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Abstract: Coffee silverskin (CS) was used to produce biocomposites, based on poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHB-HV) as polymeric matrix, by melt extrusion. CS was incorporated as filler in PHB-HV in variable amounts (5-12.5 wt.%) for evaluating its effect on thermo-mechanical properties and processability. Thermal stability of CS makes it suitable to be processed by extrusion with PHB-HV. Using the optimized formulation, coffee capsules were produced by injection molding and characterized in terms of migration tests at contact with simulants. Compared to PHB-HV-based polymeric matrix, the composites showed greater stiffness and similar thermal resistance (HDT type A of 80 °C). The overall migration in water, ethanol 10% and acetic acid at 100°C resulted below the limit (10 mg/dm²) required for plastic materials at food contact. The positive results obtained show the industrial feasibility of using one of the most abundant coffee waste products in the production of PHB-HV-based biocomposites, usable to manufacture molded items.

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polymer matrix

Pisa, 24th April 2020

Dear Editor,

the present manuscript reports the results of our research work in which we investigated the feasibility of using raw coffee silverskin (CS), one of the most abundant solid wastes produced from the coffee industry, in the production of thermoplastic PHB-HV-based composites for food-contact applications. CS is currently disposed of as a solid waste or simply burned with evident negative environmental impacts; therefore, finding more sustainable alternatives would lead to mitigating the current environmental concerns related to its disposal.

The thermal stability and the fibrous structure of CS made it suitable to be processed by melt extrusion with PHB-HV and up to 12.5 wt.% of CS, and the composites showed good processability. The elastic modulus increased, while the stress at break and the elongation at break moderately decreased with the increase of the CS content. CS behaved more like a filler than as a reinforcing fiber, and its adhesion with the PHB-HV matrix was medium-low as confirmed by the parameter B of Pukanszky's model.

However, the moderate reduction of the mechanical properties is well balanced by the environmental advantage that derives from the use of this agro-food waste in the development of biobased composites as an alternative to its actual landfilling. In addition, it is essential to consider the reduction in the cost of the final product based on PHB-HV due to the use of this waste available in large quantities at low cost. The migration tests carried on the molded capsules produced using the developed composites showed overall migrations well below the overall migration limit set by European regulation (EC 1935/2004) relating to plastic materials in contact with food.

In conclusion, on the basis of the good results in terms of processability, mechanical properties, heat resistance (HDT (type A) = 80°C) and overall migrations, the developed composites result suitable to be used in the production of items for food applications as coffee capsules.

In brief, since this work concerns the evaluation of thermal, mechanical, morphological and thermomechanical properties of a biocomposite for food applications, giving a valorization of a solid waste produced in large quantities by the coffee industry, we think that it can meet the topics addressed in Composites Part A. Accordingly, we would appreciate if this manuscript could be considered for publication in your journal.

At last, the authors declare that the present research was carried out in the project PROLIFIC "Integrated cascades of processes for the extraction and valorization of proteins and bioactive molecules from legumes, fungi and coffee agro-industrial side streams", funded by the Bio Based Industries Joint Undertaking under the European Union's Horizon2020 research and innovation programme (Grant agreement No 790157). For this reason, to better share the results of the research carried out, if the work is accepted, we would like to proceed with the **open access option**.

Best regards

Vito Gigante (on behalf of all the authors of the manuscript)

A handwritten signature in dark ink that reads "Vito Gigante". The signature is written in a cursive style with a large, stylized 'V' and 'G'.

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Utilization of coffee silverskin in the production of thermoplastic biocomposites for food contact applications

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Abstract

Coffee silverskin (CS) was used to produce biocomposites, based on poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHB-HV) as polymeric matrix, by melt extrusion. CS was incorporated as filler in PHB-HV in variable amounts (5-12.5 wt.%) for evaluating its effect on thermo-mechanical properties and processability. Thermal stability of CS makes it suitable to be processed by extrusion with PHB-HV. Using the optimized formulation, coffee capsules were produced by injection molding and characterized in terms of migration tests at contact with simulants. Compared to PHB-HV-based polymeric matrix, the composites showed greater stiffness and similar thermal resistance (HDT type A of 80 °C). The overall migration in water, ethanol 10% and acetic acid at 100°C resulted below the limit (10 mg/dm²) required for plastic materials at food contact. The positive results obtained show the industrial feasibility of

1 using one of the most abundant coffee waste products in the production of PHB-HV-
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3 based biocomposites, usable to manufacture molded items.
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6 **Keywords:** A. Polymer-matrix composites (PMCs); B. Thermomechanical; D. Thermal
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8 Analysis; E. Extrusion.
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10 11 12 13 14 **1. Introduction** 15

16
17 Coffee capsules represents a major issue in food-related waste production [1,2], since
18
19 coffee is one of the most popular beverage and traded goods, with a global production
20
21 of 105 million tons per year [3,4], and since the related market is highly driven by
22
23 increasing use of single-serve coffee in households, especially in North American and
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25 European regions [5]. Indeed, coffee capsules market largely grew in 2018, and is
26
27 predicted to show an increase of 7.1% in the period 2019-2024 [5]. Parallely, the
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29 production of coffee by-products and wastes, as coffee pulp, spent coffee grounds
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31 (SCG) and coffee silverskin (CS), is expected to grow. This trend triggers important
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33 issues in the management of these agro-industrial wastes. Recently the circular economy
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35 model, aimed at more sustainable development, encourages the reduction of the final
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37 wastes of a process, the maintenance of the value of resources and products for as long
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39 as possible, extracting the maximum value from them during use, therefore recovering
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41 and/or regenerating the products and materials at the end of their useful life [6]. In the
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43 perspective of green and circular economy, the industrial valorization of CS in
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45 alternative to its current landfilling, or use as fuel, can represent a potential opportunity
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47 for this waste, reducing even the problem of its management.
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52 Coffee silverskin is the tegument of green coffee beans, obtained as primary by-product
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54 of the coffee roasting process, and it represents about 4 wt. % of coffee beans [7]. Few
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1 studies have focused on the potential use of CS in industrial biotechnology, as a source
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3 of food additives, given its high content in antioxidant molecules, mainly phenolic
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5 compounds [8], and in soluble dietary fibers [9]. CS consists mainly of lignin (29 wt.%)
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7 and polysaccharides, i.e. cellulose (24 wt.%) and hemicellulose (17 wt.%) [10]. Gaseous
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9 products and particulate matter emissions of biomass residential boiler fired with spent
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11 coffee grounds pellets were also studied and developed [11]. Although these fibers have
12
13 been used for poultry feed and/or as a raw material for paper production, their massive
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15 use in value added applications has so far been limited. In fact, CS turns out to be a
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17 suitable starting material for obtaining high value polysaccharide derivatives, such as
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19 cellulose nanocrystals (CNC), which have attracted a lot of attention given their
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21 interesting and remarkable mechanical properties [12], such as high specific resistance
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23 (10 GPa) and a relatively high elastic modulus (150 GPa). Furthermore, their low cost,
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25 availability, renewable nature, ease of chemical and mechanical modification and high
26
27 aspect ratio have led to the use of CNCs as a reinforcing filler for polymeric
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29 composites. None of these methods used for the utilization of CS represents the most
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31 efficient solution in terms of value addition, especially if one considers the large
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33 availability of such residues. Therefore, to date most CS is simply disposed in landfill as
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35 industrial waste [13–15]. In this context, a potential alternative for the sustainable
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37 exploitation of these residues, given their great availability at low cost, can be
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39 represented by their use as a filler in polymeric matrices.

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41 However, to the best of the authors' knowledge, few works can be found dealing with
42
43 this use of CS, with the exception of the studies of Zarrinbakhsh et al. [16], Dominici et
44
45 al. [17] and Sarasini et al. [15].

1 Zarrinbakhsh et al. [16] investigated the morphology, mechanical and thermal properties
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3 of composites based on polypropylene (PP) and CS and SCG, showing that CS is a
4
5 better reinforcing agent than SCG, given its denser fibrous structure, lower fat content
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7 and higher thermal stability. Dominici et al. [17] evaluated the application of BioPE-
8
9 based composites containing CS. Grafted PE was used as compatibilizer and a
10
11 hydrophobic treatment of CS with palmitoyl chloride had a positive effect on the
12
13 interfacial adhesion, slightly positively altering the strain at break values. The amount
14
15 of CS was limited up to 20 wt.%, which resulted in an appropriate balance between the
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17 values of tensile strength and Young's modulus. Sarasini et al. [15] studied the effect of
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19 CS size, variety, distribution and content on the processability, thermal and mechanical
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21 properties of biocomposites based on biodegradable blend of poly(butylene adipate-co-
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23 terephthalate (PBAT) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate (PHB-HV),
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25 showing the feasibility of using CS in the production of biocomposites with improved
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27 stiffness and tensile strength compared to the neat blend.
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31 In this context, the present study aims to give a further contribution to the exploration of
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33 CS as filler in composites based on a biodegradable matrix such as PHB-HV and their
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35 use in the production by injection molding of coffee capsules, potentially compostable
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37 and biodegradable in various natural environments such as soil and sea water.
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41 PHB-HV and poly(3-hydroxybutyrate) (PHB) are the best-known polyesters of the
42
43 polyhydroxyalkanoates (PHAs) family, biodegradable and biocompatible polyesters
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45 produced by various microorganisms as an intracellular carbon and energy reserve from
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47 feedstocks such as sugars and plant oils under unbalanced growth conditions. PHB-HV
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49 and PHB have attracted the attention of academia and industry because of its
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51 biocompatibility, biodegradability in a wide variety of controlled and uncontrolled
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1 environments (industrial/home composting, soil, fresh water, sea water) and good
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3 thermo-plasticity [18–22]. Whilst the use of PHB-based materials is more limited due to
4
5 their severe brittleness, PHB-HVs have processability similar to polypropylene (PP),
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7 good mechanical properties and are commercially available [23,24]. Indeed, the
8
9 presence in the chains of 3-hydroxyvalerate comonomers results in considerable
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11 changes in mechanical properties: the ratio of comonomer addition is directly
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13 proportional to the toughness and inversely proportional to the stiffness and the tensile
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15 strength [25].
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20 Despite these good properties, the use of PHB-HV is still quite limited to high-value
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22 applications in the medical and pharmaceutical sectors, owing to its relatively high cost
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24 (7–12€/kg) [26], compared to traditional no-biodegradable commodity plastics and also
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26 to other biopolymers such as poly-lactic acid (PLA) (2.5–3.5€/kg) [27]. For this reason,
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28 various studies have been carried out incorporating low-value materials into PHB-HV
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30 matrices in order to reduce the cost of the final products, such as starch [28–30] and
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32 waste lignocellulose fibers, highly-available and at low-cost, sourced from agricultural
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34 and industrial crops [20,21,31–33]. In this framework, the aim of this study was to
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36 design new composites based on PHB-HV through the inclusion of raw CS to reduce
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38 the cost of the final product and, at the same time, improve their mechanical properties
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40 mitigating the current environmental concerns related to the disposal of this waste. The
41
42 PHB-HV/CS composites were produced by melt extrusion and characterized in terms of
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44 thermo-mechanical, rheological, morphological properties. The optimized composite
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46 was used to industrially produce coffee capsules by injection molding, on which
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48 migration tests in contact with foodstuffs simulants were conducted in view of its use in
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50 food contact applications.
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2. Materials and Methods

2.1 Materials

A commercial grade of PHB-HV (PHI002) by NaturePlast® (Caen, France) was used as matrix for the biocomposites, having 5 wt. % of valerate content to improve its molecular flexibility, a density of 1.25 g/cm³ and a melt flow index (190 °C, 2.16 kg) of 15-20 g/10 min. It is a semi crystalline polymer with a glass transition temperature, T_g, of around 5 °C and a melting temperature, T_m, of around 155 °C according to the supplier data sheet.

