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Utilization of coffee silverskin in the production of Poly (3-hydroxybutyrate-co-3-hydroxyvalerate) biopolymer-based thermoplastic biocomposites for food contact applications

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ABSTRACT

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) is one of the most attracting biopolymers, nevertheless, its expensiveness has hampered its uses in daily applications. In this framework, Coffee Silverskin (CS), an agricultural residue, has been embedded in variable amounts into a PHBV matrix plasticized by acetyl tributyl citrate (ATBC) to achieve a biocomposite system through melt extrusion technique. Thermal, morphological and mechanical properties have been investigated in order to validate whether these PHBV/CS-based biocomposites can be used to manufacture molded items. The increasing concentration of CS improves the crystallinity, stiffness and heat deflection temperature properties of the biocomposite. Using the optimized formulation, coffee capsules have been produced by injection molding and characterized in terms of migration properties in contact with simulants. The overall migration at 100 °C was below the limit (10 mg/dm^2) required for plastic materials at food contact. These results demonstrated the feasibility of using CS to produce high efficient PHBV/CS based biocomposites.

1. Introduction

Bio-based polymers are started blooming into the field with abilities to meet the real-time applications. Among the commercially available biopolymers, polyhydroxybutyrate (PHB) and its copolymer (polyhydroxybutyrate co-valerate) (PHBV) have attracted a significant attention of the academia and industries because of their enhanced biocompatibility, thermo-plasticity and biodegradability behavior in a wide variety of controlled and uncontrolled environments such as industrial/home composting, soil, fresh water, sea water [1–3]. PHB and PHBV are polyesters produced by microorganisms as an intracellular carbon and energy reserve from feedstocks such as sugars and plant oils under unbalanced growth conditions [4]. They show high stiffness and high crystallinity that guarantee for the good thermal resistance [5] and also good barrier to gas [6]. Whilst the use of PHB-based materials is more limited due to their severe brittleness, PHBVs possess processability similar to that of the polypropylene (PP) [7] polymer. Indeed, the incidence in the chains of 3-hydroxyvalerate comonomers results in significant variations in mechanical properties, where it is found that the ratio of comonomer addition is directly proportional to the toughness and inversely proportional to the stiffness and the tensile strength [8].

Unfortunately, its relative expensiveness [9] has hampered the research into the use of PHB and PHBV in basic practical applications such as packaging and service items. For this reason, the PHBV matrix can be modified by embedding the particulate fillers or natural fibers in order to reduce its cost and make it suitable for wider uses without losing its efficiencies. In this context, various studies have been carried out on the formulation of biocomposites by incorporating low-cost materials or food waste by-products into PHBV matrices in order to reduce their overall cost of the final products, such as waste lignocellulose fibers, which are abundant and low-cost, which can be sourced from agricultural and industrial crops [10–13]. In particular, Wei et al. [14], have reported that the mechanical properties of these fiber-matrix composites are largely dependent on their interfaces [15–17], which can fundamentally improve the mechanical resistance of PHBV by grafting with a compatibilizer the cellulose fibres by reactive extrusion for example

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with dicumyl peroxide and provide better stress transfer between the interfaces of the fiber/polymer matrix. Similarly, Madbouly et al. [18] have demonstrated that the compounds with 10% wt. of dry granules of distiller with soluble substances have a stronger effect on the biodegradation rate, which can be six times faster than the untreated PHA, in addition to the mechanical reinforcement properties.

In this framework, the aim of the present study is to design and develop new biodegradable composites based on PHBV by incorporating the raw coffee silverskin (CS), a tegument of green coffee beans, towards reducing the cost of the final product as well as to improve their properties towards mitigating the current environmental concerns related to the disposal of this waste.

In the process of waste generation connected to food packaging disposal, in fact, the coffee capsules represent a major problem since recently they are one of the most widespread ways for domestic use. Coffee production, with a global manufacture of 105 million tons per year [19], comes with a huge amount of by-products and wastes such as coffee pulp, spent coffee grounds (SCG) and coffee silverskin (CS). This trend essentially causes important issues related to the management as well as to the end life of agro-industrial wastes. In the perspective of green and circular economy, which promotes the reduction of the final wastes of a process and the longer preservation of resources, the industrial valorization of CS and SCG has become a possible opportunity for their end-use management [20].

Coffee silverskin, which is the principal by-product of the roasting process [21], could be useful as a promising source of antioxidative materials [22] and it principally consists of lignin (29 wt%), cellulose (24 wt%) and hemicellulose (17 wt%) [23]. Although CS has been used for poultry feed and/or as a raw material for paper production, its massive use in value-added applications has so far been limited. To the best of the authors' knowledge, only a few works have been reported on the use of CS embedded into the biocomposites, among which some of the noteworthy reports include the study by Zarrinbakhsh et al. [24], Dominici et al. [25] and Sarasini et al. [26]. Zarrinbakhsh et al. [24], who investigated the morphology, mechanical and thermal properties of composites based on the polypropylene (PP) and CS and SCG. Their results showed that the CS can be a better reinforcing agent as compared to SCG due to its denser fibrous structure, lower fatty acid content and higher thermal stability. Dominici et al. [25] evaluated the application of BioPE-based composites containing CS. In their study, the grafted PE was used as compatibilizer, where it was found that the hydrophobic treatment of CS with palmitoyl chloride promoted the interfacial adhesion and increased the strain at break values. The amount of CS was limited up to 20 wt%, which resulted in a balanced tensile strength and Young's modulus properties. On the other hand, Sarasini et al. [26] have studied the effect of CS size, variety, distribution and content on the processability, thermal and mechanical properties of the biodegradable biocomposites based on the blend of poly(butylene adipate-co-terephthalate (PBAT) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate (PHBV), taking into the account of end life disposal, which showed an improved stiffness as compared to the blend without CS.

In this direction, the PHBV/CS formulations reported in the present manuscript were produced by melt extrusion technique and characterized for their thermo-mechanical, rheological and morphological properties. Further, the optimized biocomposite was used to industrially produce coffee capsules by injection molding method (compared to a reference matrix), on which the migration tests in contact with foodstuffs simulants were also conducted in the perspective of its use in the food contact applications.

