot on the cacao plantation, a practice that can cause environmental problems. In contrast, their composition would provide the potential for them to be used for other purposes, for example, to obtain bioactive compounds and dietary fiber which could be used as ingredient in food processing [5, 6]. Cocoa bean shell (CBS), the thin skin immediately surrounding the cocoa nib (edible portion), constituting at least 10% of the weight of the bean, is a waste product from the chocolate manufacturing industry. The shells are normally separated from the nib by roasting. The possible use of these shells as livestock feed has been mentioned by several works [7]. Gohl [8] observed that CBS is high in nutritive value, but of limited use

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in animal feeds because of its theobromine content: when taken in modest quantities, it acts as a stimulant like caffeine: on the other hand, intake of more than 0.0279 kg per body weight is injurious to animals [9]. Hutagalung and Chang [10] observed that the amino-acid profile of CBS compares favorably with palm kernel cake, suggesting that it could be utilized as a medium protein source to substitute grain protein in livestock diets. Cocoa beans shells also have relatively high potassium content and may be used to manufacture fertilizers or composts. When used as mulch, it contains approximately 2.5% nitrogen, 1% phosphate and 3% potash, as well as a natural gum that is activated when watered: many researchers have attempted to convert such coproducts into food ingredients and for use in other value-added applications [11]. Thus, the use of these coproducts for further exploitation as food additives or supplements of high nutritional value has gained increasing interest, especially in that these are high-value products and their recovery may be economically attractive [12, 13]. Theivarasu *et al.* [14, 15] also attempted to remove methylene blue from synthetic wastewater by adsorption process using a low cost activated carbon prepared from cocoa shell agro-waste as an adsorbent.

In this context, the use of CBS as filler for polymers would possibly be considered: some works are available in the literature, which have proposed the introduction of waste from cocoa production (especially cocoa pod husks) in different polymer matrices [16–20]. The comparative introduction of different agrofillers (oat husks, cocoa shells and apple residual solids from juice pressing) in poly(lactic acid) (PLA) indicated that, in addition to the mechanical effect, all fillers promoted PLA crystallization, decreasing cold crystallization temperature [21]. In addition, it needs to be considered that CBS represents a type of nut shell, which as a general category has received some attention for its introduction into composites with variable success [22, 23].

The specific interest of the present work lies particularly in the use of a biodegradable matrix, polycaprolactone (PCL), which has a low melting temperature, in the region of 60 °C, and therefore is very suitable for easy processing. On the other hand, PCL has demonstrated effective potential in extrusion with lignin-containing material [24], therefore its use might also be suggested for compounding with CBS. In this work, the introduction of up to 30 wt% of CBS in a PCL matrix is proposed and morphological, thermal and tensile characterization is carried out to investigate the possible use of CBS in biodegradable and compostable composites.

2 MATERIALS AND METHODS

Polycaprolactone Capa™ 6500 (Mn = 50000 g/mol, Tm = 58–60 °C, MFI (2.16 kg/160 °C) = 7.90 g/10 min), supplied by Perstorp, was used as matrix. Cocoa bean shells (Lindt & Sprüngli) were ground and sieved to a particle size fraction of less than 150 µm and were dried at 98 °C in a vacuum oven for 24 h prior to the preparation of the composites.

Composites were produced with three different amounts of cocoa bean shells, 10, 20 and 30% wt. The production was carried out by using a twin-screw microextruder (DSM Xplore 5&15 CC Micro Compounder) and the following process parameters (screw rotation speed 60 rpm, mixing time 3 min and temperature profile 60–75–90 °C) have been applied with the aim to optimize the final properties of the material. To obtain samples for characterization, an injection molding system DSM Xplore 10-mL has been used (mold temperature = 25 °C, injection pressure = 9 bars, injection temperature = 100 °C) and dog-bone specimens have been produced according to ISO 527-2/1BA standard. Tensile tests have been carried out on a Lloyd Instrument LR30K, using a crosshead speed of 5 mm/min. The measurements were performed at room temperature and at least five samples were tested, expressing the results as mean value and standard deviation. Thermogravimetric measurements have been carried out using a thermobalance Seiko Exstar 6300: tests have been carried out from 30 to 900 °C at a heating rate of 10 °C/min in nitrogen atmosphere.