Acetyl tributyl citrate (ATBC), supplied by Tecnosintesi® (Bergamo, Italy), was used as plasticizer; it is widely used in food packaging. It is a colorless liquid organic, prepared by acetylation of tri-n-butyl citrate, and it is bio-based and soluble in organic solvents. It has a density of 1.05 g/cm³ and a molecular weight of 402.5 g/mol.

Coffee silverskin (CS), used as filler, was kindly supplied by illycaffè S.p.A. (Trieste, Italy) in flakes from 2 to 5 mm, bulk density of 0.18 g/cm³, and particle density of 0.71 g/cm³ [34].

Calcium carbonate (CaCO₃), purchased from Omya® (Avenza/Carrara, Italy) with trade name of Omyacarb 2-AV was used as inorganic filler; it was produced by grinding high purity white marble, having a mean particle size (d 50%) of 2.6 μm, top cut diameter (d 98%) of 15 μm, cubic shape (aspect ratio = 1) and density of 2.7 g/cm³.

2.2 Production of biocomposites

As-supplied state CS was dried in a ventilated electric oven at a temperature of 110 °C for 24 h before being processed to reduce the pre-existing humidity, then milled by an

1 automatic grinder obtaining flakes with a maximum size of 800 μm , evidenced by
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3 Scanning Electron Microscopy (SEM).
4

5
6 In order to characterize a scale-up-able formulation for the production of coffee capsule
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8 prototypes, composites containing different CS amounts were produced by using a co-
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10 rotating twin-screw extruder (EBC25HT, Comac s.r.l, Cerro Maggiore, Milan, Italy).
11

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13 The extruder, equipped with two 25 mm co-rotating screws in a barrel system with L/D
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15 = 44, has an integrated engine and a temperature control system using distilled water as
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17 refrigerant. Several proofs were carried out to define the temperature profile to avoid
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19 melt fracture instabilities, obtaining the following optimal temperature profile:
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23 150/165/170/170/170/175/175/175/175/175 $^{\circ}\text{C}$, with the die exit zone at 175 $^{\circ}\text{C}$.
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26 With the aim of maintaining the engine amperage such that neither the screws worked
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28 unloaded nor with an excessive flow of material, an empirical balance between the flow
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30 rate of the granules and the screws speed was carried out. When fully operational, the
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32 screws rate was maintained at 300 rpm and total mass feed at 15 kg/h.
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36 The blend PHB-HV/ATBC/ CaCO_3 85/10/5 w/w/w [21,35] was used as base matrix and
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38 it will be indicated in this paper as PCA. This matrix was used to produce four
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40 formulations containing different amounts of CS, 5, 7.5, 10 and 12.5 wt.% on the total
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42 weight, labeled below as PCA_5, PCA_7.5_PCA_10 and PCA_12.5, respectively. The
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44 maximum CS amount of 12.5 wt.% was due to the low bulk density and, during the
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46 extrusion processing, it was not possible to extrude compounds with a higher CS
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48 content due to the large volume occupied in the feed hopper.
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52 PHB-HV granules were fed by the main hopper, ATBC was fed into the extruder at 2/3
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54 of the screws length by using a peristaltic pump equipped with a silicon tube previously
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1 calibrated to control the flow rate. The mixture of grinded CS and calcium carbonate
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3 was fed by a tailored lateral K-Tron (Coperion, Milan, Italy) hopper for powders.
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5 The filaments at the outlet of the nozzle were continuously cooled in a tank of cool
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7 water, dried by a constant jet of air and then pelletized in a mechanical cutter obtaining
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9 pellets with a diameter of 2-3 mm. Then, the pellets were dried for 8 h in a DP 604-615
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11 dryer at 50 °C (Piovan S.p.A., Venice, Italy) and, finally, enclosed in vacuum bags to
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13 avoid the moisture capture before the subsequent tests. The granules were used to obtain
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15 ISO 527 1A dog bone specimens and ISO 179 parallelepipedal samples by an injection
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17 molding press (Megatech H18/10) for subsequent mechanical tests. In the injection
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19 molding press, temperature profile used from the screw to the injection outlet in the
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21 mold was the following: 165/170/175 °C.
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27 The optimized formulations in terms of processability were used at Femto Engineering
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29 srl (San Casciano in Val di Pesa, Florence, Italy) to produce coffee capsules on
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31 industrial scale. The following temperature profile 147/161/170 °C, from the feeding to
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33 the end of the injection point screw, with the mold at 22 °C were used in the industrial
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35 injection molding press.
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40 **2.3 Thermal and morphological characterization**

41
42 Thermogravimetric analysis (TGA) was performed on the starting PHB-HV, milled CS
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44 and the PCA blends in form of pellets using a TA Q-500 (TA Instruments, Waters LLC,
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46 New Castle, DE, USA). About 15 mg of sample were loaded into a platinum pan and
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48 heated from room temperature to 500 °C at 10°C/min under nitrogen atmosphere. TGA
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50 was used to evaluate the thermal stability of CS in view of its processing by melting
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52 extrusion with the blend PCA.
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Differential scanning calorimetry (DSC) was carried out on the produced composites in form of pellets using a Q200 TA Instrument differential scanning calorimeter equipped with an RSC cooling system. A nitrogen flow of 50 mL/min was used as purge gas for all measurements. Aluminum pan containing the sample (about 15 mg) was sealed before measurement. The sample was heated from room temperature to 200 °C at 10 °C/min under a nitrogen atmosphere and held for 5 min at 200°C to remove the previous thermal history. Then, it was cooled down to -50°C at 10°C/min and held 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 recorded at the maximum of the melting profile peak. The enthalpies of melting, ΔH_m , was evaluated from the corresponding melting peak area of the 2nd heating thermograms. The crystallinity percentage, X_c , of PHB-HV in the composites was calculated as follows:

$$X_c = \frac{\Delta H_m}{\Delta H_m^0} \cdot \frac{1}{f_{PHB-HV}} \cdot 100 \quad (1)$$

where ΔH_m is the melting enthalpy of composites, ΔH_m^0 is the melting enthalpy of 100% crystalline PHB-HV, that is 146 J/g [31,36], and f_{PHB-HV} is the weight fraction of PHB-HV in the composites.

In addition, Heat Deflection Temperature (HDT) of the neat PHB-HV, 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 constitutes 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 120 °C h⁻¹. When the sample bar deflects of 0.32 mm the corresponding bath temperature represents the HDT (Type A). Four measurements were carried and the average value was reported.

1 Morphological analysis was carried using a FEI-SEM Quanta 450 FEG on cryo-
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3 fractured surfaces of composite specimens in order to investigate the distribution of CS
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5 in the polymeric matrix. Samples were covered with an ultrathin gold layer prior to
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7 examination.
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10 **2.4 Melt flow characterization**

11 In order to evaluate the effect of CS on the fluidity of the PCA blend, the Melt Flow
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13 Rate (MFR) and Melt Volume Rate (MVR) measurements were carried out according to
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15 UNI EN ISO 1133 by a Ceast Melt Flow Tester MF20 (Instron, Canton, MA, USA)
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17 equipped with automatic weight lifting and cutting systems. MFR and MVR represent
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19 the amount of melt polymer, expressed in mass (g) and volume (cm³), respectively,
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21 flowing per 10 min through a capillary of specific diameter and length under a pressure
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23 applied at a specified temperature. 5 g of sample pellets were heated at 175°C in the
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25 barrel and extruded through the normalized die (2.095 mm) under a constant load of
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27 2.16 kg. MFR and MVR of neat PHB-HV, PCA and composite at higher CS content
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29 were measured and the melt density was evaluated by the ratio MFR/MVR.
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37 **2.5 Mechanical characterization**

38 In order to understand the effect of CS content on the mechanical properties of
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40 biocomposites, tensile tests were carried out on ISO 527 1/A dog-bone specimens at
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42 room temperature with a crosshead speed of 10 mm/min in accordance with the
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44 standard ASTM D638 using an Instron 5500 R universal testing machine (Canton, MA,
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46 USA) equipped with a 10 kN load cell and interfaced with Merlin software (version
47
48 4.42S/N-014733H). Moreover, impact tests were performed at room temperature on
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50 ISO 179 V-notched specimens (V-notch of 2 mm at 45°) using a 15 J Charpy pendulum
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52 of an Instron Ceast 9050 (Canton, MA, USA) in accordance with the method
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1 ISO179:2000. For both tests, at least five specimens for each composite were tested and
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3 the average values were reported.
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6 Dynamic mechanical thermal analysis (DMTA) was carried out on a Gabo Eplexor[®]
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8 100N (Gabo Qualimeter GmbH, Ahlden, Germany) in tensile configuration on
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10 specimens having dimensions of 40 x 10 x 1 mm in the temperature range from -60 to
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12 120°C and at frequency of 1Hz.
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15 **2.6 Migration tests on molded capsules**

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17 In view of the use of the molded capsules in contact with coffee powder and hot water,
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19 migration tests were conducted in accordance with the EC 1935/2004 directive relating
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21 to plastic materials in contact with food. This type of test involves the non-specific
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23 weight determination of the substances that are released from the container or packaging
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25 during contact with some simulants. The overall migration (OM) was determined by
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27 exposing the capsules to three chemical food simulant (water, ethanol 10% and acetic
28
29 acid) at 100°C (since the temperature of use of the capsule was estimated to be between
30
31 90 and 95 °C) for 5 min, after which the extracted residue is dried and weighed. The
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33 OM was expressed, as required, in mg per contact surface area (mg/dm²) and compared
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35 to the overall migration limit (OML) that is, in the EU Regulation 10/2011, the
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37 maximum permitted total amount of non-volatile substances that can migrate from a
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39 food packaging material or food container into food. For general plastic FCMs (Food
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41 Contact Materials), the OML is 10 mg/dm².
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49 The migration tests were carried on capsules based on PCA and PCA_12.5 and three
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51 capsules were immersed in each simulant in order to have a surface area of contact with
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53 the simulant of about 1 dm² being the surface area of each capsule of about 0.30 dm².
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3. Results and discussion

3.1. Thermal analysis

TG curves and derivative thermograms (DTG) under nitrogen atmosphere for CS and PCA are reported in **Figure 1**. For CS, the first weight loss at 50 - 100°C is attributable to the moisture removal; then, a marked mass loss occurred in the range 200-350°C related to hemicellulose and cellulose decomposition. Hemicellulose starts to decompose in the range 200 – 315 °C with a peak at about 270°C; while the cellulose decomposes at higher temperatures (315-400°C) with maximum weight loss rate at about 350°C [37]. After that, the subsequent gradual weight loss above 400°C is attributable to decomposition of lignin and proteins [15]. 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 [38] showing its suitability to be processed in the temperature range of melt processing of most commodity polymers such as PHB-HV.

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, attributable to the calcium carbonate amount present in PCA blend.

DSC heating and cooling scans for PCA and biocomposite at higher CS amount (PCA_12.5) were carried out to investigate the effect of CS on the melting temperature and crystallization behavior of PCA blend. The DSC thermograms obtained from the cooling and second heating runs and the relative crystallization and melting temperatures and heats with the PHB-HV crystallinity degree are reported in Figure 2.

