



# Preparation and characterization of a novel starch–chestnut husk biocomposite

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## Abstract

Biocomposites based on potato starch and reinforced with chestnut husks, a lignocellulosic agroforestry waste, were developed by incorporating 2.5 wt%, 5 wt% and 7.5 wt% of chestnut husks via an extrusion molding procedure. The effect of the filler on the morphology and thermos-mechanical properties were studied by scanning electron microscopy (SEM), infrared spectroscopy (FTIR) and dynamic mechanical analysis (DMA). Chestnut husks were homogeneously dispersed within the plasticized starch matrix as shown by SEM images. FTIR results shows that the peaks of pure starch samples in the 500–1500  $\text{cm}^{-1}$  region vanished as chestnut husks was incorporated, suggesting an interaction between starch and chestnut. The glass transition temperature was found to decrease at higher filler content, which indicates an improvement in segmental mobility of starch molecules. DMA tests revealed the presence of two relaxation processes. The  $\alpha$  relaxation was associated with the cooperative segmental motion of starch chains while the  $\beta$  relaxation was assigned to the segmental mobility of glycerol-rich phases.

**Keywords** Biocomposites · Starch · Chestnut husks · Glass transition

## 1 Introduction

During the last decades, natural fibers have emerged as promising elements for the development of biopolymer nanocomposites. Their combination with synthetic materials yields composites with enhanced mechanical and thermal properties. However, they are not completely biodegradable. The use of biopolymeric resources allows for the production of fully biodegradable composites. Several biopolymers including carbohydrates, polysaccharides and proteins have been used to manufacture biocomposites [1–3]. Starch has been shown to be an attractive raw material for the development of biodegradable biocomposites, due to its versatility and abundance [4–7]. It is synthesized by plants and is included in the human diet, which makes it easily available in contrast to other renewable sources. With a suitable content of water, starch can be processed as a thermoplastic using conventional

processing techniques such as extrusion, injection molding, compression molding and thermoforming [8].

However, starch-based materials feature poor mechanical properties. In order to overcome this drawback starch is usually used as matrix to prepare composites. The incorporation of an additional phase into the starch matrix may lead to the improvement of its properties, as a result of events involving local chain motions and the presence of relaxation processes.

Some studies have examined the thermal relaxation behavior of starch-based biocomposites [9–11]. Gonzalez-Gutierrez et al. [4] developed albumen/starch-based biocomposites via a thermomechanical procedure. At room temperature, samples displayed a viscoelastic behavior attributed to a large amount of interaction among chain segments. Castillo et al. [12] produced nanocomposite films based on thermoplastic corn starch reinforced with talc particles blended with glycerol. DMA analysis revealed

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the presence of two relaxation zones, one placed at low temperatures associated with a glycerol-rich phase and the other placed at high temperatures associated with a starch-rich phase. Talc nanoparticles restricted starch chains mobility, shifting the relaxation temperatures of the glycerol-rich phase to higher values. Ma et al. [13] prepared thermoplastic pea starch/carboxymethyl cellulose (CMC) composites via extrusion. The authors identified two thermal transitions: starch-rich phase and starch-poor phase. The storage modulus of the composites reinforced with CMC was superior to that for pure pea starch, with a decreasing tendency at high temperatures. Besides, CMC addition increased the glass transition.

Natural fillers offer potential advantages such as low cost, low density, low energy consumption and biodegradability [14, 15]. Chestnut is one of the resources that can be exploited by the Amazonian communities. However, its exploitation produces a large amount of waste. An individual chestnut tree yield 80 kg of chestnut, of which the 70% is formed by husks. Chestnut production represents one of the best conservation models against illegal logging for the Amazon communities. Unfortunately, the price has fallen over the last few years causing the model to become unviable. The use of chestnuts husk as a filler for biocomposites production represents an alternative economic activity for the Amazon communities. Some investigations have reported the use of chestnut husk as filler in the preparation of composites with a variety of thermoplastic matrices such as polyhydroxyalkanoate, poly(butylene succinate), poly(lactic acid), as well as thermoset polymers such as epoxy and unsaturated polyester resins. Chestnut husk contents from 5 to 30% were reported. The composites prepared exhibited acceptable mechanical properties [16–20].