2. Materials and methods

2.1. Materials

A commercial grade of PHBV (PHI002) by NaturePlast® (Caen, France) was used as the matrix for the biocomposites. This product is basically a polyhydroxybutyrate (PHB) having 5 wt% of valerate content, a density of 1.25 g/cm^3 and a melt flow index (190 °C, 2.16 kg) of 15–20 g/10 min. It is also a thermoplastic polymer with high crystallinity, due to its isotactic structure. Supplier data sheet refers to a glass transition temperature, T_g, at 5 °C and a melting temperature, T_m, at 175 °C.

Acetyl tributyl citrate (ATBC), supplied by Tecnosintesi® (Bergamo, Italy), was used as a biobased and biodegradable plasticizer. It is a colorless, odorless, organic compound and widely used additive for food packaging and for the objects intended to be in contact with food. It is soluble in organic solvents and it has a density of 1.05 g/cm^3 with a molecular weight of 402.5 g/mol.

Coffee silverskin (CS), used as the filler, was supplied by illycaffèS.p.A. (Trieste, Italy) in flakes of size from 2 to 5 mm with a bulk density of 0.18 g/cm^3 and a particle density of 0.71 g/cm^3.

It should be noted that it was necessary to use an inorganic filler (i) as a processing aid in the melt extrusion part, (ii) to enhance the friction with the mould and (iii) to facilitate the removal of the final coffee capsule. In this case, the calcium carbonate ($CaCO_3$), purchased from Omya® (Avenza/Carrara, Italy) with trade name of Omyacarb 2-AV, was chosen. It was produced by grinding the white marble, possessing an average particle size (d 50%) of 2.6 μm, top cut diameter (d 98%) of 15 μm, cubic shape and density of 2.7 g/cm^3.

2.2. Production of biocomposites

The as-supplied state CS was dried in a ventilated electric oven at a temperature of 110 °C for 24 h before subjecting into the main process.

In order to characterize the formulation for the scalable production of coffee capsule prototypes, the composites containing different CS amounts were produced by using a co-rotating twin-screw extruder (EBC25HT, Comacs.r.l, Cerro Maggiore, Milan, Italy). The extruder, equipped with two 25 mm co-rotating screws in a barrel system with L/D = 44, displayed a temperature profile of 150/165/170/170/170/175/175/175/175/175/175 °C with the die exit zone at 175 °C. The screws rate was kept at 300 rpm and mass feed at 15 kg/h.

The blend of PHBV:ATBC:$CaCO_3$with a ratio of 85:10:5 wt was developed as reported in the previous work of the same authors [27], and used as base matrix, which will be indicated as PCA (P stand for PHBV, C for Calcium Carbonate and A for ATBC) in this paper for convenience. This matrix was used to produce four formulations containing different amounts of CS such as 5, 7.5, 10 and 12.5 wt% on the total weight, which are labeled as PCA_5, PCA_7.5, PCA_10 and PCA_12.5, respectively.

The PHBV granules were fed by the main hopper and ATBC was fed into the extruder at 2/3 of the screws length by using a peristaltic pump equipped with a silicon tube previously calibrated to control the flow rate. The mixture of grinded CS and calcium carbonate was fed by a tailored lateral K-Tron (Coperion, Milan, Italy) hopper for powders.

The filaments at the exit of the nozzle were constantly cooled using cold water, dried by a constant jet of air and then pelletized using a mechanical cutter and obtained the pellets with a diameter of 2–3 mm. Then, the pellets were dried for 8 h in a DP 604–615 dryer at 50 °C (Piovan S.p.A., Venice, Italy) and finally closed in vacuum bags to avoid the humidity capture before subjecting to further tests. The granules were used to obtain ISO 527 1, which is a dog bone specimens and ISO 179, which is parallelepipedal samples by an injection molding press (Megatech H18/10) for subsequent mechanical tests. In the injection molding press, the temperature profile used from the screw to the injection outlet in the mold was set to be 165/170/175 °C.

The optimized formulations in terms of processability were used at Femto Engineering srl (San Casciano in Val di Pesa, Florence, Italy) to produce the coffee capsules on industrial scale. The following temperature profile of 147/161/170 °C, from the feeding to the end of the injection point screw, with the mold at 22 °C was used in the industrial injection molding press.

2.3. Thermal and morphological characterization

The thermogravimetric analysis (TGA) was performed for the raw untreated coffee silverskin and the PCA blends using a TA Q-500 (TA Instruments, Waters LLC, New Castle, DE, USA). In this analysis, about 15 mg of sample was taken into a platinum pan and heated from room temperature to 500 °C at 10 °C/min under nitrogen atmosphere. TGA was essentially used to evaluate the thermal stability of CS for its process by melting extrusion with the blend PCA.

Differential scanning calorimetry (DSC) analysis was performed on the developed pellets using the Q200 TA DSC instrument equipped with an RSC cooling system. A nitrogen flow of 50 mL/min was employed as purge gas. Aluminum pan holding the sample (around 15 mg) was sealed before the analysis. The sample was heated from room temperature to 200 °C at 10 °C/min and held for 5 min at 200 °C to eliminate the former thermal history. Then, it was cooled to −50 °C at 10 °C/min and kept for 5 min at −50 °C. After that, it was heated up to 200 °C at 10 °C/min to record the crystallization and melting temperatures. Melting temperature, T_m, was documented at peak of the melting profile. The enthalpy of melting, ΔH_m, was evaluated from the corresponding melting peak area of the 2nd heating thermograms. The crystallinity percentage, X_c, of PHBV in the composites was calculated as follows:

$$X_c = \frac{\Delta H_m}{\Delta H_m^0} \cdot \frac{1}{f_{PHBV}} \cdot 100 \tag{1}$$

where ΔH_m is the melting enthalpy of composites, $\Delta H^0{}_m$ is the melting enthalpy of 100% crystalline PHBV, that is 143 J/g [28], and $f_{PHBV}$is the weight fraction of PHBV in the composites.