DSC (TA Instrument, Q200) measurements were performed in the temperature range from –25 to 100 °C at 10 °C/min under nitrogen flow; samples were heated from –25 to 100 °C at 10 °C/min; after that an isothermal step was also considered (100 °C for 2 min) to erase the thermal history (1st scan), then they were cooled to –25 at 10 °C/min and reheated under the same conditions (2nd scan). Peak temperatures for melting and crystallization were evaluated and the degree of cristallinity of the sample was calculated taking as reference 139.5 J/g [25] as melting heat of the fully crystalline PCL sample. The shell's microstructure and the morphology of composites fractured surfaces were investigated by field emission scanning electron microscopy (FESEM, Supra 25-Zeiss, Germany). All specimens were sputter coated with gold prior to examination.

3 RESULTS AND DISCUSSION

Different structures have been observed by scanning electron microscopy on cocoa bean shells surface (Figure 1). Thin-walled parenchyma cells and large amounts of vascular tissue were observed to be

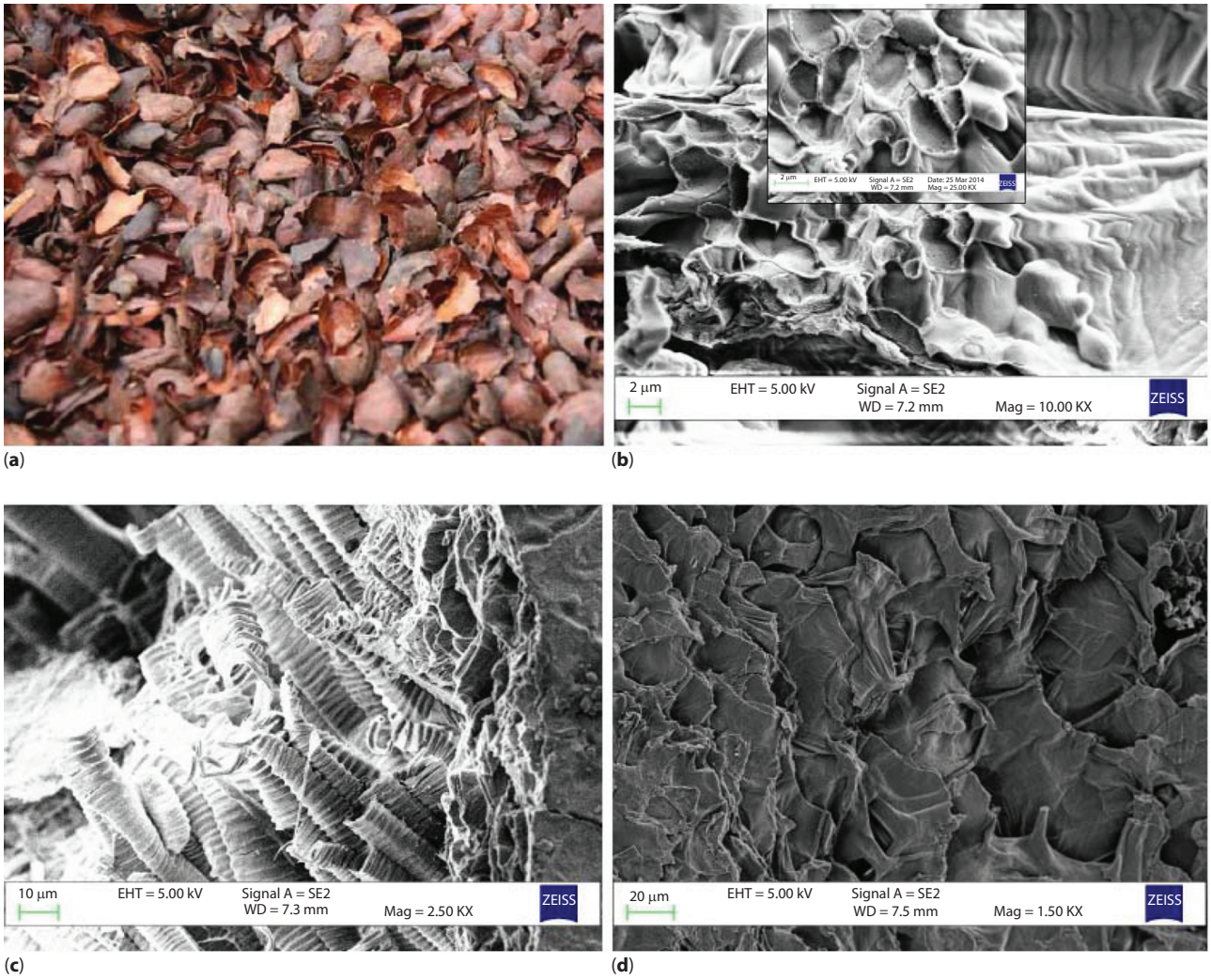

Figure 1 Visual appearance of roasted beans shells (**a**) and FESEM images of different morphologies detected in ground cocoa bean shells (granular structures with inset (**b**), parenchyma cells (**c**), and cuticular layer (**d**)).

composed of tracheary elements with helical secondary thickenings [26]. The parenchyma cells contain cocoa butter, aleurone grains, and starch granules. It appeared that fat within the parenchyma cells existed in a globular form, so the internal structure of the cotyledon