The work reported here describes the development of a novel starch–chestnut husks biocomposite. The influence of chestnut husks content on the thermomechanical properties of these biocomposites is evaluated. Morphological as well as mechanical characterization, that included tensile tests as well as dynamic mechanical analysis were carried out to establish the structure property relationships in the composites.

## 2 Materials and methods

### 2.1 Materials

Commercial potato starch was used. Chestnut husks (*Bertholletia excelsa*) were extracted from the agronomical wastes found in Peruvian Amazon. The husks were grounded with a manual grinder machine.

### 2.2 Biocomposite formation

The biocomposites were obtained following the same processing route used for the preparation of starch based biocomposites reinforced with natural fibers such as sisal, yute and cabuya with a filler content ranging 2.5–7.5 wt% reported previously elsewhere [21]. Chestnut husks were grounded and sieved in a 400 ASTM mesh. The blending of ingredients (starch, chestnut, glycerol, and water) was performed in a glass container subjected to constant stirring at 50 rpm. The pure starch biocomposite was prepared by mixing 85 wt% starch, 14.25 wt% water, and 0.75 wt% glycerol. The biocomposites were produced by adding 2.5, 5, and 7.5 wt% of the filler (chestnut husks) with respect to the total mass. The biocomposites were manufactured using a standard extrusion process [22]. The extrusion process was carried out using an open-barrel single screw extruder, followed by a compression molding process, sample was compressed the sample for 30 min at a gauge pressure of 2000 psi and temperature of 95 °C.

### 2.3 Characterization techniques

The morphology of the fracture surface of the samples after the tensile tests was investigated by scanning electron microscopy (SEM). A FEI QUANTA (FEI, United Kingdom) SEM operated at 20 kV was used. The fractured surface of the samples was coated with gold.

FTIR spectra were acquired using a Lambda Scientific FTIR equipped with a universal ATR sampling accessory. The acquisition covered a spectral range of 500–4000  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ .

Tensile tests were performed in a 23-5D INSTRON equipment. Rectangular strips (14 mm × 8 mm) were tested (using at least 5 samples per composition) with a 100 N load cell. A crosshead speed of 1 mm/min was used. The ultimate tensile strength, Young's modulus and maximum strain values were recorded.

Dynamic mechanical analysis (DMA) was performed in a RSA-G2 equipment (TA Instrument, New Castle, DE, USA). The three-point bending mode was selected for experiments, with temperature sweeps at a constant frequency (1 Hz). The chosen temperature was between –50 and 150 °C with a heating rate of 5 °C/min. All tests were performed in triplicate.

Differential scanning calorimetry (DSC) tests were carried out in a Perkin Elmer DSC 4000 calorimeter. Samples weighing 10 mg were encapsulated in standard aluminum pans, and were heated from –50 to 200 °C at 5 °C/min under an N<sub>2</sub> atmosphere (flow rate of