In literature Krook et al. [39] pointed out that the crystallinity immediately after the cooling procedure is above 50% for PHBV molded and this data was confirmed by our

1 tests; moreover, as shown, the addition of CS to PCA matrix determined a small
2
3 increase of the degree of crystallinity, in accordance with other research activities
4
5 dealing with the use of CS in composites based on PHB-HV [15].
6
7

8 This evidence affects the crystallization temperature as highlighted in DSC
9
10 thermograms in **Figure 2a**, which is lower for the composite with CS because, being the
11
12 most crystalline material, it needs more time to reorganize during the cooling. As
13
14 expected, ATBC plasticizer lowers the melting temperature (**Figure 2b**) compared to
15
16 neat PHB-HV, because it improves the molecular mobility of the polymer as reported in
17
18 several works [40,41].
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22 The average values of HDT (Type A) obtained in accordance with the standardized ISO
23
24 75 method for neat PHB-HV, the base matrix PCA and the composite at higher CS
25
26 content (PCA_12.5) were 92.2°C, 78.3°C and 80.5°C, respectively. As expected, the
27
28 addition of ATBC to the PHB-HV matrix reduced the HDT of neat PHB-HV (this value
29
30 is comparable with that reported by Peelman et al. [42] for PHB-HV); in fact, the
31
32 addition of ATBC lowers the processability temperature of PHB-HV by reducing the
33
34 stiffness of the polymer, widening the chains, resulting in greater mobility of the chains
35
36 with consequent crystallinity reduction.
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41 The reduced crystallinity affects HDT [43], anyway, the formulation with 12.5 wt.% of
42
43 CS showed similar HDT than that of PCA, this guarantees a good heat resistance. Both
44
45 values show that from a thermo-mechanical point of view both PCA and PCA_12.5
46
47 result suitable to the production of coffee capsules.
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51 **3.2 Morphological analysis**

52 **Figure 3** shows the morphology of cryo-fractured sections of dog-bone specimens for
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54 PCA and PCA_12.5. As shown, CS was uniformly distributed in the polymer matrix,
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1 due probably to the presence of plasticizer in PCA; but it exhibited a poor but not absent
2
3 interfacial adhesion with the matrix. These weak interfacial interactions are typical of
4
5 the composites containing natural fibers. Natural fibers tend to be active polar
6
7 hydrophilic materials, whereas polymeric materials are nonpolar and show considerable
8
9 hydrophobicity [44]. Consequently, the hydrophilic nature of natural fillers reduces the
10
11 adhesion to a hydrophobic matrix and, as a result, a loss in strength may be induced as
12
13 showed by the results of mechanical tests reported below. The surface free energy of
14
15 both the filler and the polymer is very small [45], therefore the phenomenon of stress
16
17 transfer occurs in a more difficult way and the filler particles become sources of stress
18
19 concentration which can lead to an accelerated breakage [46]. To prevent this
20
21 phenomenon, the silverskin surface could be modified by several methods proposed in
22
23 the literature, such as wax treatments [47].
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30 **3.3 Melt flow properties**

31
32 Melt fluidity measurements of the neat PHB-HV, PCA and PCA_1.5 are reported in
33
34 **Table 1** in terms of MFR and MVR values obtained at 175°C, i.e. the temperature used
35
36 in the extrusion process.
37
38
39

40 As shown, the addition of ATBC and then CS content decreased the melt viscosity at
41
42 low shear rate. This is in accordance with what reported by Ren et al. [48] that since
43
44 PHB-HV is a viscoelastic polymer, the addition of plasticizer and naturals fibers lowers
45
46 its viscosity and increases its dimensional stability. The melt flow rate obtained for the
47
48 composite is in the range of values (5-20 g/10 min) appropriate for injection molding
49
50 applications as confirmed by their good processability showed in the subsequent
51
52 industrial injection molding [49].
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57 **3.4 Mechanical properties**

1 The mechanical properties of PCA and the different developed composites are
2
3 summarized in **Table 2**. It is to be noted that with the incorporation of CS from 5 to
4
5 12.5 wt.% the Young's modulus increases almost linearly with the CS amount up to 10
6
7 wt.% then slightly flattens. This stiffening increase is rather common due of the
8
9 incorporation of stiff lignocellulosic fillers that restrict the molecular mobility of
10
11 polymer chains [15]. The incremental addition of CS leads to a limited reduction of
12
13 break strength. The lower tensile strength of the composites is typically due to a poor
14
15 interfacial adhesion between natural filler and polymeric matrix. In fact, the strength of
16
17 a composite is a function of the weakest fracture path throughout the material. Hard
18
19 fillers can affect the strength in two ways: weakening caused by the stress concentration
20
21 or reinforcing effect since they may serve as barriers to crack growth [50].
22
23

24
25 The stress resistance fell within a typical range of materials for injection molding issues,
26
27 included coffee capsules [51], but the property that is most affected by the introduction
28
29 of grinded CS was the elongation at break compared to the matrix without filler (PCA).
30
31 Nevertheless, the maximum CS content, which noteworthy lowers the price of the final
32
33 material and ensures better biodegradability kinetics [52], is in line with other
34
35 biocomposites [53]. PCA_12.5 shows also the greatest impact resistance value,
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37 probably because it guarantees a better obstacle to crack advancement, typical fracture
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39 behavior of composites.
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46 ***3.4.1 Predictive models for tensile results***

47
48 In order to understand the micromechanics mechanisms that explain the tensile data
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50 obtained and correlate them to the filler and matrix characteristics, analytical predictive
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52 models were applied. Many empirical equations have been proposed in literature to
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1 predict the modulus of particulate - polymer systems [54,55]. In this work, due to the
2
3 low filler concentrations, the Einstein's equation [56] was used:
4

$$5 \quad E_c = E_m(1 + 2.5V_p) \quad (2)$$

6
7
8 where E_c and E_m is the composite and matrix elastic modulus, respectively, and V_p is the
9
10 particle volume fraction. This equation implies that the composite modulus is
11
12 independent of particle size and predicts a linear relationship between E_c and V_p . As
13
14 shown in **Figure 4a**, the Einstein's model fitted well with the experimental data.
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18 As far as concern the behavior of composite strength, for micro-particulate composites,
19
20 relies on the effectiveness of stress transfer between matrix and fillers that depends
21
22 strongly on the particle size, particle–matrix interface adhesion and particle loading
23
24 [57,58]. Assuming that the strength of a particulate filled polymer composite is
25
26 determined from the effective sectional area of load-bearing matrix in the absence of the
27
28 particles, a very simple expression for the composite strength is given by the following
29
30 simple equation [59]:
31
32

$$33 \quad \sigma_c = \sigma_m(1 - V_p) \quad (3)$$

34
35 where σ_c and σ_m are the composite and matrix strength, respectively.
36
37

38
39 On the basis of the hypothesis that there is no adhesion between filler and matrix and
40
41 the load is sustained exclusively by the polymer, another predictive model was
42
43 developed with simple geometric considerations [60]:
44
45

$$46 \quad \sigma_c = \sigma_m \left(1 - 1.21V_p^{2/3}\right) \quad (4)$$

47
48 which gives a lower-bound strength of the composite.
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52 **Figure 4b** shows the comparison of the experimental data obtained for PCA and the
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54 PCA/CS composites with the two models (Eq. 3 and 4).
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1 As shown, the experimental values are close to the upper bound (Eq.3), and the lower
2 decrease with the filler loading can be attributed to a weak adhesion filler/matrix. To
3 better investigate the interfacial properties that strongly affect the composite strength
4 [61], Pukánszky's model [62] was taken into account. This model is one of the most
5 used predictive models for composites containing short fibers as the used CS particles
6 can be considered. In Pukánszky's model the effect of decreasing load-bearing cross-
7 section of the polymer is considered as an effect of filling:
8
9

$$10 \ln\sigma_{c,red} = \ln \frac{\sigma_c(1 + 2.5V_p)}{1 - V_p} = \ln\sigma_m + BV_p \quad (5)$$

11 where B is an empirical parameter which depends on particle surface area, particle
12 density and interfacial bonding energy [63]. For poor interfacial bonding, the particles
13 do not carry any load, so B is almost zero [64]. Plotting the logarithm of the reduced
14 stress $\ln\sigma_{c,red}$, against the filler volume fraction, the slope of the line obtained gives the
15 value of the B parameter. **Figure 4c** shows the fitting of the experimental values with
16 Pukánszky's model. A value of the interaction B parameter of about 2 was obtained,
17 indicating a not so poor interfacial bonding from matrix and particles. This result is
18 coherent with the low decrease in the composite strength with increasing CS loading.
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41 **3.4.2 DMTA analysis**

42 DMTA characterization was carried out to investigate the effect of different amount of
43 CS into the PCA matrix on the glass transition of the composite. Indeed, the glass
44 transition temperature, T_g , is a direct measurement of molecular mobility and it can be
45 evaluated in several ways. One of them is the dynamic mechanical thermal analysis
46 (DMTA) performed at a fixed heating rate considering the peak of $\tan \delta$ (ratio of
47 viscous and elastic response) as index of T_g . Saba et al. [65] stated that $\tan \delta$ peak is
48 one of the most sensitive methods to evaluate T_g for semi-crystalline polymers.
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1 Nevertheless, all the data depend greatly on the cooling (or heating) rate, and on the
2
3 loading frequency [66].
4

5 For PHB-HV the T_g values reported in literature vary from 4 to 16 °C, depending on the
6
7 valerate content [67]. In particular, Mofokeng et al. [68], Torres-Tello et al. [69] and
8
9 Rosario et al. [70] stated that with a valerate weight percentage of 6%, T_g evaluated
10
11 with DMTA varied from 11 to 16°C. Instead, for the same valerate content, from DSC
12
13 measurements T_g of PHB-HV was evaluated to be near 5°C [43]. These discrepancies
14
15 between DSC and DMTA measurements have been reported and discussed by many
16
17 authors for various polymeric systems [71]. These differences are ascribed to the kinetic
18
19 nature of the glass transition, heating rate and loading frequency utilized in DSC and
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21 DMTA experiments being different in terms of molecular mobility [72].
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27 In this work, the DMTA measurements were carried out in the range from -25 to 45 °C
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29 to evaluate the T_g and, also, the drop of storage modulus, E' , with the temperature
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31 increasing. In **Figure 5a** it is possible to note that T_g values for all the composites were
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33 in the range from 0 to 5°C. The presence of plasticizer ATBC lowers T_g compared to T_g
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35 of neat PHB-HV (about 15°C, in accordance with the values evaluated by DMTA for
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37 PHB-HV with similar valerate content reported in literature [68]). It is possible to note
38
39 that these data were confirmed also by the change of slope of the E' curves, which
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41 occurs at approximately the same temperature at which the $\tan \delta$ peaks are located. The
42
43 presence of CS showed no evident influence on the T_g and this is in accordance with
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45 other works [73,74] where natural fillers did not influence T_g but only the stiffness for
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47 semi-crystalline polymers.
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54 Moreover, as shown, the energy dissipation ratio decreased due to the amount of filler
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56 dispersed in the polymeric matrix, increasing the stiffness of the composite. More
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1 specifically, the viscous response was predominant compared to the elastic one for
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 3 composites with the highest CS content. Increasing the temperature, the storage module
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 5 continued to decrease but the $\tan \delta$ was constant because the loss modulus, that is the
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 7 viscous response to vibrational stress, was more significant as the temperature increases.
 8
 9 Storage modulus at room temperature in this case is slightly higher, but the trend is in
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 11 line with that calculated with the uniaxial tensile test.
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 13

14
 15 After confirming that the effect of the filling influenced the stiffness of the composite
 16
 17 and not the T_g , it was interesting to investigate how the efficiency of the filling affected
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 19 the increase in temperature. The effectiveness of fillers on the storage modulus can be
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 21 described by the so-called C coefficient determined by the following equation [75]:
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$$C = \frac{\left(\frac{E'_g}{E'_r} \right)_{composite}}{\left(\frac{E'_g}{E'_r} \right)_{matrix}} \quad (6)$$

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 composite strength. It defines the aptitude to interrupt the increasing motion
 of polymer chains in composites at elevated temperatures.
 The storage module in the glassy state was taken constant at -10°C while the rubbery
 one was considered at three different temperatures (25, 35 and 45°C) to evaluate its
 progress. As shown in **Figure 5b**, the estimated C coefficient was very similar for
 systems with the higher quantity of natural fibers [73,75,76] in which there was a lower
 ability to stress transfer as in the present study.