parenchyma had a "honeycomb" appearance due to the presence of fat globules embedded within the cell matrix. A continuous structure is also visible as a section of cuticular layer, which usually imparts water impermeability to seed coats [27].

Results from thermogravimetric analysis carried out on micronized cocoa shells (Figure 2a) evidenced five weight loss peaks, located at 58, 161, 215, 260 and 313 °C, respectively (Figure 2b). The first peak corresponds to the evaporation of moisture and water linked with the structure, which takes place till around 100 °C and corresponds to a weight loss of about 7–8%. The three subsequent peaks (161, 215 and 260 °C) can be referred to the degradation of pectin and hemicellulose, while the final peak at 313 °C corresponds to the degradation of cellulose. The test has been carried out up to 900 °C in nitrogen atmosphere and the remaining mass at the end corresponded to the 33.3% of initial weight, which represents the residue, formed by ashes, of the material. As a whole, the holocellulose, formed by cellulose, hemicellulose and pectin, constitutes over 60% of the material. These peaks match closely with what was described by Du *et al.* [28] and Pereira *et al.* [29].

Comparing the amount of holocellulose with that of other lignin-based shells, in walnut shells this is lower, being around 48% [30]. In contrast, this is around 64% for almond shells [31] and 68% for peanut hulls [32]: these sources of biomass have been selected for their structural similarity with CBS so as to allow for comparison among mechanical properties of the composites obtained.