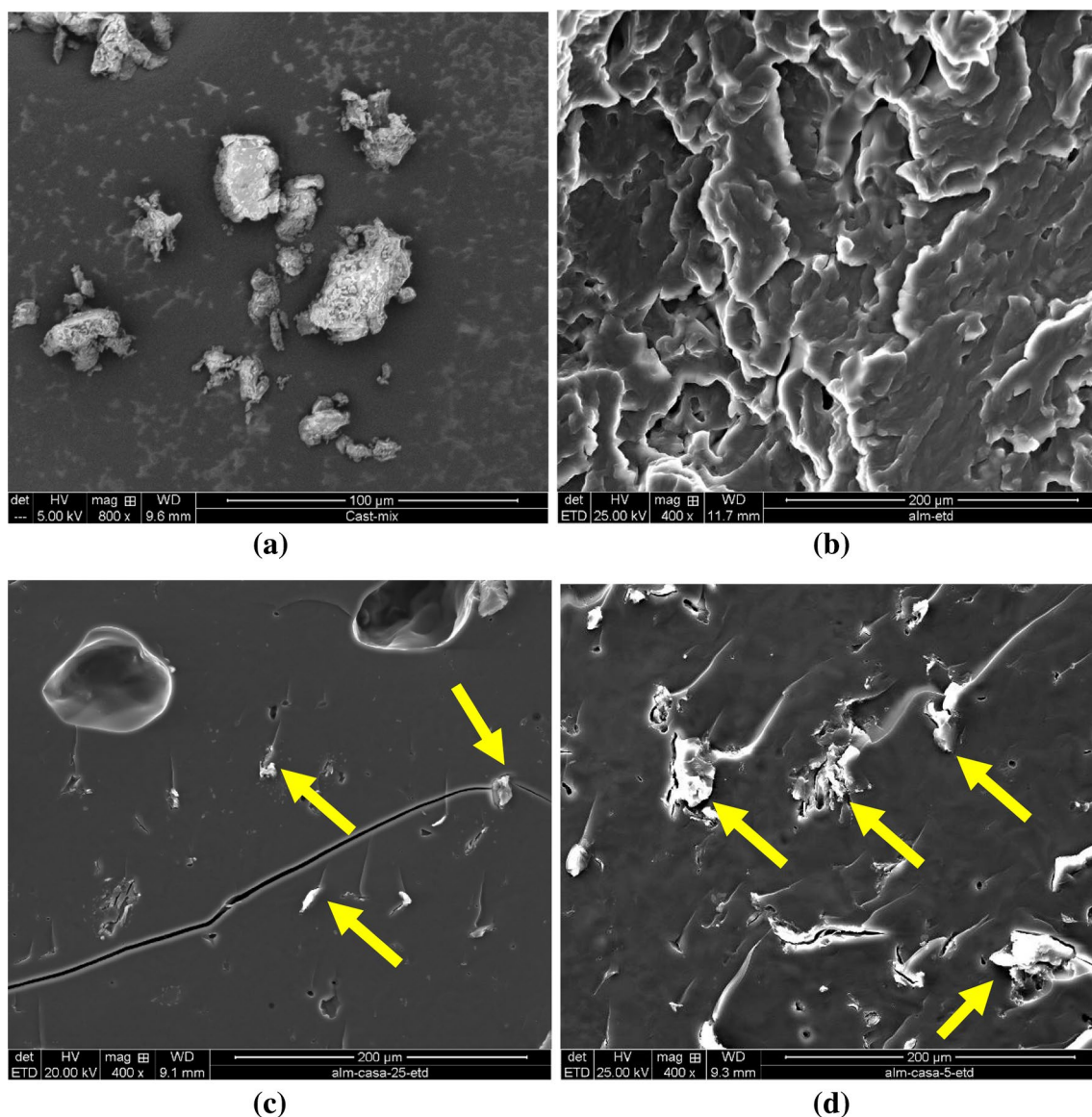
20 ml/min). The particular temperature scanning range was selected in order to include avoid dehydration of hydroxyl groups [23].

### 3 Results and conclusions

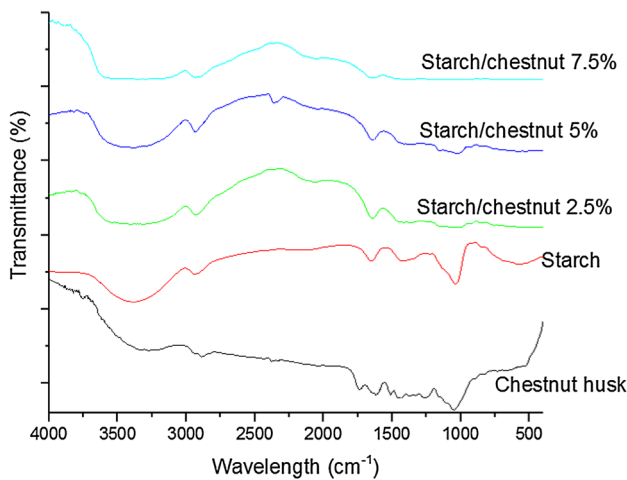
Figure 1a shows a representative SEM image of grounded chestnut husks, which have irregular shapes with sizes ranging from 210 to 400  $\mu\text{m}$ . Cross-sectional SEM images of a pure starch samples and starch–chestnut biocomposites are depicted in Fig. 1b–d. The biocomposites show a homogenous starch phase which means that the molding process was successful. It is also possible to observe

cracks that occur after the molding process, due to the high remaining moisture content of the specimens [24].