1 Nevertheless, the composite with the greatest possible processing quantity of CS
2
3 (PCA_12.5) not only showed the lowest C coefficient value (efficiency index of the
4
5 reinforcement) but also the minor growth slope with increasing temperature. This can be
6
7 explained stating that the influence of the matrix was minor, compared to the CS flakes,
8
9 as the temperature increases. On the basis of these results, PCA_12.5 was chosen for the
10
11 production of coffee capsules together with PCA. The most inefficient behavior was
12
13 showed by the composite PCA_10. This may explain, the lower Charpy impact strength
14
15 obtained for the PCA_10 (**Table 2**).
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20 **3.5 Migration tests**

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22 The results of the OM obtained with molded capsules based on PCA and PCA_12.5, the
23
24 composite at highest CS content, are reported in **Table 3**. As shown, all the tested
25
26 samples were compliant with current legislation, for all the used simulants, even in the
27
28 most aggressive environment represented by acetic acid since the average migration
29
30 values of both formulations are far from the allowed limit of 10 mg/dm².
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32
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35 These results show that during use at medium and high temperatures, the migration of
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37 substances from the molded capsules towards the food content, in this case the coffee, is
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39 totally below the permitted limits. So, the formulation PCA and PCA_12.5 resulted "ok
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41 food contact" and, consequently, they are suitable to produce coffee capsules.
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46 **4. Conclusions**

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48 In the present work, coffee silverskin, a waste material from coffee production, was
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50 incorporate in different amounts (5-12.5 wt.%) to a polymeric matrix based on PHB-
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52 HV/ATBC/CaCO₃ to produce thermoplastic composites for food-contact applications.
53
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55 The composites were characterized in terms of processability and thermal-mechanical
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1 properties in order to investigate the effect of CS addition and the possibility to produce
2 items by injection molding such as coffee capsules.
3

4
5 In presence of ATBC as a plasticizer and CaCO_3 as inorganic filler, the developed
6 composites containing CS showed good processability. The elastic modulus increased,
7 while the stress at break and the elongation at break moderately decreased with the
8 increase of the CS content. CS behaved more like a filler than as a reinforcing fiber, and
9 its adhesion with the PHB-HV matrix is medium-low as confirmed by the parameter B
10 of Pukanszky's model.
11

12
13 However, the moderate reduction of the mechanical properties is well balanced by the
14 environmental advantage that derives from the use of this agro-food waste in the
15 development of biobased composites as an alternative to its landfilling. In addition, it is
16 essential to consider the reduction in the cost of the final product based on PHB-HV due
17 to the use of this waste available at low cost.
18

19
20 On the basis of the good results of migration tests, all the developed composites resulted
21 "ok food contact" and, consequently, they can be used to produce items for food
22 applications as coffee capsules, adopting a circular economy approach.
23

24
25 Even if the mechanical properties of the developed composites can be improved by
26 using appropriate compatibilizers, the molded products showed good processability,
27 mechanical properties and heat resistance suitable for their consequent introduction into
28 the market.
29

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32
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34 of processes for the extraction and valorization of proteins and bioactive molecules from
35 legumes, fungi and coffee agro-industrial side streams". This project has received
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16 **References**

- 17
18 [1] Cincotta F, Tripodi G, Merlino M, Verzera A, Condurso C. Variety and shelf-life
19 of coffee packaged in capsules. *LWT* 2020;118:108718.
20 [2] Gandia RM, Sugano JY, Boas LH de BV, Mesquita DL. Beverage capsule
21 consumption: A laddering study. *Br Food J* 2018.
22 [3] Esquivel P, Jiménez VM. Functional properties of coffee and coffee by-products.
23 *Food Res Int* 2012;46:488–95.
24 [4] Toschi TG, Cardenia V, Bonaga G, Mandrioli M, Rodriguez-Estrada MT. Coffee
25 silverskin: characterization, possible uses, and safety aspects. *J Agric Food Chem*
26 2014;62:10836–44.
27 [5] Forsythe SJ. *The microbiology of safe food*. John Wiley & Sons; 2020.
28 [6] Kaur G, Uisan K, Ong KL, Lin CSK. Recent trends in green and sustainable
29 chemistry & waste valorisation: rethinking plastics in a circular economy. *Curr*
30 *Opin Green Sustain Chem* 2018;9:30–9.
31 [7] Ballesteros LF, Teixeira JA, Mussatto SI. Chemical, functional, and structural
32 properties of spent coffee grounds and coffee silverskin. *Food Bioprocess*
33 *Technol* 2014;7:3493–503.
34 [8] Napolitano A, Fogliano V, Tafuri A, Ritieni A. Natural occurrence of ochratoxin
35 A and antioxidant activities of green and roasted coffees and corresponding
36 byproducts. *J Agric Food Chem* 2007;55:10499–504.
37 [9] Pourfarzad A, Mahdavian-Mehr H, Sedaghat N. Coffee silverskin as a source of
38 dietary fiber in bread-making: Optimization of chemical treatment using response
39 surface methodology. *LWT-Food Sci Technol* 2013;50:599–606.
40 [10] Iriundo-DeHond A, Haza AI, Ávalos A, del Castillo MD, Morales P. Validation
41 of coffee silverskin extract as a food ingredient by the analysis of cytotoxicity
42 and genotoxicity. *Food Res Int* 2017;100:791–7.
43 <https://doi.org/10.1016/j.foodres.2017.08.012>.
44 [11] Limousy L, Jeguirim M, Dutournié P, Kraiem N, Lajili M, Said R. Gaseous
45 products and particulate matter emissions of biomass residential boiler fired with
46 spent coffee grounds pellets. *Fuel* 2013;107:323–9.
47 [12] Trache D, Donnot A, Khimeche K, Benelmir R, Brosse N. Physico-chemical
48 properties and thermal stability of microcrystalline cellulose isolated from Alfa
49 fibres. *Carbohydr Polym* 2014;104:223–30.
50 [13] Sung SH, Chang Y, Han J. Development of polylactic acid nanocomposite films
51 reinforced with cellulose nanocrystals derived from coffee silverskin. *Carbohydr*
52
53
54
55
56
57
58
59
60
61
62
63
64
65

- 1 Polym 2017;169:495–503.
- 2 [14] Sarasini F, Luzi F, Dominici F, Maffei G, Iannone A, Zuorro A, et al. Effect of
3 different compatibilizers on sustainable composites based on a PHBV/PBAT
4 matrix filled with coffee silverskin. *Polymers (Basel)* 2018;10:1256.
5 <https://doi.org/10.3390/polym10111256>.
- 6 [15] Sarasini F, Tirillò J, Zuorro A, Maffei G, Lavecchia R, Puglia D, et al. Recycling
7 coffee silverskin in sustainable composites based on a poly(butylene adipate-co-
8 terephthalate)/poly(3-hydroxybutyrate-co-3-hydroxyvalerate) matrix. *Ind Crops*
9 *Prod* 2018;118:311–20. <https://doi.org/10.1016/j.indcrop.2018.03.070>.
- 10 [16] Zarrinbakhsh N, Wang T, Rodriguez-Urbe A, Misra M, Mohanty AK.
11 Characterization of wastes and coproducts from the coffee industry for composite
12 material production. *BioResources* 2016;11:7637–53.
- 13 [17] Dominici F, García García D, Fombuena V, Luzi F, Puglia D, Torre L, et al. Bio-
14 Polyethylene-Based Composites Reinforced with Alkali and Palmitoyl Chloride-
15 Treated Coffee Silverskin. *Molecules* 2019;24:3113.
- 16 [18] Deroiné M, Le Duigou A, Corre Y-M, Le Gac P-Y, Davies P, César G, et al.
17 Seawater accelerated ageing of poly(3-hydroxybutyrate-co-3-hydroxyvalerate).
18 *Polym Degrad Stab* 2014;105:237–47.
19 <https://doi.org/https://doi.org/10.1016/j.polymdegradstab.2014.04.026>.
- 20 [19] Volova TG, Boyandin AN, Vasiliev AD, Karpov VA, Prudnikova S V,
21 Mishukova O V, et al. Biodegradation of polyhydroxyalkanoates (PHAs) in
22 tropical coastal waters and identification of PHA-degrading bacteria. *Polym*
23 *Degrad Stab* 2010;95:2350–9.
24 <https://doi.org/https://doi.org/10.1016/j.polymdegradstab.2010.08.023>.
- 25 [20] Seggiani M, Cinelli P, Mallegni N, Balestri E, Puccini M, Vitolo S, et al. New
26 Bio-Composites Based on Polyhydroxyalkanoates and *Posidonia oceanica* Fibres
27 for Applications in a Marine Environment. *Materials (Basel)* 2017;10:326.
28 <https://doi.org/10.3390/ma10040326>.
- 29 [21] Cinelli P, Mallegni N, Gigante V, Montanari A, Seggiani M, Coltelli B, et al.
30 Biocomposites Based on Polyhydroxyalkanoates and Natural Fibres from
31 Renewable Byproducts. *Appl Food Biotechnol* 2019;6:35–43.
32 <https://doi.org/10.22037/afb.v6i1.22039>.
- 33 [22] Zhang K, Mohanty AK, Misra M. Fully biodegradable and biorenewable ternary
34 blends from polylactide, poly(3-hydroxybutyrate-co-hydroxyvalerate) and
35 poly(butylene succinate) with balanced properties. *ACS Appl Mater Interfaces*
36 2012;4:3091–101. <https://doi.org/10.1021/am3004522>.
- 37 [23] Koller I, Owen AJ. Starch- Filled PHB and PHB/HV copolymer. *Polym Int*
38 1996;39:175–81.
- 39 [24] Haugaard VK, Danielsen B, Bertelsen G. Impact of polylactate and poly
40 (hydroxybutyrate) on food quality. *Eur Food Res Technol* 2003;216:233–40.
- 41 [25] Bugnicourt E, Cinelli P, Lazzeri A, Alvarez V. Polyhydroxyalkanoate (PHA):
42 Review of synthesis, characteristics, processing and potential applications in
43 packaging. *Express Polym Lett* 2014;8:791–808.
44 <https://doi.org/10.3144/expresspolymlett.2014.82>.
- 45 [26] Jayakumar A, Prabhu K, Shah L, Radha P. Biologically and environmentally
46 benign approach for PHB-silver nanocomposite synthesis and its
47 characterization. *Polym Test* 2020;81:106197.
- 48 [27] Messin T, Marais S, Follain N, Guinault A, Gaucher V, Delpouve N, et al.
- 49
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- 51
- 52
- 53
- 54
- 55
- 56
- 57
- 58
- 59
- 60
- 61
- 62
- 63
- 64
- 65