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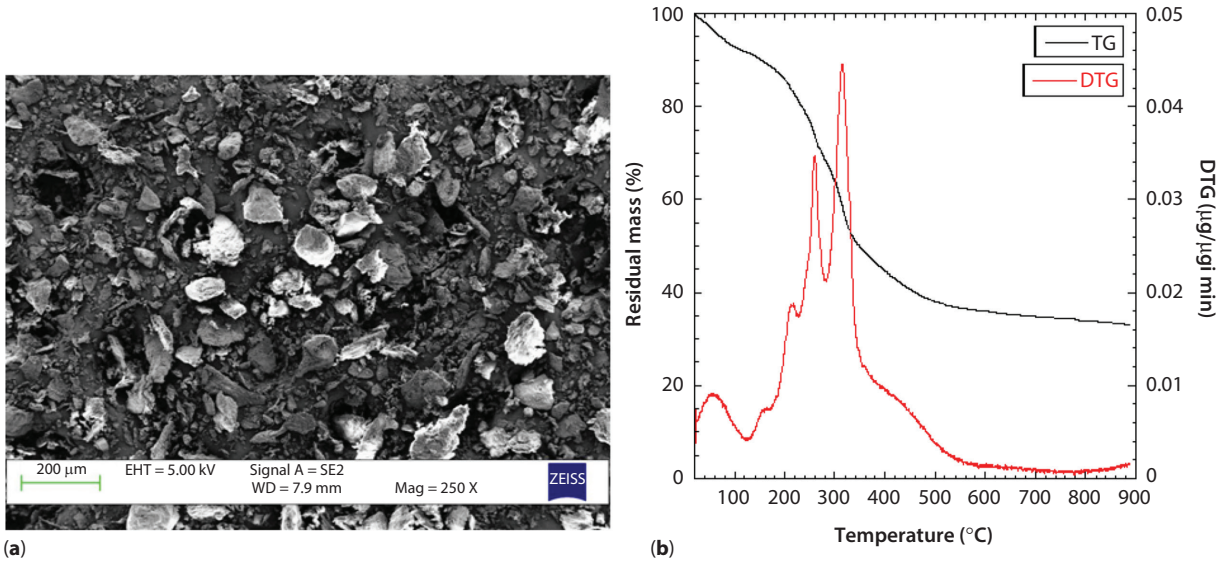

Figure 2 FESEM image (**a**) and results of thermogravimetric analysis (**b**) of ground cocoa bean shells.

Table 1 Results of tensile tests for PCL/CBS composites at different weight percent (E, Young's Modulus; σ_y, yield strength; ε_y, strain at yield; σ_b, strength at break; ε_b, strain at break).

	PCL	PCL10CBS	PCL20CBS	PCL30CBS
E (MPa)	439 ± 16	528 ± 43	652 ± 4	740 ± 14
σ_y (MPa)	16.1 ± 0.9	15.5 ± 0.6	14.5 ± 0.1	14.8 ± 0.5
ε_y (%)	8.9 ± 0.3	7.6 ± 0.9	5.4 ± 0.2	3.9 ± 0.3
σ_b (MPa)	30.2 ± 1	27.9 ± 0.9	18.2 ± 1.4	5.4 ± 1.2
ε_b (%)	672 ± 23	656 ± 48.2	388 ± 40.3	16 ± 4.2

The results of tensile tests are reported in Table 1 and Figure 3a: for PCL composites with up to 30 wt% of CBS (PCL30CBS), a slight decrease of tensile strength was observed, with an average value of 16.1 ± 0.9 MPa for neat PCL to 14.8 ± 0.5 MPa for PCL30CBS. The non-uniform distribution of CBS particles in the microstructure of the composite is the major factor responsible for the decrease in strength, when compared with the control sample having 0% wt. of CBS. Another factor could nevertheless be related to the differences in polarities between the polar agro-waste filler and nonpolar PCL matrix, which could initiate and propagate sites for failures.

Young's modulus of the CBS-based composites increased with increasing content of filler with respect to neat PCL (439 ± 1 MPa). The presence of fillers hindered the polymer chain mobility of PCL matrix; moreover, the rigidity of the composite could also be linked to the cellulose contents of the cocoa shells. The Young's modulus increase with filler content was in agreement with other reported works [33].

Quite obviously, the introduction of the filler does reduce elongation of the polymer, however, the brittle failure with ultimate strain around 15–20%, which was measured for the introduction of 10 or 20% wt. of CBS in the polymer, has no practical consequences. Brittle fracture is also particularly evident for the surface fracture observed under SEM for 30% wt. of CBS (Figure 3b), where, however, particularly irregular structures appear, in which the pull-out and the fibrillation of cocoa shells is observable. To allow for comparison with other similar situations, the use of MAPP enabled the introduction of up to 60 wt% of walnut shell flour ground at a size retained on an 80 mesh sieve. It was found that, despite the sufficient interfacial adhesion obtained, decrease in tensile and flexural strength with higher fiber content was significant, while stiffness consistently increased: the best compromise was found with 40 wt% of filler using 3 wt% of maleic anhydride [34]. In another case, the use of argan nut shell particles up to 40 wt% in an HDPE matrix equally resorted in an increase of stiffness by 58% [35].