The FTIR spectra of chestnut husk particles, pure starch and starch biocomposites with different chestnut husk contents are shown in Fig. 2. The chestnut husk spectrum shows absorption bands at around  $3400\text{ cm}^{-1}$  and  $2900\text{ cm}^{-1}$  related to O–H and C–H vibrations, respectively. The peaks at  $1750\text{ cm}^{-1}$  are accounted for the C=O band in carbonyl groups, whereas the peaks between  $1050$  and  $1350\text{ cm}^{-1}$  correspond to the C–O band found in ester, phenol, and ethers which are active groups of their constituent compounds (lignin, tannins, cellulose and hemicelluloses) [25, 26]. The spectra of pure starch samples show a broad peak at  $3200\text{ cm}^{-1}$  that is attributed



**Fig. 1** SEM images of **a** chestnut husk particles, **b** pure starch sample, **c** starch–2.5 wt% chestnut husk biocomposite and **d** starch–5 wt% chestnut husk biocomposite. The arrows depict the location of chest husk particles



**Fig. 2** FTIR spectra of samples: **a** chestnut husk, **b** pure starch, **c** starch with 2.5 wt% husk, **d** starch with 5 wt% husk and **e** starch with 7.5 wt% husk

to O–H stretching due to the presence of hydroxyl groups in the starch molecules [27–29]. The peak at 2936  $\text{cm}^{-1}$  corresponds to the C–H stretching whereas the peaks at 1650  $\text{cm}^{-1}$  and 1455  $\text{cm}^{-1}$  are related to  $\delta(\text{O–H})$  bending [30–32]. The peak at 1030  $\text{cm}^{-1}$  corresponds to C–O stretching vibration [33, 34].

There is a decrease in the intensity of the OH  $\delta(\text{O–H})$  bending and C–O stretching vibration at 1650  $\text{cm}^{-1}$ , 1450  $\text{cm}^{-1}$  and 1030  $\text{cm}^{-1}$  in the spectra of starch–chestnut husk biocomposites. The intensity of these peaks decreases as the chestnut husk content increases. Zulkifli et al. [35] reported a similar observation in the FTIR spectra of polypropylene–cellulose composites. They related this result to an improved interfacial adhesion between the matrix and the reinforcement. Zaaba et al. [36] studied the effect of the peanut shell powder content on the properties of recycled polypropylene composites. The FTIR spectra of peanut shell–polypropylene composites showed a decrease in the intensity of OH stretching bands at 3200–3600  $\text{cm}^{-1}$  and through this result the authors confirmed the interaction between the matrix and the fibers. The change in the intensity of the peak at 1030  $\text{cm}^{-1}$  might be related to the cleavage of glycosidic

bonds in starch. It has been reported that the extrusion process affects the molecular weight of starch which is related to molecular chain breakage [37, 38].

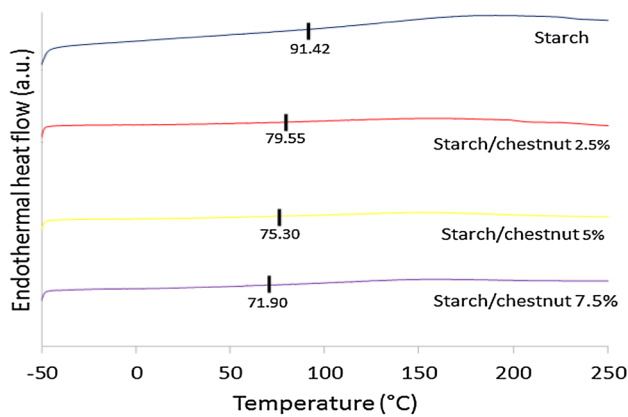
An overview of the results of the tensile tests carried out on pure starch samples and starch–chestnut husk biocomposites is given in Table 1. The incorporation of chestnut husks led to an increase in the elastic moduli of the biocomposites with regard to the unreinforced matrix. Pure starch samples have an average elastic modulus of 3.30 MPa, while starch with 7.5 wt% of chestnut husks displayed an average elastic modulus of 4.85 MPa. On the other hand, the value of the ultimate tensile strength is independent from the chestnut husk content while the elongation at break decreased as the filler content increased. These results are in agreement with previous reports of starch-based biocomposites reinforced with cellulosic fillers such as cotton, hemp and winceyette fibers [39–41]. The effect of the incorporation of cellulosic fillers usually results in an increase of the elastic modulus value and a decrease of the elongation at break. From Table 1, we can also point out that the ultimate tensile strength decreases at a 2.5% content of chestnut husks and remains constant at 5% and 7.5% with regard to the unreinforced polymer. In general, it can be considered that the mechanical strength is not compromised due to the addition of chestnut husks to the polymer.