- 1 Biodegradable PLA/PBS multilayer membrane with enhanced barrier
2 performances. *J Memb Sci* 2020;598:117777.
- 3 [28] Reis KC, Pereira J, Smith AC, Carvalho CWP, Wellner N, Yakimets I.
4 Characterization of polyhydroxybutyrate-hydroxyvalerate (PHB-HV)/maize
5 starch blend films. *J Food Eng* 2008;89:361–9.
6 <https://doi.org/https://doi.org/10.1016/j.jfoodeng.2008.04.022>.
- 7 [29] Zhang K, Misra M, Mohanty AK. Toughened sustainable green composites from
8 poly (3-hydroxybutyrate-co-3-hydroxyvalerate) based ternary blends and
9 miscanthus biofiber. *ACS Sustain Chem Eng* 2014;2:2345–54.
- 10 [30] Godbole S, Gote S, Latkar M, Chakrabarti T. Preparation and characterization of
11 biodegradable poly-3-hydroxybutyrate–starch blend films. *Bioresour Technol*
12 2003;86:33–7. [https://doi.org/https://doi.org/10.1016/S0960-8524\(02\)00110-4](https://doi.org/https://doi.org/10.1016/S0960-8524(02)00110-4).
- 13 [31] Righetti MC, Cinelli P, Mallegni N, Stäbler A, Lazzeri A. Thermal and
14 mechanical properties of biocomposites made of poly(3-hydroxybutyrate-co-3-
15 hydroxyvalerate) and potato pulp powder. *Polymers (Basel)* 2019;11.
16 <https://doi.org/10.3390/polym11020308>.
- 17 [32] Zhao H, Turng L-S. *Biocomposites*. Elsevier; 2015.
18 <https://doi.org/10.1016/B978-1-78242-373-7.00015-9>.
- 19 [33] Tănase EE, Popa ME, Râpă M, Popa O. PHB/Cellulose Fibers Based Materials:
20 Physical, Mechanical and Barrier Properties. *Agric Agric Sci Procedia*
21 2015;6:608–15. <https://doi.org/https://doi.org/10.1016/j.aaspro.2015.08.099>.
- 22 [34] Galanakis CM. *Handbook of coffee processing by-products: sustainable*
23 *applications*. Academic Press; 2017.
- 24 [35] Cinelli P, Seggiani M, Mallegni N, Gigante V, Lazzeri A. Processability and
25 Degradability of PHA-Based Composites in Terrestrial Environments. *Int J Mol*
26 *Sci* 2019;20:284. <https://doi.org/10.3390/ijms20020284>.
- 27 [36] Barham PJ, Keller A. The relationship between microstructure and mode of
28 fracture in polyhydroxybutyrate. *J Polym Sci Part B Polym Phys* 1986;24:69–77.
29 <https://doi.org/10.1002/polb.1986.180240108>.
- 30 [37] Yang H, Yan R, Chen H, Lee DH, Zheng C. Characteristics of hemicellulose,
31 cellulose and lignin pyrolysis. *Fuel* 2007;86:1781–8.
- 32 [38] Yao F, Wu Q, Lei Y, Guo W, Xu Y. Thermal decomposition kinetics of natural
33 fibers: activation energy with dynamic thermogravimetric analysis. *Polym*
34 *Degrad Stab* 2008;93:90–8.
- 35 [39] Krook M, Hedenqvist MS, Albertsson A, Hellman A, Iversen T, Gedde UW.
36 Barrier and mechanical properties of pulp fiber/polymer laminates and blends.
37 *Polym Eng Sci* 2000;40:143–56.
- 38 [40] Quero E, Müller AJ, Signori F, Coltelli MB, Bronco S. Isothermal cold-
39 crystallization of PLA/PBAT blends with and without the addition of acetyl
40 tributyl citrate. *Macromol Chem Phys* 2012;213:36–48.
41 <https://doi.org/10.1002/macp.201100437>.
- 42 [41] Gigante V, Coltelli M-B, Vannozzi A, Panariello L, Fusco A, Trombi L, et al.
43 Flat Die Extruded Biocompatible Poly(Lactic Acid) (PLA)/Poly(Butylene
44 Succinate) (PBS) Based Films. *Polymers (Basel)* 2019;11:1857.
45 <https://doi.org/10.3390/polym11111857>.
- 46 [42] Peelman N, Ragaert P, Ragaert K, Meulenaer B De, Devlieghere F, Cardon L.
47 Heat resistance of new biobased polymeric materials, focusing on starch,
48 cellulose, PLA, and PHA. *J Appl Polym Sci* 2015;132:42305.
- 49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

- 1 <https://doi.org/10.1002/app.42889>.
- 2 [43] Bugnicourt E, Cinelli P, Lazzeri A, Alvarez V. The main characteristics,
3 properties, improvements, and market data of polyhydroxyalkanoates. *Handb*
4 *Sustain Polym Process Appl* Thakur, VK, Thaku, MK, Eds 2016:899–928.
- 5 [44] Belgacem MN, Gandini A. The surface modification of cellulose fibres for use as
6 reinforcing elements in composite materials. *Compos Interfaces* 2005;12:41–75.
7 <https://doi.org/10.1163/1568554053542188>.
- 8 [45] Zhang L, Deng X, Zhao S, Huang Z. Biodegradable polymer blends of poly(3-
9 hydroxybutyrate) and hydroxyethyl cellulose acetate. *Polymer (Guildf)*
10 1997;38:6001–7. [https://doi.org/https://doi.org/10.1016/S0032-3861\(97\)00158-4](https://doi.org/https://doi.org/10.1016/S0032-3861(97)00158-4).
- 11 [46] Mieck K-P, Reußmann T, Hauspurg C. Correlations for the fracture work and
12 falling weight impact properties of thermoplastic natural / long fibre composites.
13 *Mater Sci Eng Technol* 2000;31:169–74. [https://doi.org/10.1002/\(SICI\)1521-4052\(200002\)31:2<169::AID-MAWE169>3.0.CO;2-S](https://doi.org/10.1002/(SICI)1521-4052(200002)31:2<169::AID-MAWE169>3.0.CO;2-S).
- 14 [47] Righetti MC, Cinelli P, Mallegni N, Massa CA, Aliotta L, Lazzeri A. Thermal,
15 mechanical, viscoelastic and morphological properties of poly (lactic acid) based
16 biocomposites with potato pulp powder treated with waxes. *Materials (Basel)*
17 2019;12:990.
- 18 [48] Ren H, Zhang Y, Zhai H, Chen J. Production and evaluation of biodegradable
19 composites based on polyhydroxybutyrate and polylactic acid reinforced with
20 short and long pulp fibers. *Cellul Chem Technol* 2015;49:641–52.
- 21 [49] Richardson SM. Injection moulding of thermoplastics: Freezing during mould
22 filling. *Rheol Acta* 1983;22:223–36.
- 23 [50] Hashemi S, O'Brien D. The essential work of plane-stress ductile fracture of
24 poly(ether-ether ketone) thermoplastic. *J Mater Sci* 1993;28:3977–82.
25 <https://doi.org/10.1007/BF00351217>.
- 26 [51] Yoakim A, Perentes A, Gerbaulet A. EP2230195A1 - Capsule with filtering
27 insert for preparing a coffee beverage. EP2230195A1, 2014.
- 28 [52] Avella M, Martuscelli E, Raimo M. Properties of blends and composites based on
29 poly(3-hydroxy)butyrate (PHB) and poly(3-hydroxybutyrate-hydroxyvalerate)
30 (PHBV) copolymers. *J Mater Sci* 2000;35:523–45.
31 <https://doi.org/10.1023/A:1004740522751>.
- 32 [53] Seggiani M, Cinelli P, Balestri E, Mallegni N, Stefanelli E, Rossi A, et al. Novel
33 Sustainable Composites Based on Poly(hydroxybutyrate-co-hydroxyvalerate) and
34 Seagrass Beach-CAST Fibers: Performance and Degradability in Marine
35 Environments. *Materials (Basel)* 2018;11:772.
36 <https://doi.org/10.3390/ma11050772>.
- 37 [54] Fu SY, Feng XQ, Lauke B, Mai YW. Effects of particle size, particle/matrix
38 interface adhesion and particle loading on mechanical properties of particulate-
39 polymer composites. *Compos Part B Eng* 2008;39:933–61.
40 <https://doi.org/10.1016/j.compositesb.2008.01.002>.
- 41 [55] Bourkas G, Prassianakis I, Kytopoulos V, Sideridis E, Younis C. Estimation of
42 Elastic Moduli of Particulate Composites by New Models and Comparison with
43 Moduli Measured by Tension , Dynamic , and Ultrasonic Tests. *Adv Mater Sci*
44 *Eng* 2010;10:13. <https://doi.org/10.1155/2010/891824>.
- 45 [56] Einstein A, Fürth R. Investigations on the theory of Brownian movement. New
46 York, N.Y.: Dover Publications; 1956.
- 47 [57] Lazzeri A, Zebarjad SM, Pracella M, Cavalier K, Rosa R. Filler toughening of
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

- 1 plastics. Part 1—the effect of surface interactions on physico-mechanical
2 properties and rheological behaviour of ultrafine CaCO₃/HDPE nanocomposites.
3 *Polymer (Guildf)* 2005;46:827–44.
- 4 [58] Zhang Q, Tian M, Wu Y, Lin G, Zhang L. Effect of particle size on the properties
5 of Mg (OH) 2- filled rubber composites. *J Appl Polym Sci* 2004;94:2341–6.
- 6 [59] Levita G, Marchetti A, Lazzeri A. Fracture of ultrafine calcium
7 carbonate/polypropylene composites. *Polym Compos* 1989;10:39–43.
- 8 [60] Nicolais L, Narkis M. Stress- strain behavior of styrene- acrylonitrile/glass bead
9 composites in the glassy region. *Polym Eng Sci* 1971;11:194–9.
- 10 [61] Renner K, Kenyó C, Móczó J, Pukánszky B. Micromechanical deformation
11 processes in PP/wood composites: Particle characteristics, adhesion,
12 mechanisms. *Compos Part A Appl Sci Manuf* 2010;41:1653–61.
13 <https://doi.org/https://doi.org/10.1016/j.compositesa.2010.08.001>.
- 14 [62] Turcsányi B, Pukánszky B, Tüdős F. Composition dependence of tensile yield
15 stress in filled polymers. *J Mater Sci Lett* 1988;7:160–2.
16 <https://doi.org/10.1007/BF01730605>.
- 17 [63] Aliotta L, Gigante V, Coltelli MB, Cinelli P, Lazzeri A, Seggiani M. Thermo-
18 mechanical properties of PLA/short flax fiber biocomposites. *Appl Sci*
19 2019;9:3797. <https://doi.org/10.3390/app9183797>.
- 20 [64] Liang JZ, Li RKY. Prediction of tensile yield strength of rigid inorganic
21 particulate filled thermoplastic composites. *J Mater Process Technol*
22 1998;83:127–30.
- 23 [65] Saba N, Jawaid M, Alothman OY, Paridah MT. A review on dynamic
24 mechanical properties of natural fibre reinforced polymer composites. *Constr*
25 *Build Mater* 2016;106:149–59.
- 26 [66] Malkin AY. The state of the art in the rheology of polymers: Achievements and
27 challenges. *Polym Sci Ser A* 2009;51:80–102.
- 28 [67] Pearce RP, Marchessault RH. Melting and Crystallization in Bacterial Poly(β -
29 hydroxyvalerate), PHV, and Blends with Poly(β -hydroxybutyrate-co-
30 hydroxyvalerate). *Macromolecules* 1994;27:3869–74.
31 <https://doi.org/10.1021/ma00092a029>.
- 32 [68] Mofokeng JP, Luyt AS. Dynamic mechanical properties of PLA/PHBV,
33 PLA/PCL, PHBV/PCL blends and their nanocomposites with TiO₂ as nanofiller.
34 *Thermochim Acta* 2015;613:41–53.
35 <https://doi.org/https://doi.org/10.1016/j.tca.2015.05.019>.
- 36 [69] Torres-Tello E V, Robledo-Ortíz JR, González-García Y, Pérez-Fonseca AA,
37 Jasso-Gastinel CF, Mendizábal E. Effect of agave fiber content in the thermal and
38 mechanical properties of green composites based on polyhydroxybutyrate or
39 poly(hydroxybutyrate-co-hydroxyvalerate). *Ind Crops Prod* 2017;99:117–25.
40 <https://doi.org/https://doi.org/10.1016/j.indcrop.2017.01.035>.
- 41 [70] Rosário F, Corradini E, Casarin SA, Agnelli JAM. Effect of Gamma Radiation
42 on the Properties of Poly(3-Hydroxybutyrate-co-3-Hydroxyvalerate)/Poly(ϵ -
43 Caprolactone) Blends. *J Polym Environ* 2013;21:789–94.
44 <https://doi.org/10.1007/s10924-013-0573-3>.
- 45 [71] Rieger J. The glass transition temperature T_g of polymers—comparison of the
46 values from differential thermal analysis (DTA, DSC) and dynamic mechanical
47 measurements (torsion pendulum). *Polym Test* 2001;20:199–204.
- 48 [72] Rahman MS, Al-Marhubi IM, Al-Mahrouqi A. Measurement of glass transition
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