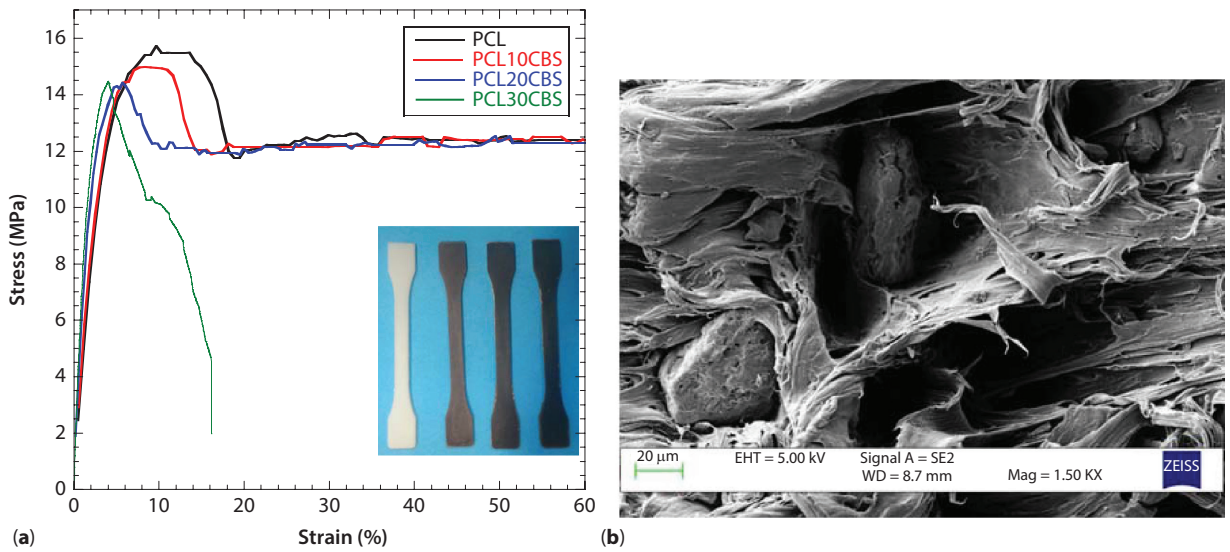

Figure 3 Results of tensile test for PCL/CBS composites (samples in the inset) (**a**) and FESEM image of the tensile fractured surface of PCL30CBS composite (**b**).