We next assessed the transitions in starch and the influence of chestnut husks on these transitions. First, we used DSC to study the thermal transitions. Starch is a semicrystalline polymer. It is formed by crystalline and amorphous regions. The extrusion-molding procedure used to prepare the biocomposite disrupts most of the crystalline domains, and the amorphous regions are blended with water and glycerol. The thermograms depicted in Fig. 3 show a step related to glass transition. The glass transition was measured using the graphical tangent method [42]. The  $T_g$  has been one of the material properties used to compare the thermal behavior of starch-based biocomposites [43, 44]. The  $T_g$  is associated with the primary,  $\alpha$ -relaxation of the material suggesting a difference in the molecular mobility between the glassy and rubbery states. In order to assess such relaxation mechanisms DMA tests were performed.

**Table 1** Elastic modulus, ultimate tensile strength and elongation at break of the pure starch and starch–chestnut husk biocomposites

Sample	Elastic modulus (MPa)	Ultimate tensile strength (UTS) (MPa)	Elongation at break (%)
Pure starch	3.3 ± 0.05	0.24 ± 0.12	22.10 ± 0.56
Starch–2.5 wt% chestnut husk	3.87 ± 0.18	0.165 ± 0.01	17.75 ± 0.35
Starch–5 wt% chestnut husk	3.97 ± 0.19	0.25 ± 0.04	17.33 ± 0.67
Starch–7.5 wt% chestnut husk	4.85 ± 0.43	0.25 ± 0.05	14.43 ± 1.10





**Fig. 3** Thermal analysis of starch–chestnut husk composites by DSC of pure starch, starch with 2.5 wt% husk, starch with 5 wt% husk and starch with 7.5 wt% husk biocomposites

The storage modulus as a function of temperature is displayed in Fig. 4a. It can be observed that, for all samples, the storage modulus decreases slightly as the temperature increases in agreement with previous reports of starch-based materials [45–47]. In the region corresponding to a maximum in  $\tan \delta$  plots (Fig. 4b), a sharp decrease in storage modulus can be observed, which is associated to the glass transition of the polymer [44, 45]. This relaxation process is labeled as  $\alpha$  and involves the cooperative motions of polymeric chains.

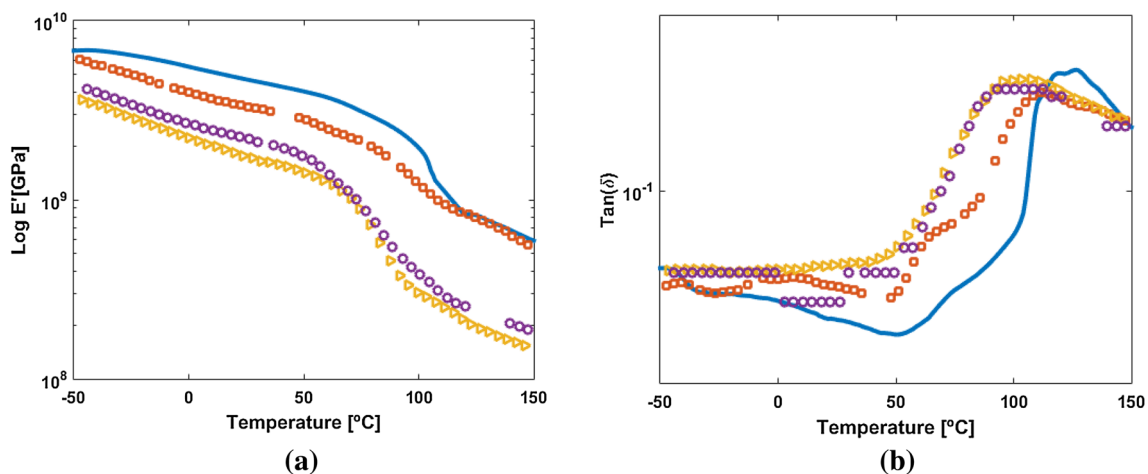
The  $T_g$  measured with DSC and DMA tests follow the same trend (Table 2).  $T_g$  decreases as the filler content increases. Previous reports of starch-based composites have shown a similar result [48, 49]. According to Follain et al. [48] the addition of cellulosic fillers to a starch/