In addition, the Heat Deflection Temperature (HDT) of the neat PHBV, PCA blend and composites was evaluated. HDT represents the temperature at which a standardized test bar deflects of a specified distance under an imposed load value. HDT therefore can be an effective way to evaluate the heat resistance of plastics. HDT measurements were performed on a CEAST HV 3 according to the standard ISO 75 method, with a pressure of 1.81 MPa and a bath heating rate of 2 °C/min. When the sample bar deflects of 0.32 mm, the corresponding bath temperature represents the HDT (Type A). Four measurements were carried out and the average value was reported.

Morphological analysis was carried out using a FEI-SEM Quanta 450 FEG on cryo-fractured surfaces of composite specimens in order to investigate the distribution of CS in the polymeric matrix. Samples were covered with an ultrathin gold layer prior to the imaging.

2.4. Melt flow characterization

In order to evaluate the effect of CS on the fluidity of the PCA blend, the Melt Flow Rate (MFR) and Melt Volume Rate (MVR) measurements were carried out according to UNI EN ISO 1133 by a CEAST Melt Flow Tester MF20 (Instron, Canton, MA, USA). In this analysis, MFR and MVR of neat PHBV, PCA and composite with higher CS content were measured and the melt density was evaluated by the ratio of MFR/MVR. Five grams of sample pellets were charged into the chamber, heated at 175 °C in the barrel and extruded through the normalized die (2.095 mm) under a constant load of 2.16 kg and the values achieved were normalized to attain measurements units of g/10 min and cm^3/10 min.

2.5. Mechanical characterization

In order to understand the effect of CS content on the mechanical properties of biocomposites, tensile tests were carried out on ISO 527 1/A dog-bone specimens at room temperature with a crosshead speed of 10 mm/min in accordance with the standard ASTM D638 using an Instron 5500 R universal testing machine (Canton, MA, USA) equipped with a 10 kN load cell and interfaced with Merlin software (version 4.42S/N-014733H). Moreover, the impact tests were performed at room temperature on ISO 179 V-notched specimens (V-notch of 2 mm at 45°) using a 15 J Charpy pendulum of an Instron Ceast 9050 (Canton, MA, USA) in accordance with the method ISO179:2000. For both tests, at least five specimens for each composite were tested and the average values were reported.

Dynamic mechanical thermal analysis (DMTA) was accomplished on a Gabo Eplexor® 100 N (Gabo Qualimeter GmbH, Ahlden, Germany) in tensile configuration on specimens having dimensions of 40 × 10 × 1 mm in the temperature range from −60 to 120 °C and at frequency of 1 Hz.

2.6. Migration tests on molded capsules

To characterize the use of the molded capsules in contact with coffee powder and hot water, the migration tests were conducted in accordance with the EC 1935/2004 directive relating to plastic materials in contact with food. This type of test involves the non-specific weight determination of the substances that are released from the container or packaging during contact with some food-simulants. The overall migration (OM) was determined by exposing the capsules to three chemical food simulants (water, ethanol 10% and acetic acid) at 100 °C (since the temperature of use of the capsule was estimated to be between 90 and 95 °C) for 5 min, after which the extracted residue is dried and weighed. The OM was expressed in mg per contact surface area (mg/dm^2) and compared to the overall migration limit (OML) as per the EU Regulation 10/2011, which describes the maximum permitted total amount of non-volatile substances that can migrate from a food packaging material or food container into food. For general plastic FCMs (Food Contact Materials), the OML is 10 mg/dm^2.

The migration tests were carried on capsules based on PCA and PCA_12.5 and three capsules were immersed in each simulant in order to have a surface area of contact with the simulant of about 1 dm^2 being the surface area of each capsule of about 0.30 dm^2.

3. Results and discussion

3.1. Thermal analysis

Thermo gravimetric (TG) curves and derivative thermograms (DTG) under nitrogen atmosphere for CS and PCA are displayed in Fig. 1. For CS, the first weight loss at 50–100 °C is attributed to the removal of moisture; then, a notable weight-loss occurred in the range of 200–350 °C related to the decomposition of hemicellulose and cellulose components. Hemicellulose starts decomposing in the range of

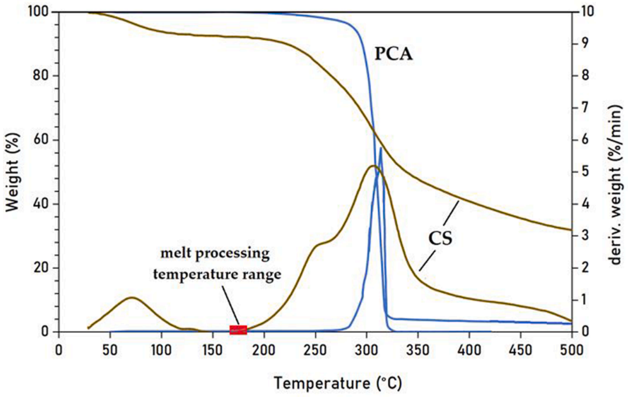

Fig. 1. TG and DTG curves of PCA and CS. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

200–315 °C with a peak decomposition at about 270°Cand the cellulose decomposes at higher temperatures (315–400 °C) with maximum weight loss rate at about 350 °C [29]. Further, the subsequent gradual weight-loss above 400 °C is attributed to the decomposition of lignin and proteins [26]. These results show that CS has a similar thermal stability if not superior to the most common natural fibers used in composites that exhibit an onset decomposition temperature of about 215 ± 10 °C [30] showing its suitability to be processed in the temperature range of melt processing of most commodity polymers such as PHBV.

The TG curve of PCA blend showed thermal stability up to 250 °C and then a single-stage thermal degradation with peak close to 320 °C. A residue of about 4% was observed at 500 °C, attributed to the residual calcium carbonate present in PCA.