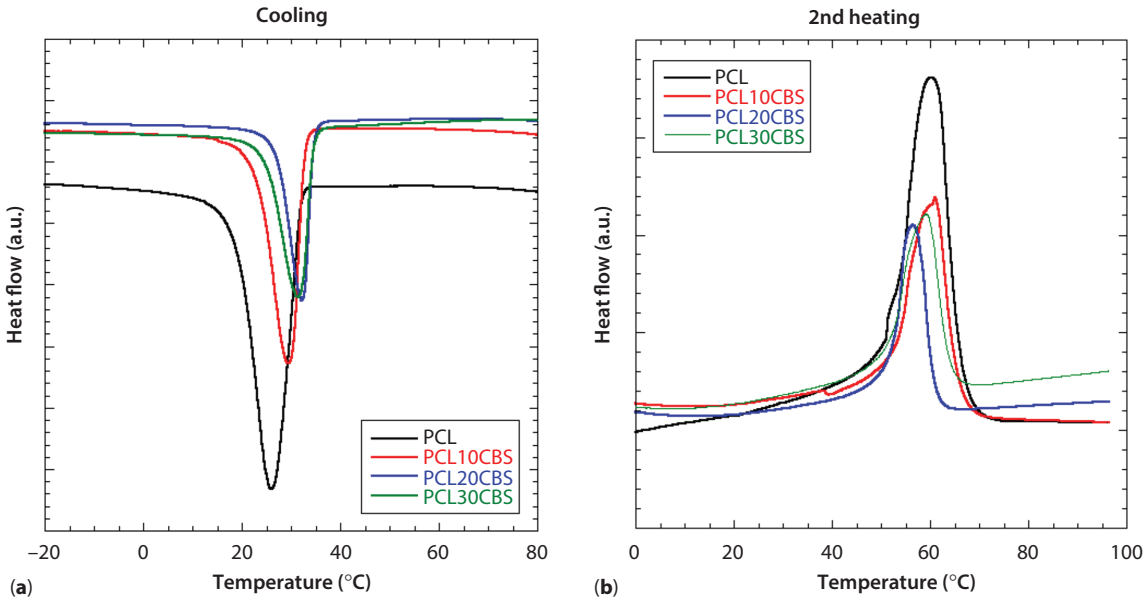

Figure 4 Cooling scan (**a**) and second heating scan (**b**) DSC curves for PCL/CBS composites.

The thermal characterization of PCL-based composites was carried out using DSC. From the thermograms (Figure 4, cooling and 2nd heating scan and Table 2), melting temperature (T_m), associated heat of melting (ΔH_m), degree of crystallinity (X_c) and crystallization temperature (T_c) were measured. For all the composites, the crystallization temperature is slightly increased when compared to the neat matrix, which can be translated as a difficulty for the PCL chains to rearrange themselves in the presence of the shells' residue.

The incorporation at the different weight levels into PCL induced a change in the crystallization temperature with respect to neat PCL, indicating the occurrence of a nucleating effect on the crystal growth of PCL. The reduced decrease in melting parameters (temperature and enthalpy) can be seen as a restriction of the periodic arrangements of PCL chains into its lattice, leading to some loss in the polymer crystallinity in biocomposites with respect to neat PCL. As the concentration of the CBS shells was increased, the relative weight percent of

Table 2 Results of DSC tests for PCL/CBS composites at different weight percent (T_m, melting temperature; T_c, crystallization temperature; ΔH_m, heat of melting; degree of cristallinity, X_c).

	T_c (°C)	T_m (°C)	ΔH_m (J/g)	X_c (%)
PCL	24.9 ± 0.3	60.9 ± 0.2	95.5 ± 2.2	68.5 ± 1.6
PCL10CBS	29.4 ± 0.6	60.2 ± 0.5	60.7 ± 0.3	48.4 ± 0.3
PCL20CBS	31.4 ± 0.2	59.2 ± 0.3	58.5 ± 0.4	52.4 ± 0.8
PCL30CBS	32.3 ± 0.3	56.5 ± 0.8	52.1 ± 0.8	53.4 ± 0.4

the PCL in the compound was decreased, leading to lower values for endothermic area (J/g). On the contrary, the degree of crystallinity of PCL is markedly influenced by the presence of CBS. In particular, the presence of ground CBS particles seems to restrict the periodic arrangements of PCL chains into its lattice, leading to a decrease in crystallinity of neat PCL with the increase in CBS content. This behaviour was observed in other studies on PCL reinforced with lignocellulosic reinforcements [36].

4 CONCLUSIONS

The introduction of ground cocoa bean shells (CBS) into a biodegradable matrix, such as polycaprolactone, proved to be rather successful in terms of the achievement of a sufficiently strong interface and provided enhanced rigidity to the polymer. The maximum amount of filler introduced, 30% wt., was demonstrated to be not easily exceeded with the production process adopted. However, it is likely that the implementation of compatibilization processes, such as starch grafting on polycaprolactone, would possibly lead to the prospective introduction of a higher amount of filler. Compatibilization would allow to control the high occurrence of pullout and fibrillation of CBS in composites with the highest amount of filler. The results shown in this study confirm that, the possibility to reuse a waste, such as CBS, formed by a quite rigid and impermeable lignocellulosic structure yet comprising a significant amount of parenchymal tissue, therefore not very brittle, in a composite, appears promising.

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