- 1 temperature by mechanical (DMTA), thermal (DSC and MDSC), water diffusion
2 and density methods: a comparison study. *Chem Phys Lett* 2007;440:372–7.
3 [73] Adam J, Korneliusz BA, Agnieszka M. Dynamic mechanical thermal analysis of
4 biocomposites based on PLA and PHBV - A comparative study to PP
5 counterparts. *J Appl Polym Sci* 2013;130:3175–83.
6 <https://doi.org/10.1002/app.39562>.
7 [74] Gatenholm P, Kubát J, Mathiasson A. Biodegradable natural composites. I.
8 Processing and properties. *J Appl Polym Sci* 1992;45:1667–77.
9 <https://doi.org/10.1002/app.1992.070450918>.
10 [75] Pothan LA, Oommen Z, Thomas S. Dynamic mechanical analysis of banana fiber
11 reinforced polyester composites. *Compos Sci Technol* 2003;63:283–93.
12 [76] Singh S, Mohanty AK. Wood fiber reinforced bacterial bioplastic composites:
13 Fabrication and performance evaluation. *Compos Sci Technol* 2007;67:1753–63.
14
15
16
17
18
19
20
21
22
23
24
25
26
27
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29
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1 **Figures captions**
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8 **Figure 1.** TG and DTG curves of PCA and CS.
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12 **Figure 2.** DSC thermograms of the cooling (a) and second heating run (b) of neat PHB-
13 HV, PCA and PCA 12.5.
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18 **Figure 3.** SEM images of cryofractured section of dog-bone specimens of a) PCA; b)
19 PCA_12.5 at two magnifications: 280X (left) and 2400X (right).
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23 **Figure 4.** Fitting of the experimental data with a) predictive Einstein's model for elastic
24 modulus of the composites; b) predictive models for composite strength and c)
25 Pukanszky's model to predict the interfacial B parameter.
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28 **Figure 5.** a) DMTA measurements and b) the consequent estimated C coefficient
29 versus temperature for the different composites.
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Tables

Table 1. MFR and MVR values obtained at 175 °C for neat PHB-HV, PCA and the composites at higher CS amount.

Sample	MFR (g/10 min)	MVR (cm³/10 min)	Melt density (g/cm³)
PHB-HV	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

Table 2. 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/m²)
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

Table 3. Overall migration test results (100°C, 5 min).

Formulation	Simulant	OM (mg/dm²)	Limit (mg/dm²)
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

Figure 1
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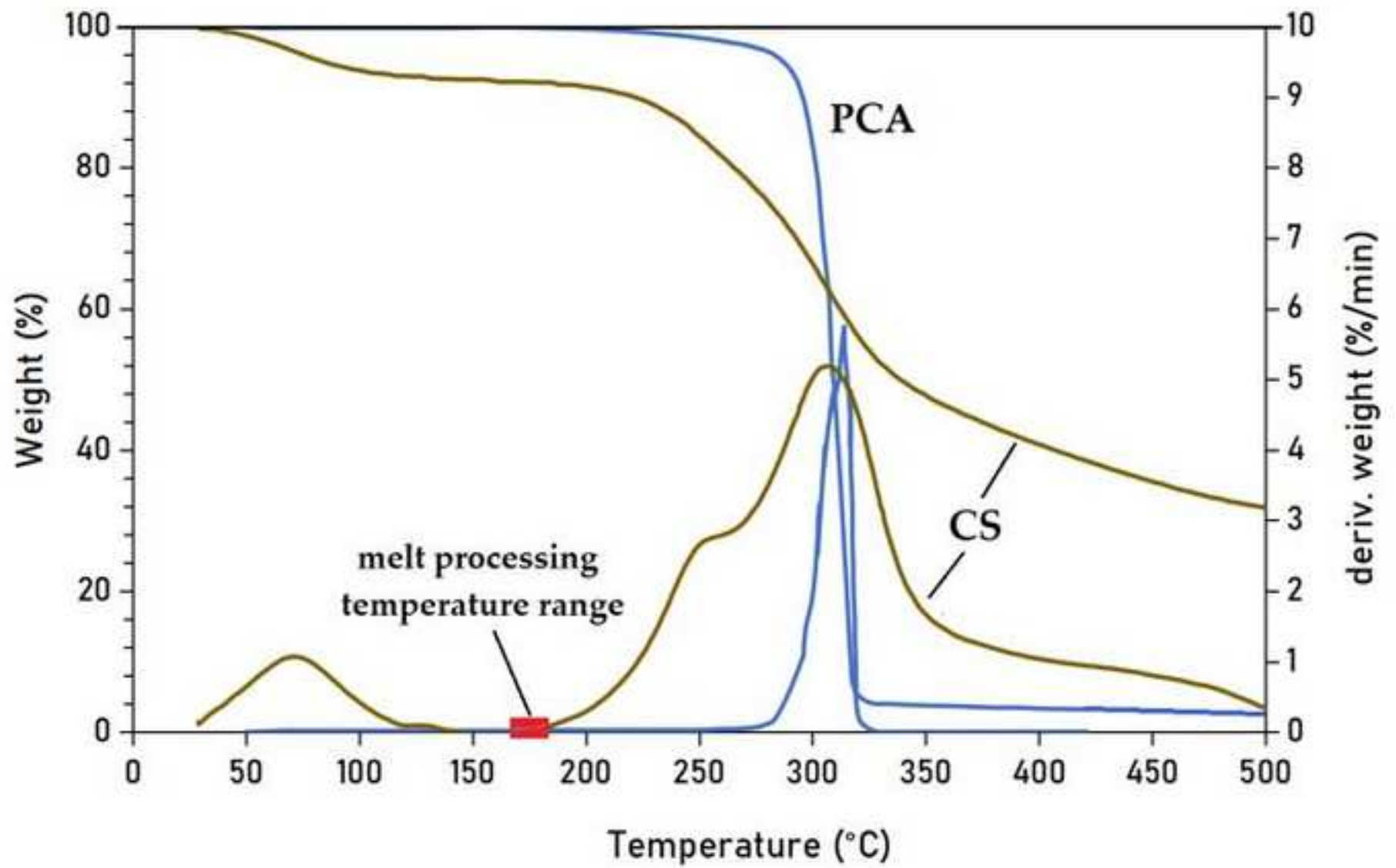