**Table 2** Glass transition of the biocomposite samples measured by DSC and DMA

Matrix	Filler	Filler content (wt%)	$T_g$ (°C) DMA	$T_g$ (°C) DSC
Starch	–		117.8	91.42
	Chestnut husk	2.5	112.3	79.55
		5	99.33	75.3
		7.5	92.93	71.9

water/glycerol system can lead to a plasticizing effect. In fact, the  $T_g$  of a polymeric system can change due to a number of reasons such as changes in tacticity, molecular weight, and retained monomer [50]. However, in the case of polymeric composites the reason is usually accounted to the interaction of the polymeric matrix with the filler particles [51, 52]. It seems that the interaction of the starch chains with the surface of the chestnut particles was able to alter the chain kinetics. The chestnut particles facilitate the mobility of starch chains, increasing the free volume. As a result,  $T_g$  decreases with the filler addition. In addition, a widening of the  $\alpha$  relaxation peak with the addition of reinforcements is observed, which confirms the improvement of the segmental mobility compared to the neat starch matrix [53].

The secondary relaxation process observed in Fig. 4b is named  $\beta$  relaxation and occurs at the second maximum of the  $\tan \delta$  curve. This relaxation has been reported to take place between  $-50$  and  $-70$  °C [44, 45]. In particular, this secondary relaxation process is highly related to the plasticizer concentration (glycerol), the so-called glycerol-rich domain [12, 54].



**Fig. 4** DMA curves for the chestnut husk-reinforced starch biocomposites. **a** storage modulus and **b**  $\tan \delta$ . Solid blue line: unfilled starch matrix; red squares: 2.5 wt% filler; yellow triangles: 5 wt% filler; purple circles: 7.5 wt% filler

### 3.1 Relation between DSC and DMA measurements

The second order transition  $T_g$  was calculated following the tangent method from thermograms (Fig. 3), and are presented in Table 2. The  $T_g$  values derived from DSC curves differ from those extracted by DMA. The variation between both results can be ascribed to the difference in the working mechanisms of DSC and DMA.

DSC requires a minimum amount of samples (~ 10 mg), in contrast to larger samples used in DMA. When heating/cooling, independently of rate, a gradient of temperature will be observed in larger samples. As a consequence, the DMA result can be considered as an average response of individual constituents of the whole sample.

It has also been reported the dependence of  $T_g$  on the heating rate. Kinetic events governing the macromolecules behavior during temperature transitions induce relaxation on polymeric chains. Since relaxation on polymeric chains is a time-dependent phenomenon, a different heating ratio may yield different  $T_g$  results [55]. Moreover, particular values of pans heat capacity, thermal conductivity and mass will affect kinetics events. For instance, pans with larger mass and poorer conductivity shift the peak temperature [55]. Despite the variation in results given by DSC and DMA, the  $T_g$  tendency to decrease with increasing filler content was assessed by both techniques.

## 4 Conclusions

The results showed that chestnut husks can be used as suitable fillers for the development of starch-based biocomposites. The incorporation of chestnut husk increases the elastic modulus of the samples. Differential scanning calorimetry and dynamic-mechanical analysis have provided a clear assessment of the thermo-mechanical relaxation processes of novel starch–chestnut husk biocomposites. Two relaxation processes were identified from loss tangent curves: a relaxation involving the cooperative segmental motion, and  $\beta$  relaxation assigned to glycerol segmental mobility. The chestnut husk addition simultaneously shifted the glass transition temperature  $T_g$  toward low temperatures, reduced the peak height of the  $\alpha$  relaxation and broadened its domain. This behavior revealed an incremental filler–matrix interfacial region, which enhances the cooperative segmental mobility. SEM images confirmed that the chestnut husks were homogeneously distributed in the starch host matrix, increasing the rigid phase of the composite. The existence of interfacial interaction was showed by FTIR results, confirming good compatibility between the components.

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### Compliance with ethical standards

**Conflict of interest** On behalf of all authors, the corresponding author states that there is no conflict of interest.

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