DSC heating and cooling scans for PHBV, PCA and biocomposites were carried out to investigate the effect of increasing content of CS on the melting temperature and crystallization behavior of the biocomposites. The DSC thermograms obtained from the cooling and second heating runs (in order to evaluate the thermal properties erasing the injection molding effect) are given in Fig. 2 and the relative crystallization temperature, melting temperatures, enthalpies and crystallinity degrees are listed out in Table 1. It can be noticed that the increasing amount of CS to PCA matrix led to a small but significant increase in the degree of crystallinity, which is in well accordance with other reports dealing with the use of CS in PHBV based composites [26]. This result can be ascribed to a slight nucleating effect of the CS, which is an effect that encountered in several other natural residues embedded in polymer matrices [31,32]. This statement was confirmed by the result obtained from the cooling scan process, where all the curves displayed an intense crystallization peak, which shifted progressively towards lower temperatures with increasing percentage of coffee silverskin, attesting the nucleating action employed on the crystallization of PHBV. This process essentially affects the crystallization temperature as highlighted in DSC thermograms, which is lower for the composite with CS as being the

Table 1
Crystallization Temperature (Tc), Melting Temperature (Tm), Crystallization Enthalpy (ΔHc),Melting Enthalpy (ΔHm) and crystallinity fraction (Xc) for PHBV, PCA and CS/PCA biocomposites.

Sample	Tc (°C)	Tm (°C)	ΔHc (J/g)	ΔHm, (J/g)	Xc (%)
PHBV	121.9	173.1	97.2	99.9	69.9
PCA	116.4	168.4	77.6	83.3	68.5
PCA_5	115.0	168.3	77.2	82.1	71.8
PCA_7.5	114.3	166.8	76.8	79.9	72.1
PCA_10	114.1	166.5	76.1	78.5	73.2
PCA_12.5	112.0	166.3	75.7	78.4	74.6

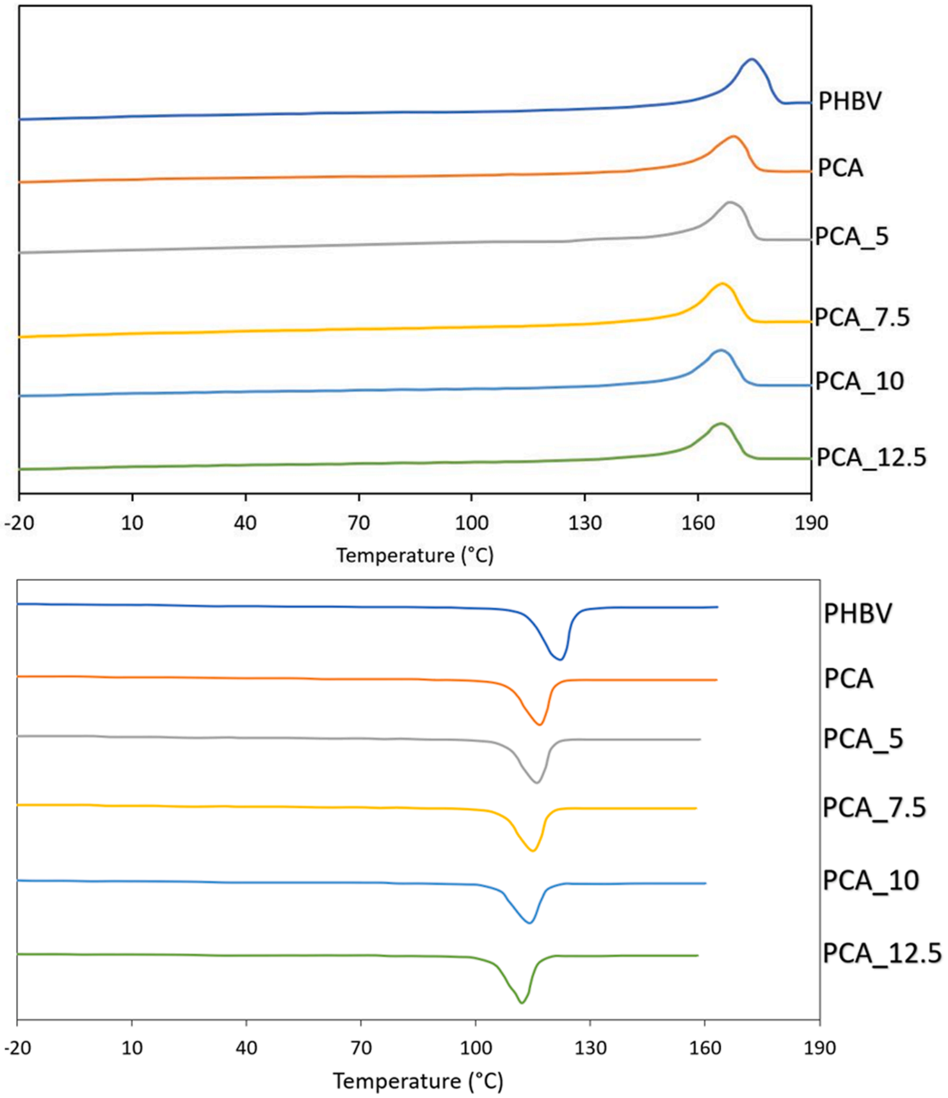

Fig. 2. DSC thermograms of the second heating run (a) and cooling (b) of neat PHBV, PCA/CS biocomposites. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

most crystalline material which needs more time to reorganize during the cooling process. A fluctuation in melting temperature is initially occurred with the addition of the plasticizer with respect to pure PHBV (as expected, ATBC plasticizer lowers the melting temperature improving the molecular mobility of the polymer [33]) and then the T_m is settled around 166–168 °C for all the formulations.

These calorimetric results led to a conclusion that the coffee residue did not affect the thermal stability but it has slightly increased the crystallinity of the formulations. These results were also confirmed by the data of HDT test made on neat PHBV, PCA and PCA_12.5 samples. These tests were carried out in order to evaluate the ability to resist the deflection at high temperatures for the composite at higher CS content as compared to the neat matrices. From the results, the average values of HDT (Type A) for the neat PHBV, base matrix PCA and the composite at higher CS content (PCA_12.5) were found to be 92.2, 78.3 and 80.5 °C, respectively. As expected, the addition of ATBC to the PHBV matrix reduced the HDT of neat PHBV (this value is comparable with that reported by Peelman et al. [34] for PHBV) and in fact, the addition of ATBC lowers the processability temperature of the PHBV by reducing the stiffness of the polymer, resulting in greater mobility of the chains with consequent crystallinity reduction. However,

the formulation with 12.5 wt% of CS did not show huge differences as compare to the PCA matrix. The observed slight increment in the HDT of PCA_12.5 with respect to PCA could be due to its higher crystallinity, which ensures a good heat resistance in the sample. Overall, the HDT studies demonstrated that both PCA and PCA_12.5 are suitable for their usage as biocomposite formulation for the coffee capsules.

3.2. Melt flow properties

The melt fluidity measurements of the neat PHBV, PCA and PCA_12.5 are reported in Table 2 in terms of MFR and MVR values obtained at 175 °C, i.e. the temperature used in the extrusion process.

As shown in Table 2, the addition of ATBC and CS has decreased the melt viscosity at low shear rate.

PCA_12.5 has the lowest flow index values compared to the other tested formulations. It is believed that the insertion of silverskin disturbed the molecular chain, moreover the hydrophilic characteristics of the natural fibers induced the hydrolytic degradation of the PHBV during the time of testing; this reduced the polymer's molecular length, and flow is easier with a shorter length. Despite the silverskin's drying pretreatment, the residual inner moisture probably remained, causing the melt flow value to rise slightly. Similar results were achieved by Gorrasi et al. [35], by Lee et al. [36] (in their work presented similar results concerning modification of Floreon by kenaf fibers) and above all by Barczewski et al. [37] in which the MFI value grows along with increasing chestnut content (occurrence of significant wall slip during capillary flowand for the sample containing 30 wt% of the ground chestnut shell it is over 5 times higher than in case of the neat resin.

The melt flow rate obtained for the composite is in the range which is appropriate for injection molding applications as confirmed by their good processability as observed in the subsequent industrial injection molding.

3.3. Mechanical properties

The mechanical properties of PHBV, PCA and the developed biocomposites with varying amount of CS are summarized in Table 3. The addition of plasticizer to the PHBV caused a three folds-increment in the elongation at break and in the Charpy impact strength, leading to the formation of a material with a lower elastic modulus and lower stress at break. Regarding the biocomposites, it can be noticed that the incremental addition of CS (that is a waste residue made of mainly lignin (29 wt%), cellulose (24 wt%) and hemicellulose (17 wt%) [21]) led to a growing elastic modulus, which reflected the behaviour observed during the DSC test, in which a slight increase of crystallinity with the content of CS was noted. This observation highlights a close correlation between the two properties as described in other PHBV/natural residual systems in the literature [16]. Contemporary with the stiffness increase, a reduction of break strength with increasing CS content was noticed, suggesting the limited interfacial interaction, low compatibility and substantially inefficient load transfer between the polymer matrix and the unmodified agricultural residue [38,39], which has also been noted in recent works on the untreated coffee silverskin of a comparable dimensional distribution and microstructural appearance that embedded into several polymeric matrices [24–26]. Poor interaction and low compatibility is typical behavior when untreated agricultural residues or industrial wastes are embedded into polymeric matrices, not only PHBV [40–42]. In all these studies, the resulting biocomposites exhibited lower tensile strength as compared to the neat matrix but with an enhanced modulus.

Table 2
MFR and MVR values obtained at 175 °C for neat PHBV, PCA and the composites at higher CS amount.

Sample	MFR (g/10 min)	MVR (cm^3/10 min)	Melt density (g/cm^3)
PHBV	10.1 ± 0.68	8.1 ± 0.27	1.25
PCA	11.1 ± 0.52	11.0 ± 0.31	0.98
PCA_12.5	13.2 ± 1.86	13.5 ± 0.95	1.01

Nevertheless, the PCA with 12.5 wt% CS content, which notably lowers the price of the final material and ensures the better biodegradability kinetics [43], which showed a stress resistance and a stiffness within a typical range of materials for injection molding issues, included coffee capsules [44]. Moreover, it also displayed the greatest impact resistance value, which is around 1.5 times higher than PHBV.

3.3.1. Predictive models for tensile results

In order to understand the micromechanics mechanisms behind the tensile data obtained and correlate them to the CS and matrix characteristics, analytical predictive models were applied. Many empirical equations have been proposed in the literature to predict the modulus of "similar particulate shaped fillers-polymer systems" [45]. In this work, due to the low concentrations of CS, the Einstein's equation [46] was used:

$$E_c = E_m\left(1 + 2.5V_p\right) \tag{2}$$

where E_c and E_m is the composite and matrix elastic modulus, respectively, and V_p is the particle volume fraction. This equation implies that the composite modulus is independent of particle size and predicts a linear relationship between E_c and V_p. As shown in Fig. 3a, the Einstein's model fitted well with the experimental data.

From the obtained data, it has been evidenced that the tensile strength decreased with the CS content; for those systems in which the inner material did not guarantee a reinforcement effect, whereas the upper bound of the tensile stress can be predicted by the following simple equation [46,47]:

$$\sigma_c = \sigma_m\left(1 - V_p\right) \tag{3}$$

Table 3
Summary of tensile and impact properties for the PCA/CS composites.

Sample	Elastic Modulus (GPa)	Break Strength (MPa)	Elongation at break (%)	Charpy Impact Strength (kJ/m^2)
PHBV	2.61 ± 0.05	34.8 ± 1.1	2.6 ± 0.3	2.5 ± 0.9
PCA	1.30 ± 0.06	23.0 ± 0.2	6.2 ± 0.9	5.8 ± 0.6
PCA_5	1.73 ± 0.16	20.8 ± 0.7	4.0 ± 0.3	3.7 ± 0.5
PCA_7.5	1.93 ± 0.17	19.7 ± 0.7	2.9 ± 0.3	3.7 ± 0.4
PCA_10	2.03 ± 0.14	18.4 ± 0.9	2.5 ± 0.4	3.2 ± 0.3
PCA_12.5	2.05 ± 0.12	17.3 ± 0.8	2.3 ± 0.3	3.8 ± 0.2

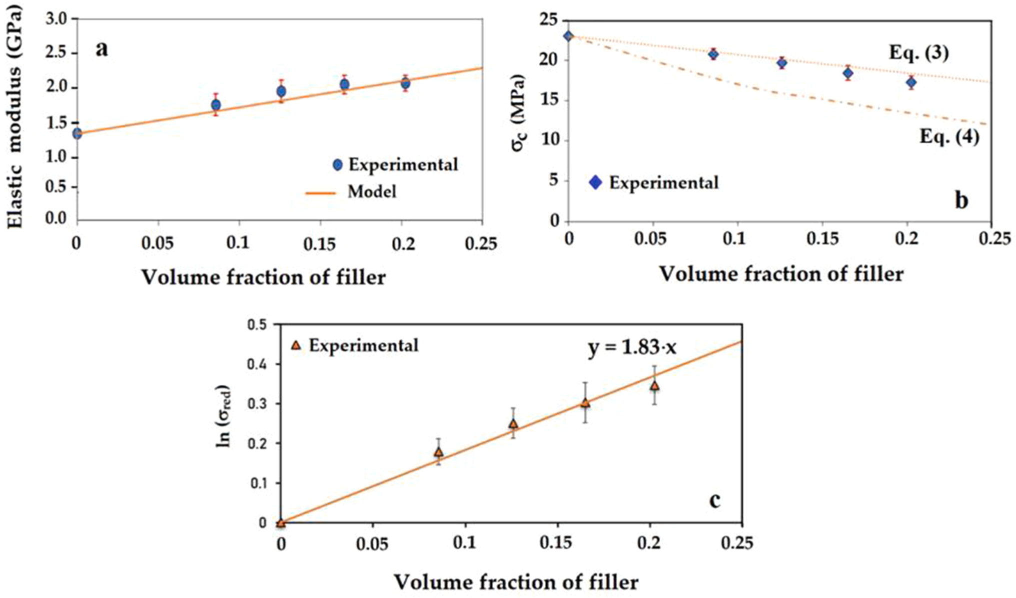

Fig. 3. Fitting of the experimental data with (a) predictive Einstein's model for elastic modulus of the composites; (b) predictive models for composite strength and (c) Pukanszky's model to predict the interfacial B parameter. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

where σ_c and σ_m are the composite and matrix strength, respectively.

Hypothesizing that there is no adhesion between CS and matrix and the load is sustained exclusively by the polymer, another predictive equation was found with geometric assumptions [48]:

$$\sigma_c = \sigma_m\left(1 - 1.21V_p^{2/3}\right) \tag{4}$$

which gives thelower-bound strength of the composite.

Fig. 3b shows the comparison of the experimental data obtained for PCA and the PCA/CS composites with two models (Eqs. (3) and (4)). As obtained, the experimental values are similar to the upper limit (Eq. (3)) and the lower reduction with the filling load can be attributed to a weak adhesion. In order to better study the properties of the interface that strongly influence the strength of the composition, the Pukánszky's model is considered [49]. This equation is used for one of the most widely used short fibers composites, as the biocomposites with CS particles can be assimilated by hypothesis. In Pukánszky's model, the effect of reducing the section of the polymer is considered as a filling effect:

$$ln\sigma_{c,red} = ln\frac{\sigma_c(1 + 2.5V_p)}{\sigma_m(1 - V_p)} = BV_p \tag{5}$$

where B is an empirical parameter which depends on density, particle surface area, and interfacial bonding energy. For poor interfacial bonding, the particles do not carry any load, so B is almost zero [50]. Plotting the logarithm of the reduced stress $ln\sigma_{c,red}$, against the filler volume fraction, the slope of the line achieved gives the value of the B parameter. Fig. 3c shows the fitting of the experimental values with Pukánszky's model. A value of the interaction B parameter of about 2 was obtained, indicating a poor interfacial bonding between PCA and CS. This result is coherent with the decrease in the composite strength with increasing CS loading.

3.3.2. DMTA analysis

DMTA characterization was carried out to investigate the effect of different amount of CS into the PCA matrix on the glass transition of the composite. Indeed, the glass transition temperature, T_g, is a direct measurement of molecular mobility and it can be evaluated in several ways. One of them is the dynamic mechanical thermal analysis (DMTA) performed at a fixed heating rate considering the peak of Tan δ (ratio of viscous and elastic response) as index of Tg. Saba et al. [51] stated that Tan δ peak is one of the most sensitive methods to evaluate T_g for semi-crystalline polymers. Nevertheless, all the data depend greatly on the cooling (or heating) rate and on the loading frequency.

For PHBV, the T_g values reported in the literature vary from 4 to 16 °C, depending on the valerate content [52]. In particular, Mofokeng et al. [53], Torres-Tello et al. [54] and Rosario et al. [55] stated that with a valerate weight percentage of 6%, the T_g was evaluated with DMTA varied from 11 to 16 °C. Instead, for the same valerate content, T_g of PHBV was evaluated to be near 5 °C from DSC measurements [56]. These discrepancies between DSC and DMTA measurements have been reported and discussed by many researchers for various polymeric systems [57]. These differences are ascribed to the kinetic nature of the glass transition, heating rate and loading frequency utilized in DSC and DMTA experiments being different in terms of molecular mobility.

In this work, the DMTA measurements were carried out in the range from −25 to 45 °C to evaluate the T_g and also the drop of storage modulus (E') with increasing temperature. In Fig. 4a, it is possible to note that the T_g values for all the composites were in the range from 0 to 5 °C. The presence of plasticizer ATBC lowers the T_g as compared to T_g of neat PHBV (about 15 °C, in accordance with the values evaluated by DMTA for PHBV with similar valerate content reported in literature [53]). These data can be confirmed by the change of slope of the E' curves, which occurs at approximately the same temperature at which the tan δ peaks are located. The presence of CS showed no evident influence on the T_g and this is in accordance with other works [58] where the natural fillers did not influence T_g but only the stiffness for semi-crystalline polymers.

Moreover, as shown, the energy dissipation ratio is decreased due to the amount of CS dispersed in the polymeric matrix with increasing stiffness of the composite. More specifically, the viscous response was predominant as compared to the elastic one for the composites with the highest CS content. Notably, with increasing temperature, the storage modulus was continued to decrease but the Tan δ was constant because of the loss modulus (which is the viscous response to vibrational stress) was more significant as the temperature increases. Storage modulus at room temperature in this case is slightly higher, but the trend is in line with that calculated with the uniaxial tensile test.

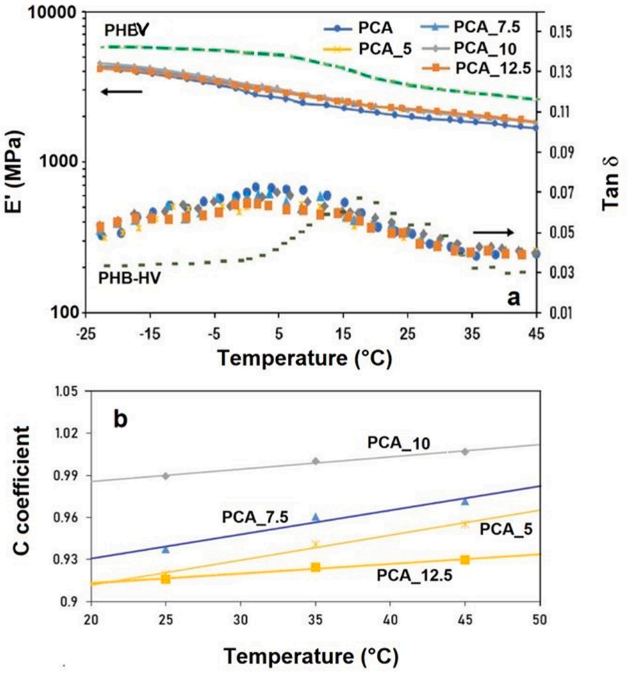

Fig. 4. (a) DMTA measurements and (b) the consequent estimated C coefficient versus temperature for the different composites. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

After confirming that the CS insertion influenced the stiffness of the composite and not the T_g, it was interesting to investigate how its efficiency affected the increase in temperature. The effectiveness of fillers on the storage modulus can be described by the so-called C coefficient determined by the following equation [59]:

$$C = \frac{\left(E'_g/E'_r\right)_{composite}}{\left(E'_g/E'_r\right)_{matrix}} \tag{6}$$

where E'_g and E'_r are the storage modulus of glassy and rubbery state, respectively. Basically, the lower is the C coefficient the higher is the effectiveness of reinforcement. However, the C coefficient corresponds only to storage modulus, without any direct relation to the composite strength. It defines the aptitude to interrupt the increasing motion of polymer chains in composites at elevated temperatures.

The storage modulus in the glassy state was taken constant at $-10\,^{\circ}$C, while the rubbery one was considered at three different temperatures (25, 35 and 45 °C) to evaluate its progress. As shown in Fig. 4b, the estimated C coefficient was very similar for the systems with the higher quantity of natural fibers [58] in which there was a lower ability to stress transfer as observed in the present study.

Nevertheless, the composite with the greatest possible processing quantity of CS (PCA_12.5) is not only showing the lowest C coefficient value (efficiency index of the reinforcement) but also the minor growth slope with increasing temperature. This can be explained by stating that the influence of the matrix was minor as compared to the CS flakes with increasing temperature. On the basis of these results, PCA_12.5 was chosen for the production of coffee capsules together with PCA. The most inefficient behavior was showed by the composite PCA_10. This may be due to the lower Charpy impact strength of the PCA_10 (Table 2).

3.4. Morphological analysis

In order to better understand the thermal and mechanical properties of the biocomposites with coffee silverskin and for evaluating the microstructure of the agricultural residue after grinding, the SEM image of the cryofractured samples were carried out. In addition, the dimensional distribution of the milled and sieved CS was also evaluated. More than 500 particles were examined from five micrographs acquired by SEM analysis (one of them is showed in Fig. 3A) using ImageJ® software. Fig. 3A showed that the grinding and sieving of the CS flakes could lead to the formation of micrometric powder (in Fig. 3b the average dimensional distribution is around 250 µm) with a “lamella” shape.

Fig. 5c and d show the morphology of cryo-fractured sections of dogbone specimens of PCA_12.5, which is the biocomposite with the maximum content of CS, at different magnifications (280x and 2400x respectively) to validate the coupling between matrix and CS. As shown in the images, the CS lamellae were uniformly distributed in the polymer matrix, but they exhibited a poor interfacial adhesion with the matrix as shown in the circled enlargement in Fig. 5d. These weak interfacial interactions are typical for the composites containing natural residues and they tend to be the active polar hydrophilic materials, whereas the polymeric materials are nonpolar and show considerable hydrophobicity [60]. Consequently, the hydrophilic nature of the dispersed phase reduces the adhesion to a hydrophobic matrix and as a result, a loss in strength may be induced as showed by the results of mechanical tests as reported in the following section.

3.5. Migration tests

The results of the overall migration (OM) obtained for molded capsules based on PCA and PCA_12.5 (Fig. 6) are reported in Table 4. As shown in Table 4, all the tested samples were compliant with current legislation for all the used simulants even in the most aggressive environment as created by acetic acid since the average migration values of both formulations are far from the allowed limit of 10 mg/dm^2.

These results show that during its use at medium and high temperatures, the migration of substances from the molded capsules towards the food content (coffee as in this case) is totally below the permitted limits. So, the formulations PCA and PCA_12.5 are possibly found to be suitable for the food contact applications and therefore, they are also suitable to produce coffee capsules, as taking into the account that PHBV is moisture sensitive, and higher temperature would elevate the degradation/chain scissoring. For this reason, more detailed analysis on this aspect must be carried out in future works.

4. Conclusions

In the present work, coffee silverskin- a waste material from coffee production was incorporated in different amounts (5–12.5 wt%) to a polymeric matrix based on PHBV/ATBC/$CaCO_3$ to produce thermoplastic biocomposites for food-contact applications. The synthesized biocomposites were characterized in terms of processability, thermal and mechanical properties in order to investigate whether these PHBV-based biocomposites could be used to manufacture molded items to give a new life to a waste residue and to yield biopolyesters based formulation at more affordable costs and the possibility to produce items by injection molding such as coffee capsules.

In presence of ATBC as a plasticizer and $CaCO_3$ as an inorganic filler, the developed composites containing CS showed good processability. It is observed that the elastic modulus was increased with increasing crystallinity as evidenced by DSC results, while the stress at break and the elongation at break were moderately decreased with the increase of the CS content. These observations suggested that the developed material show limited interfacial interactions, low compatibility and substantially inefficient load transfer between the polymer matrix and the unmodified agricultural residue. The adhesion of CS to the matrix was found to be low as confirmed by SEM images and by the analytical prediction of parameter B of Pukanszky’s model.

However, the moderate reduction of the mechanical properties was well balanced by the environmental advantage that derived from the use of this agro-food waste in the development of biobased composites as an

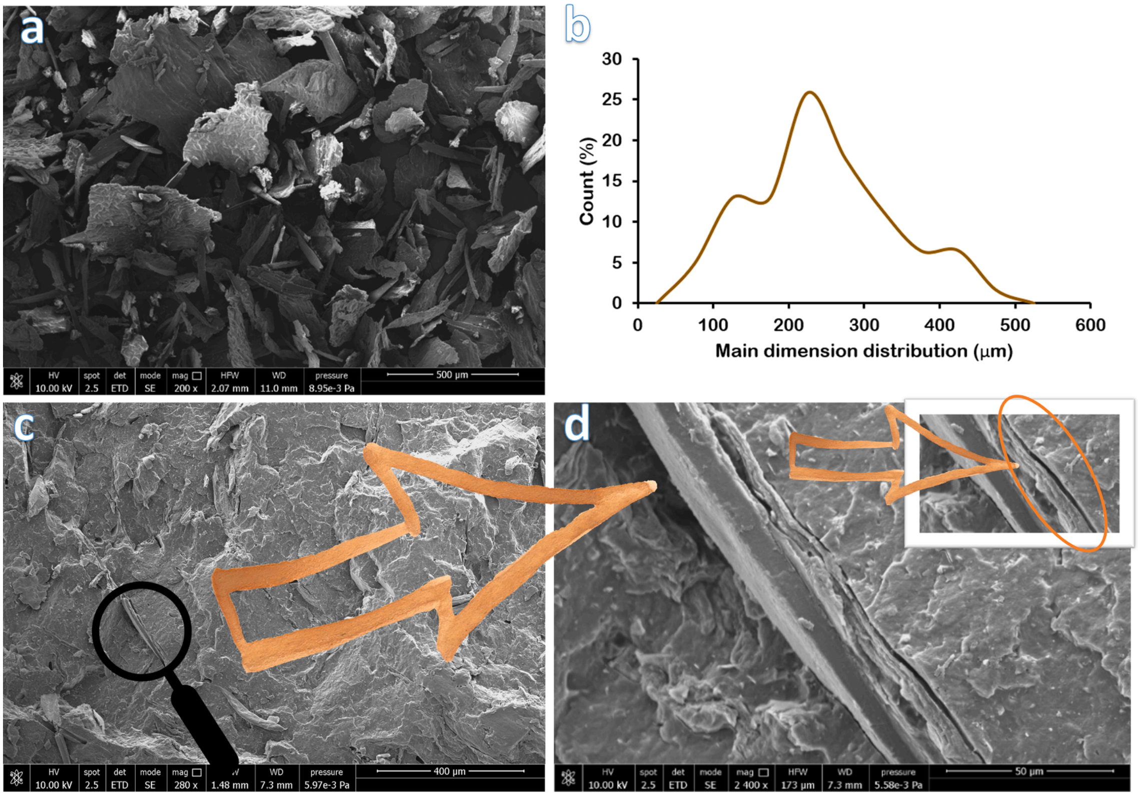

Fig. 5. (a) SEM images of CS as it is (b) Mean dimension distribution of coffee silverskin filler (c) SEM image of cryofractured section of dog-bone specimens of PCA_12.5 at two magnifications: 280X (c) and 2400X (d). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

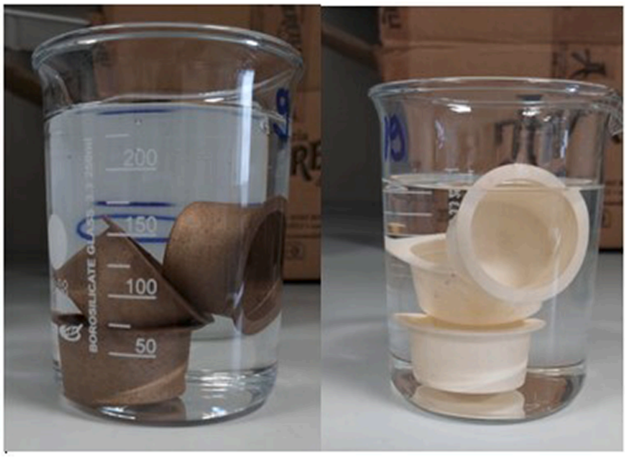

Fig. 6. Coffee capsules migration tests. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 4
Overall migration test results (100 °C, 5 min).

Formulation	Simulant	OM (mg/dm^2)	Limit (mg/dm^2)
PCA	Water	0.52 ± 0.16	10
PCA	Ethanol 10%	0.55 ± 0.20	10
PCA	Acetic Acid	3.53 ± 1.41	10
PCA_12.5	Water	0.99 ± 0.35	10
PCA_12.5	Ethanol 10%	0.78 ± 0.39	10
PCA_12.5	Acetic Acid	2.77 ± 0.82	10

alternative to its land-filling. In addition, it is essential to consider the reduction in the cost of the final product based on PHBV due to the use of this waste available at low cost.

On the basis of the obtained good results of migration tests, all the developed composites can possibly be suitable for the food contact applications and therefore they can be used to produce items for food applications as coffee capsules, adopting a circular economy approach.

Even if the mechanical properties of the developed composites can still be improved by using appropriate compatibilizers, the developed composites showed good processability, mechanical properties and heat resistance properties suitable for their introduction into the market.

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CRediT authorship contribution statement

Vito Gigante: Methodology, Investigation, Writing - original draft. **Maurizia Seggiani:** Conceptualization, Writing - original draft, Writing - review & editing. **Patrizia Cinelli:** Conceptualization, Writing - review & editing. **Francesca Signori:** Methodology, Investigation, Writing - original draft. **Alice Vania:** Methodology, Investigation. **Luciano Navarini:** Validation, Resources. **Giuseppe Amato:** Validation. **Andrea Lazzeri:** Resources.

Declaration of Competing Interest

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