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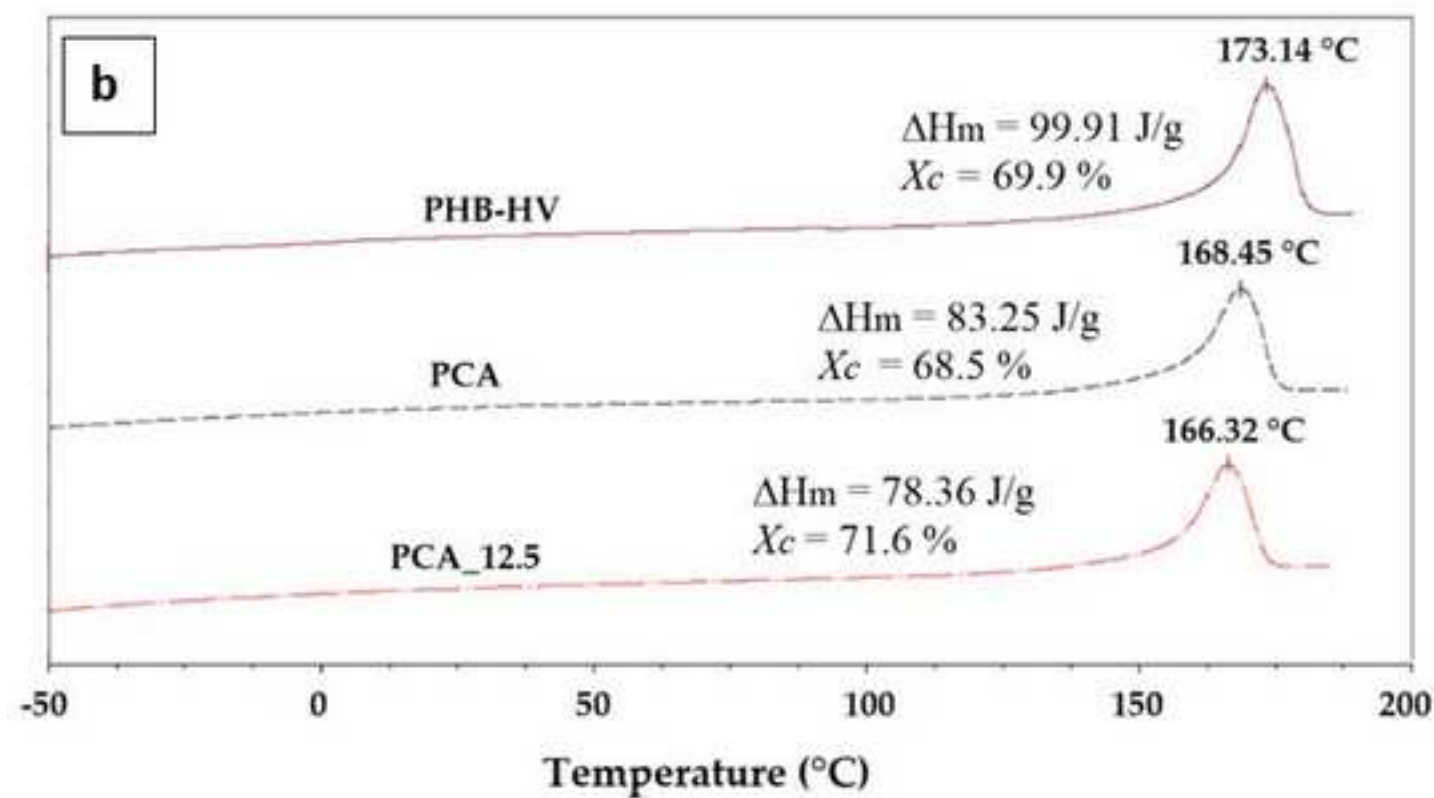
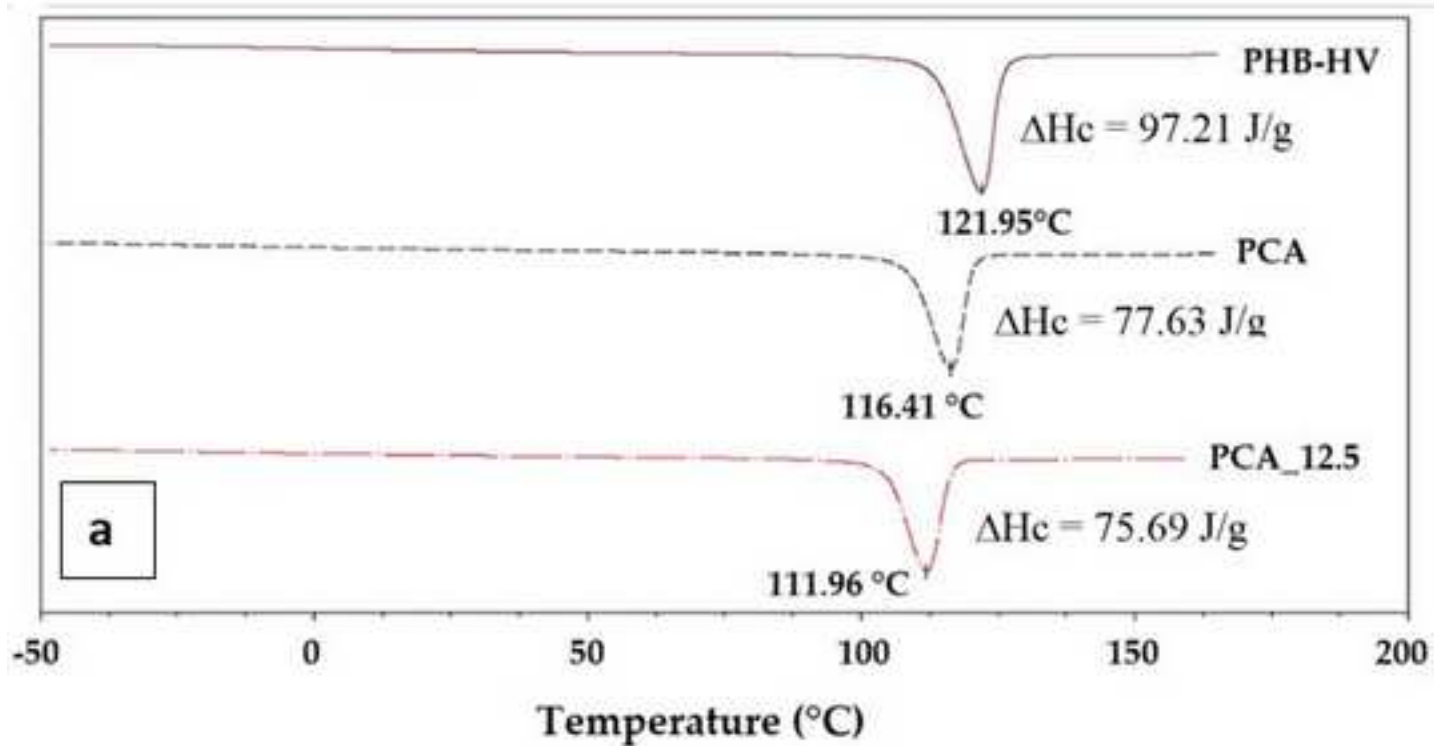


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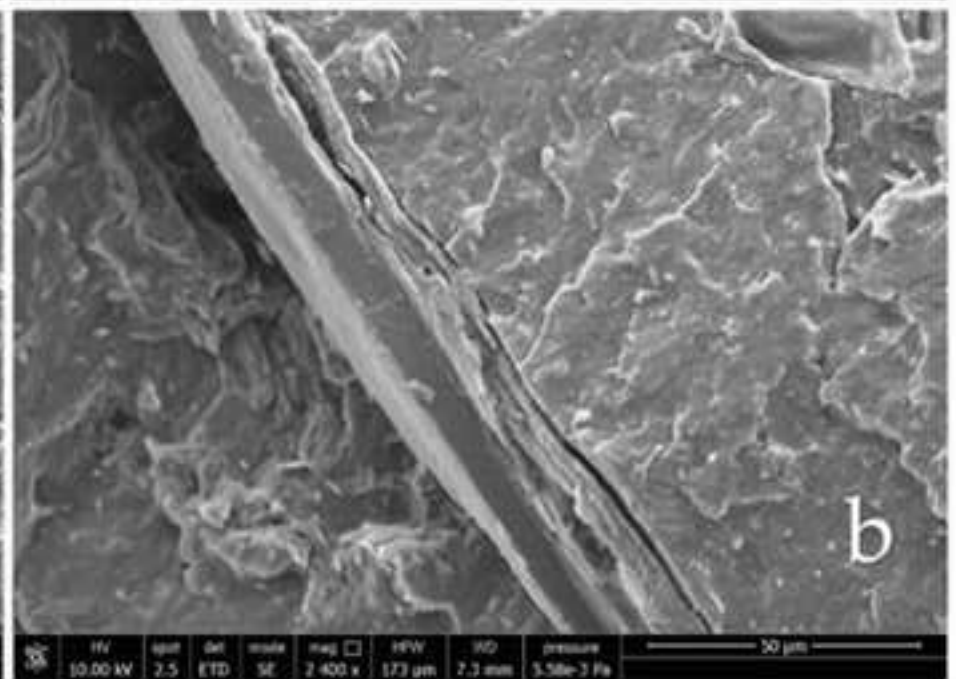
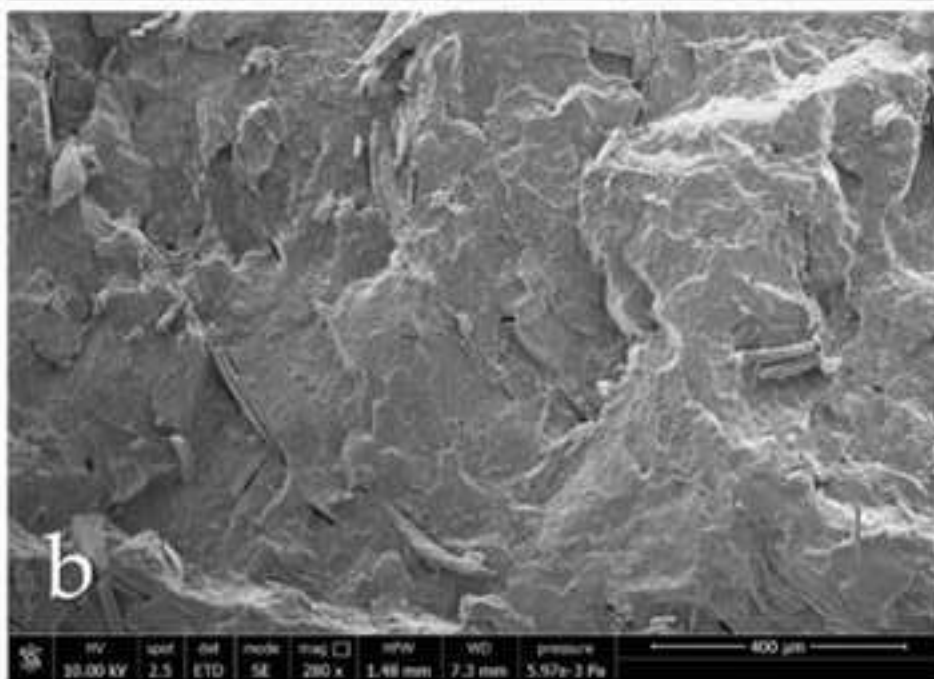
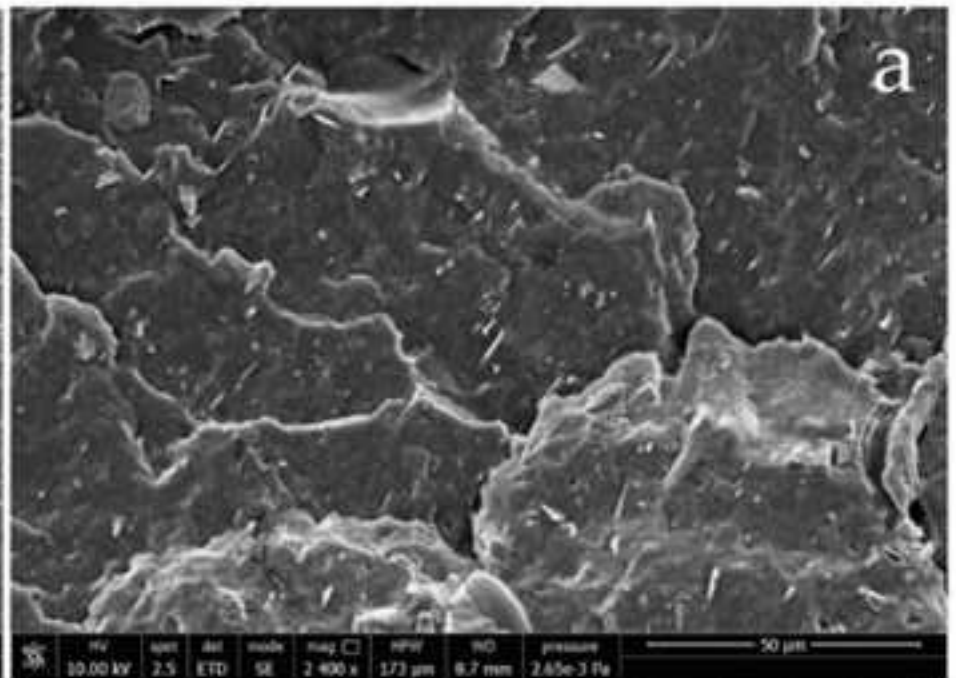
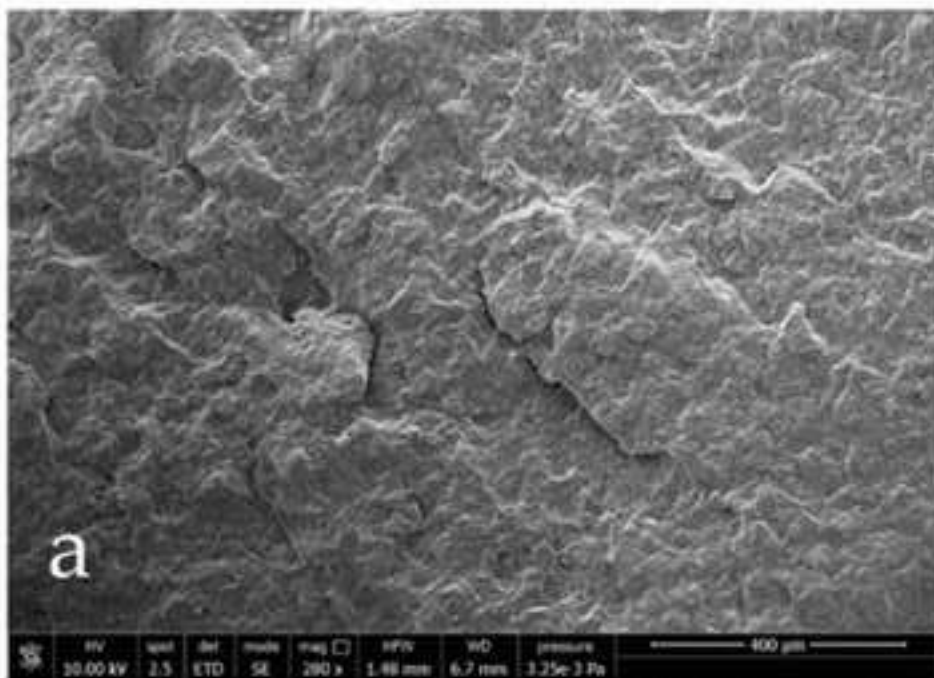


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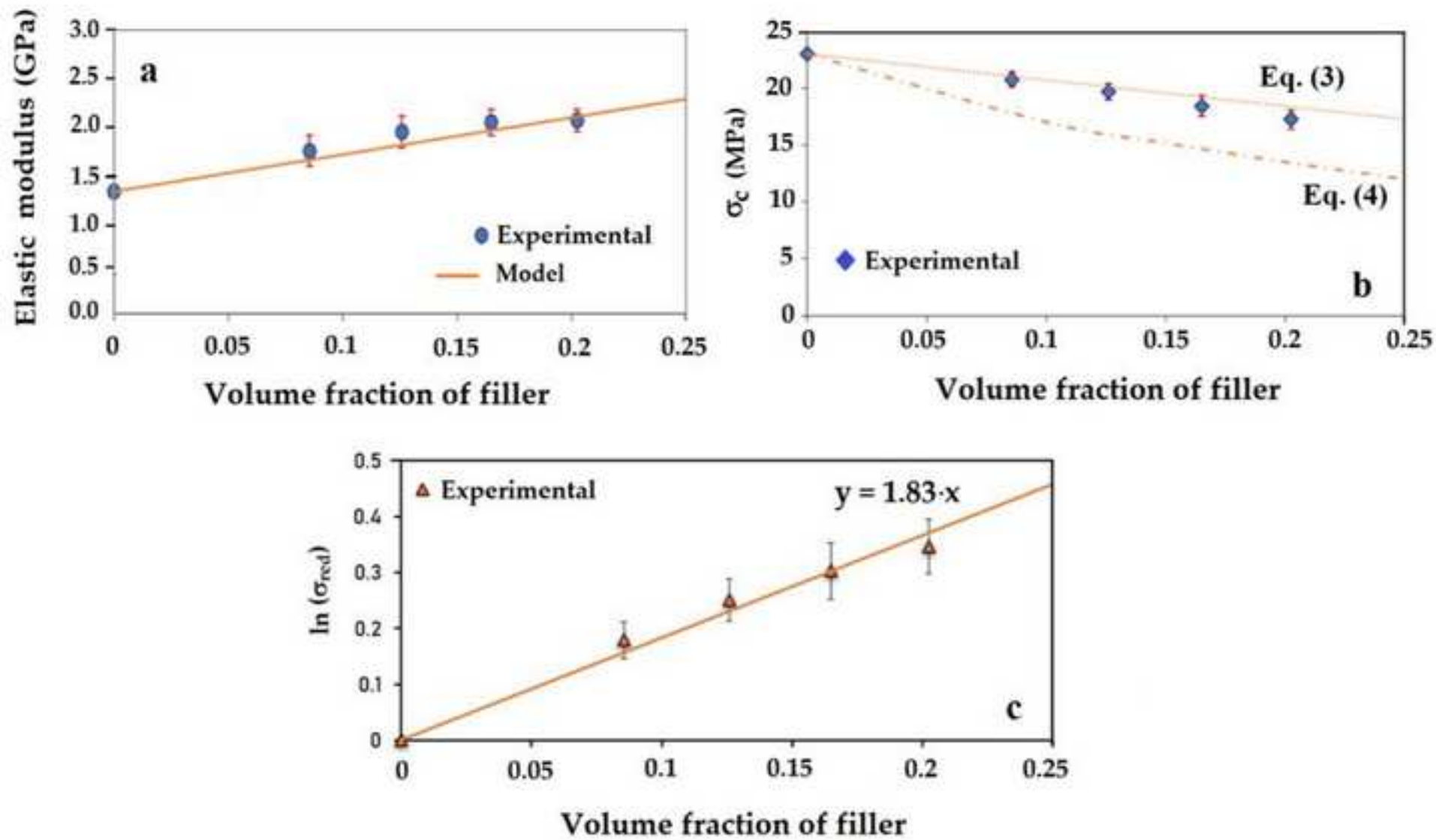
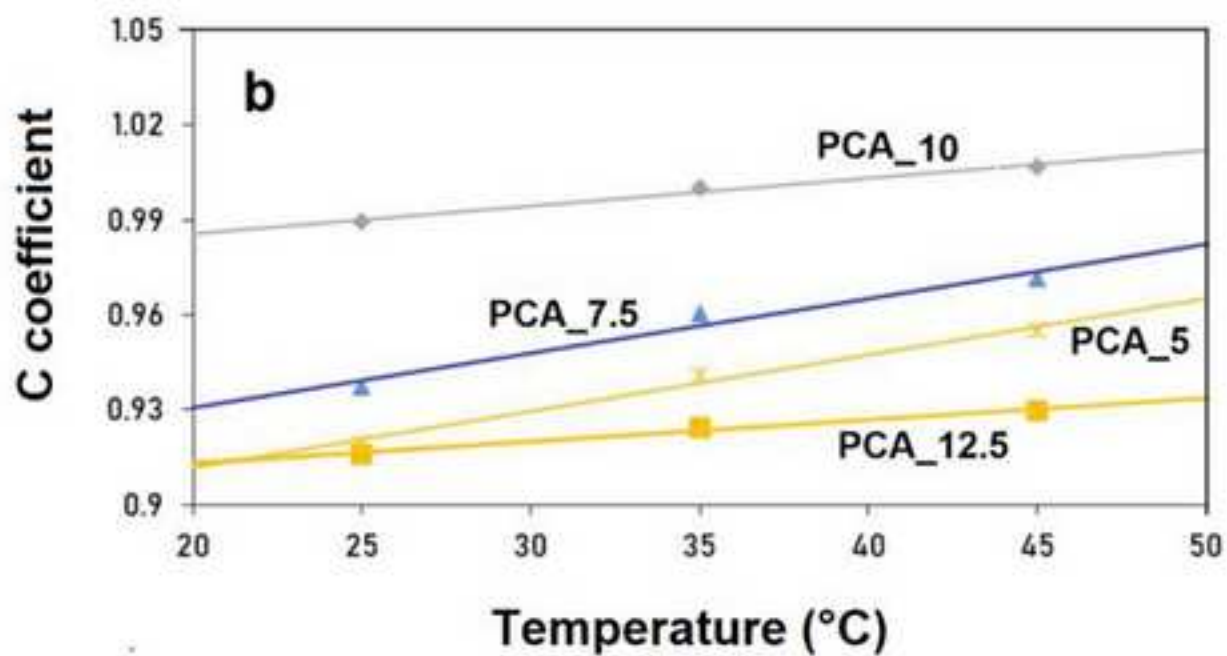
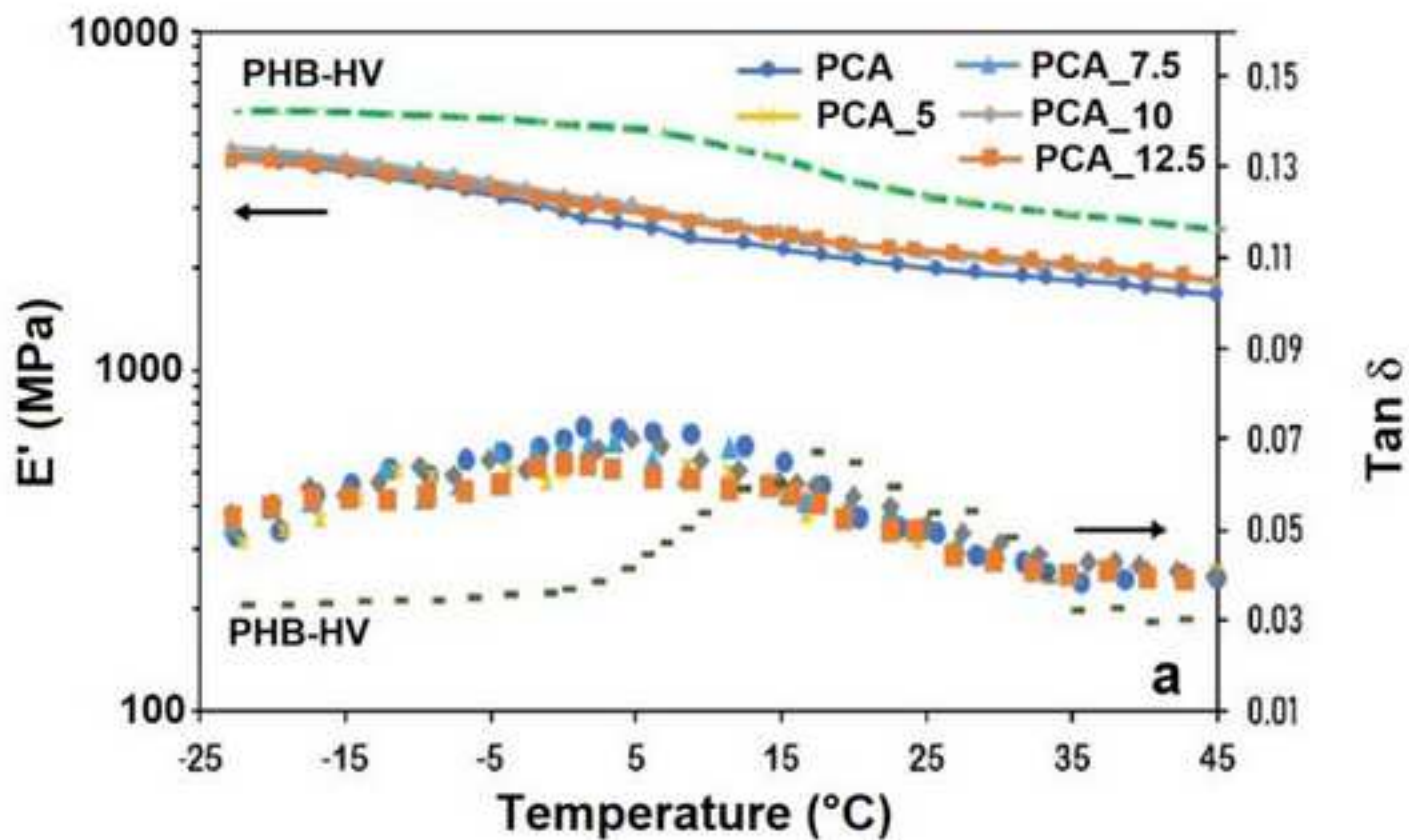


Figure 5

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Utilization of coffee silverskin in the production of thermoplastic biocomposites for food contact applications

Highlights

- Raw coffee silverskin (CS) was successfully processed with PHB-HV by melt extrusion
- Thermoplastic PHB-HV/CS composites up to 12.5 wt.% CS were produced and characterized
- CS behaved as filler showing medium-low adhesion with the PHB-HV matrix
- Coffee capsules were produced by injection molding using the PHB-HV/CS composites
- Overall migrations of coffee capsules at 100°C in different simulants were below the required limit.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: