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ARTICLE

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An investigation on the possible use of coffee silverskin in PLA/PBS composites

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Abstract

The production of degradable packaging materials is a task that can be no longer postponed. Moreover, high amounts of agricultural wastes are landfilled without any recycling. In this research, the possibility to formulate particulate composites made of biopolymers filled with coffee waste with acceptable physical and mechanical characteristics that will degrade is investigated. The addition of this agricultural waste, by reducing the requested amount of biopolymer, can decrease the overall price of the material presently the main limiting factor to the use of biopolymers in the packaging industry. Silverskin, the integument of coffee beans discarded during the roasting process, after a milling step, is added up to a 30 wt% either to polylactic acid (PLA) or to a blend of PLA and polybutylene succinate. The filler can be homogeneously dispersed in both systems. The data shows that the silverskin filler increases the elastic modulus but decreases the tensile strength of the material and helps the development of crystal phase in the matrix. The thermal stability and the hydrophobicity of the materials stay almost unchanged on filler addition. Moreover, data shows that the addition of silverskin increases the materials susceptibility to microbial attack.

KEYWORDS

coffee waste, durability, particulate composites, PLA/PBS blends

1 | INTRODUCTION

The drive for green production systems and materials for developing circular economy scenarios requires a careful assessment and a change in materials used. A key concern is the use of fossil fuel-based plastics that are persistent and non-degradable in the environment.[1–3] Therefore, the use of polymers deriving from renewable sources, capable of being degraded if dispersed in the environment or that can be exploited in compost production is a valid alternative to the use of oil derived commodities.[4–6] Among the different choices, polylactic acid (PLA) has attracted significant interest and is one of the biopolymers more widespread in use.[7–9] Whilst PLA is a useful polymer, in many cases it can be too brittle for specific end uses[1] and so it is often blended with other biopolymers such as polybutylene succinate (PBS) or poly (butylene adipate-co-terephthalate) (PBAT).[10–18] This blending can change, among other characteristics, the plasticity of the resultant blend making it more suitable

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for a wider range of uses. Another mechanism to change the properties of biopolymers is by the addition of fillers; when this filler is derived from agricultural or food wastes, the environmental benefits can be even more significant, and also reduce the overall amount of polymer needed which may have economic benefits. On the agricultural side, lignocellulosic plant fibers have been used to produce wood flour[19,20] or pure cellulose, in the form of microfibrillated or nanocellulose,[21,22] which has then been used to formulate composites. The main source of food waste is generally from industrial processing rather than domestic waste, but a wide range of food wastes have been investigated for producing plastic composites; for example wine harvest residues,[23,24] eggshells,[25] tea waste,[26] shellfish shell,[27] orange peel,[28] lemon peel,[29] garlic skin.[30] One industry that does produce considerable worldwide waste is the coffee industry where 45% of the bean goes to waste[31] either as husk, peel, pulp, or silverskin. The coffee silverskin is the thin covering skin on coffee beans and is a by-product of the beans roasting process. For each ton of treated beans, around 20–30 kg of silver skin are produced and with 9.5 million tons of coffee produced in 2018,[32] this forms a considerable waste stream. The chemical composition of silver skin is mainly based on soluble and insoluble dietary fibers, carbohydrates, and fatty acids.[33,34] They also contain phenolic and melanoidin[35] compounds that could be used as antioxidant additives. Whilst there are a number of approaches for the reuse of coffee waste, for example, for production of bioplastics such as polyhydroxyalkanoates[36] this paper concentrates on the use of coffee waste as a filler material for bioplastic blending. This use of spent coffee grounds and silver skin has been proposed in the formulation of several bioplastics with the majority of these utilizing polypropylene[37] or polyethylene[38,39] due to their good properties and widespread use. However, the use of alternative biodegradable polymers such as PLA[40–42] or PBAT[43,44] has been investigated. Use of coffee waste has been shown to reduce tensile strength but increase the young's modulus when used with polypropylene. However, with PLA or PBAT, whilst Young modulus is still increased, the tensile strength can be either increased or decreased based on processing parameters and rigor of any preprocessing of the coffee waste, although some advantage to using silverskin over spent grounds was reported.[31]

The present research investigates the use of coffee silverskin (up to a 30 wt% fraction) as a filler with PLA as it is presently one of the most commonly used biopolymers and with a blend of PLA/PBS. A blend containing 90% wt PLA and 10% PBS is selected, since higher amounts of PBS lead to an incomplete miscibility. The aim of using this blend is to increase the plastic deformation of PLA as well as to increase both its processing capabilities and its tendency towards hydrolytic degradation. Moreover, the waste addition is performed in order to produce a bioplastic with improved or comparable physical characteristics compared to PLA that can also degrade naturally over time. To improve the environmental credentials no chemical treatments were performed on the filler. An overall characterization of the composites has been carried out to study the effect of natural filler addition. The mechanical properties of the derived composites as well as their thermal properties were determined. Since the most likely use of these materials is in the packaging industry, the interaction with moisture (hydrophobicity) and the effect of microbial activity in soil were also investigated.

2 | MATERIALS AND METHODS

2.1 | Materials

Poly lactic acid (PLA) (Ingeo™ Biopolymer 2003D) with specific gravity of 1.24 g.cm^{-3} and melt flow index (MFR) equal to 6 g.10 min^{-1} (210 C, 2.16 kg) was obtained from NatureWorks LLC CO., USA. Bio-based polybutylene succinate (PBS) (BioPBS™ FZ91PM) with specific gravity of 1.26 g.cm^{-3} and MFR equal to 5 g.10 min^{-1} (190 C, 2.16 kg) was supplied by PTT MCC Biochem Co., Thailand.

Coffee silverskin was obtained from roasting process of coffee beans (a mixture of about 30%wt of Robusta and 70%wt of Arabica), provided by Caffe'Cagliari spa Co., in Modena, Italy. The elemental analysis of coffee silverskin can be summarized as it follows: N% 3.24; C% 44.07; H% 5.81; S% 0.00, ashes 9.32 wt% (550°C after 4 h). Coffee silverskin was ball milled in a rotary mill (MMS, Nonantola, Italy) at 200 rpm for 20 min in a 300 ml Alubit jar at room temperature, with the final particle size distribution obtained by laser granulometry using a Malvern Mastersizer 2000 model (produced by Malvern Instruments, UK) as shown in Figure 1. Hereafter, the coffee silverskin will be simply referred to as CS.

2.2 | Sample preparation

Prior to compounding, PLA, PBS, and CS powders were oven-dried at 60 C under vacuum for 12 h to eliminate moisture and any absorbed gases. The compounding process for each of the different polymer/blend compositions was performed using a plasti-corder apparatus (Produced by Brabender Co, Germany) at 190 C for 10 min with a rotational speed of 60 rpm.

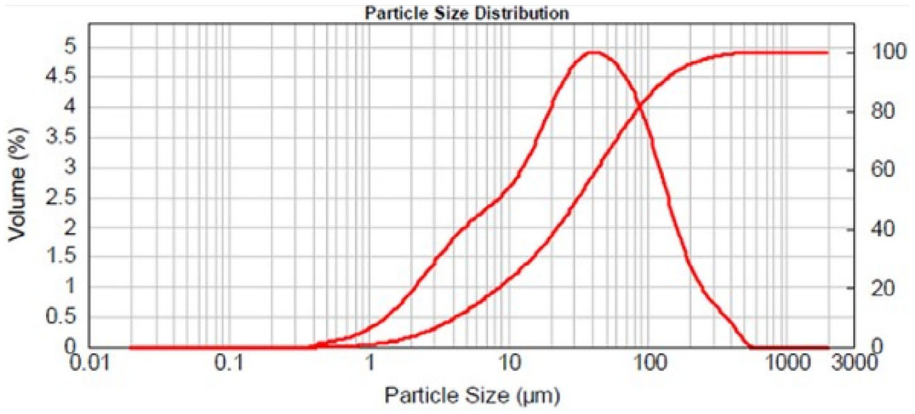

FIGURE 1 Particles size distribution (cumulative and retained) of coffee silverskin after milling [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 1 Composition (wt%) and sample codes of the investigated materials

Sample code	PLA (wt%)	PBS (wt%)	CS (wt%)
PLA	100	0	0
PLA-20CS	80	0	20
PLA-30CS	70	0	30
PLA/PBS	90	10	0
PLA/PBS-20CS	72	8	20
PLA/PBS-30CS	63	7	30

From this compounded material "dog-bone" shaped samples with dimensions of 25°×°5°×°2 mm, were produced by injection molding using Haake minijet pro (Produced by Thermo scientific Ltd.) for Tensile test. Film samples were obtained from the compounded blends by sheet formation via extrusion using a twin-screw extruder (Labtech scientific type LTE −26-40) and a film casting line (Labtech LCR-300), with screw speed of 120 rpm at a temperature maintained between 160 and 185 C for biodegradability test and determination of water contact angle.

The samples are coded to show the base polymer (PLA or blend) with the percent of silverskin added such that PLA-20CS is PLA with 20 wt% of silverskin and PLA/PBS-20CS is the blend filled with a 20 wt% of silverskin. Table 1 shows the composition of all the investigated composites and summarizes the relevant codes.

2.3 | Isothermal crystallization

Differential scanning calorimetry thermal analysis was performed on the compounded material using a Thermal Analysis instruments model TA Q10, under nitrogen flow. Samples (10–11 mg) of each investigated material were submitted to the following thermal cycle:

1. Heating at 175°C
2. Isothermal treatment for 5 min
3. Rapid quenching to 90°C
4. Isothermal treatment for 90 min

The exothermic peak related to the crystallization was recorded. Three different replicate measurements were performed. The time corresponding to half of the crystallization, $t½$, as well as the enthalpy of the process were determined taking advantage on the internal software of the TA instrument (TA Universal Analysis software).

2.4 | Thermal gravimetric analysis

The thermal stability of materials was carried out using a thermogravimetric analyzer (TGA/DSC 1 Star System produced by Mettler Toledo, USA) under a nitrogen atmosphere with a gas flow rate of 100 ml.min^{-1}. The samples (10 mg) were heated from 50 to 800°C with a rate of 10°C.min^{-1}. The degradation temperature (T_{onset}), defined as the initial temperature of degradation, corresponding to the intercept of the tangent drawn at the inflection point of the decomposition step with the horizontal zero-line of the thermogravimetric curve was determined, as well as the temperature (T_{max}) at which the rate of weight loss reaches its maximum. The plot of the derivative of the mass loss (DTG) is usually reported to better underline the different steps of degradation.

2.5 | Mechanical properties

Tensile tests were performed on the dog-bone shaped samples using an INSTRON 5966 series test apparatus, without preloading and with speed of 5 mm per minute following the standard ISO 527-1, on five replicate samples for each composition. The instrument reported the stress–strain graph for each composition, and the value of Young's modulus calculated by means of the slope of

linear part of these curves without the use of an extensometer.

2.6 | Scanning electron microscopy

The morphology of the tensile fractured specimens was observed by SEM, (FEI, XL20 microscope, secondary electron detector, at 15 kV) after aluminum sputtering on the sample surfaces (Quorum 150R ES).

2.7 | Biodegradability

The potential for microbial breakdown of the samples was evaluated with a soil jar method using unsterile soil and samples (15°×°2°×°thickness) that were cut from composite films. Samples of the composite films were placed inside jars filled with the soil (John Innes No 2) at approximately 40% moisture content. The samples were placed so that half of each of the samples was below the soil level and half above. Five replicate samples were used for each composite and the jars were maintained at 21°C and 65% relative humidity for 6 weeks, before assessment by visual and mass loss criteria. This test is a non-standard test developed from methods described by Curling[45] and the standard method ENV807,[46] which a method devised for testing wood preservatives but which, with material specific adjustments can be used for general testing of microbial action in soil contact. This method can be used to determine whether microbial action affects the material and therefore whether longer term biodegradation or composting trials would be advisable.

2.8 | Water contact angle

In order to investigate the value of water contact angle for different samples, Drop shape analyzer DSA30S produced by KRUSS Co. was used. Prior to performing the test, samples were kept under vacuum for 40 h at room temperature. A 4-μl distilled water drop was measured out from the syringe and dropped on the surface of the samples. The drop was allowed to reach equilibrium before measurement was recorded and before evaporation occurs. Five replicate drops for each sample were used and the final value of contact angle calculated as the mean of the values.

2.9 | Statistical analysis

Statistical analysis of data was performed using one-way analysis of variance (ANOVA) tests a significance level of $p = 0.05$ followed by Tukey's HSD test to examine intra-group pair means for statistical significance.

3 | RESULTS AND DISCUSSION

3.1 | Isothermal crystallization

The PLA sample shows only a limited tendency towards crystallization. This feature has been underlined in literature,[47,48] and in our case, it may derive from its high molecular weight. This is shown by the results of the isothermal crystallization tests (Figure 2), in that the PLA has a high t ½ value (the time required to reach half of the overall isothermal crystallization), and a low crystallization enthalpy applying to the amount of polymer in the sample. However, the data shows that by adding a faster crystallizing polymer (PBS Figure 2) in the blend development of the ordered crystalline phase is encouraged. A similar effect is also shown by the addition of the silverskin filler both in the pure PLA and in the blend. The PBS/filler appears to be acting as a nucleating agent in a similar way that has been previously reported in literature for lignin-based fillers.[49] Also polyphenols, present in the filler, have been found to have a promoting effect on PLA crystallization[50,51] The effect of the filler is progressive; the level of crystallization increases as the amount of silver skin increases (Figure 2) particularly with the pure PLA but also in the blend, although to a lesser extent. However, there does not appear to be any synergic effect derived from the concurrent addition of PBS and CS, as found elsewhere.[52] Indeed, PBS preferentially interacts with the cellulose surface creating an interference effect with co-polymers. Hence, the PBS preferentially interacts with the CS precluding a synergic increase of PLA crystallinity. Therefore, in terms of crystallinity adding only one of either the PBS or silverskin would appear to be the most beneficial.

3.2 | Thermal gravimetric analysis

PLA and PLA/PBS samples degrade in a single step process between 350 and 400°C and the behavior is unchanged by the presence of PBS (Figure 3). This degradation is due to the scission of the ester linkages present in the main chains of both polymers.[53]

In contrast, the thermal stability curve of the silverskin shows three different degradation steps which can be attributed as follows,

50 to 110°C Moisture loss from the sample

200 to 400°C Decomposition of hemicellulose (around 260°C) and cellulose (around 340°C).[54]

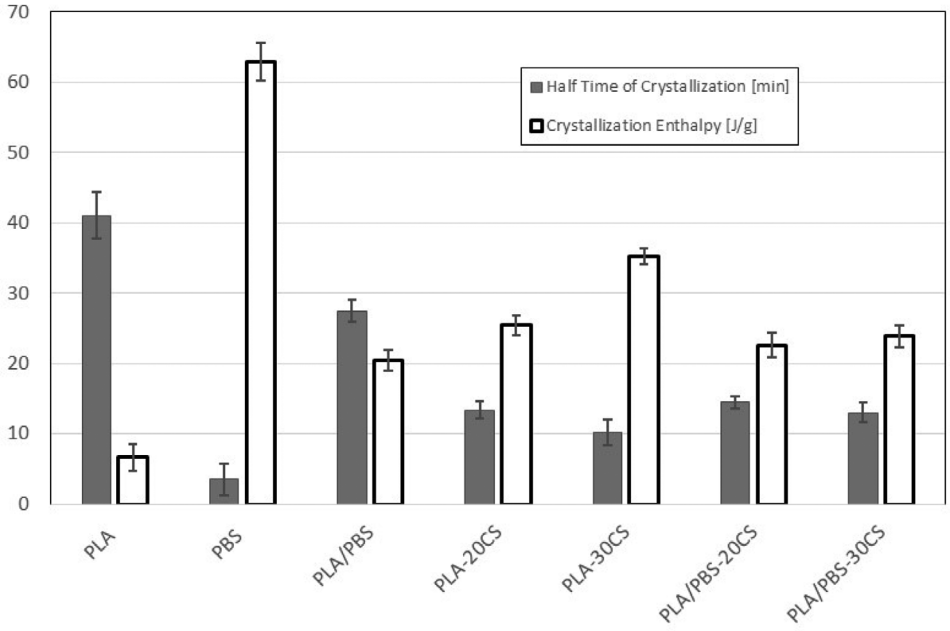

FIGURE 2 Half time of crystallization and crystallization enthalpy of the isothermal peak recorded in isothermal conditions at 90°C. (PLA = polylactic acid; PBS=polybutylene succinate; PLA/PBS = blend of the two polymers; PLA-20CS = polylactic acid +20% silverskin; PLA-30CS = polylactic acid +30% silverskin; PLA/PBS-20CS = blend +20% silverskin; PLA/PBS-30CS = blend +30% silverskin)

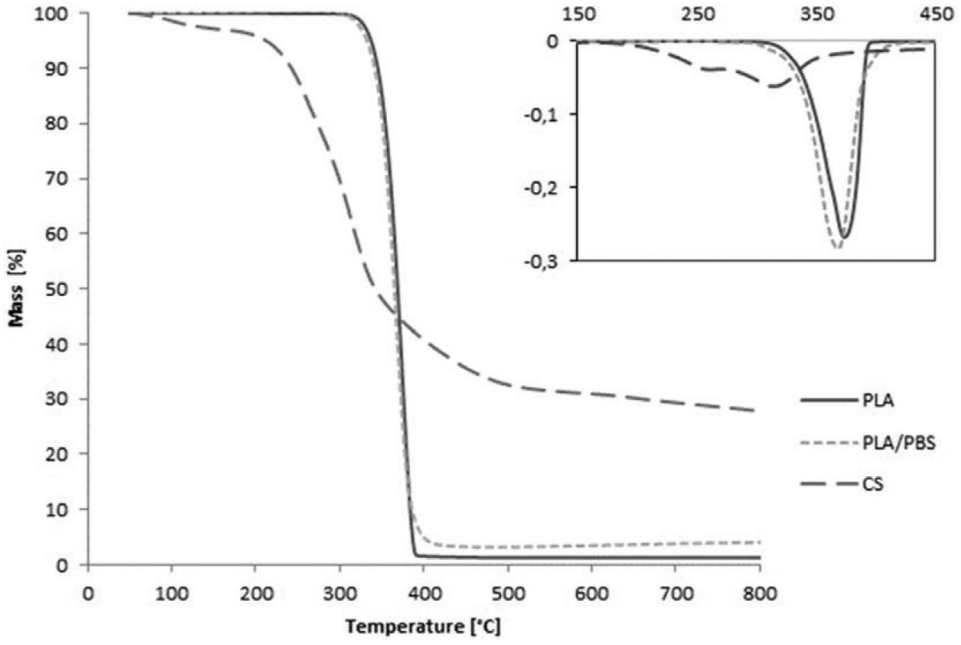

FIGURE 3 TGA curves and their first derivatives for polylactic acid, polylactic acid/polybutylene succinate blend (PLA/PBS), and coffee silverskin

400°C and over Degradation of lignin

The DTG shows the overlapping of the peaks relevant to hemicellulose and cellulose. The degradation of the silverskin leaves a residue of inorganic ash as shown by the higher residual mass for the silverskin as compared with the polymers.

The thermal degradation of the composites again takes place in a rapid single step similar to the pure PLA and PLA/PBS samples (Figure 4) with the three-step degradation of the silverskin generally masked by the higher proportion of PLA, demonstrating the PLA component has the key role in thermal stability of the bio composites.

However, we can see that the increase in the amount of silverskin in the samples leads to a limited decrease in the onset temperature of the decomposition of the materials (Table 2). The slight effect could derive from the degradation of the hemicellulose components of the natural material that is however enveloped by the PLA matrix. The mass of the final residue (Table 2 and Figure 3) at high temperatures increases as the amount of silver skin increases compared to that observed for the polymers, again due to the ash of the silverskin. PBS reduces the thermal values slightly but appears to have no effect on values when the silverskin is added, as the

values at 20% and 30% addition are almost coincident with or without PBS. Hence it can be said that the small amount of PBS (10%wt) does not affect the processing thermal properties of the final polymer blend.

3.3 | Mechanical properties

The addition of both the PBS and the silverskin have clear effects on the mechanical properties of the compounded materials (Table 3). The data shows that the Youngs modulus increases in all the composites when compared with the pure PLA and PLA/PBS matrices. However, it should be noted that adding PBS reduces the Youngs modulus when compared to the pure PLA samples. Adding silverskin to the polymers increased the Young's modulus by 20% for PLA-20CS and 31% for PLA-30CS as compared with the base PLA. In comparison silverskin addition only increases Youngs modulus by 18% for PLA/PBS-20CS and 28% for PLA/PBS-30CS in

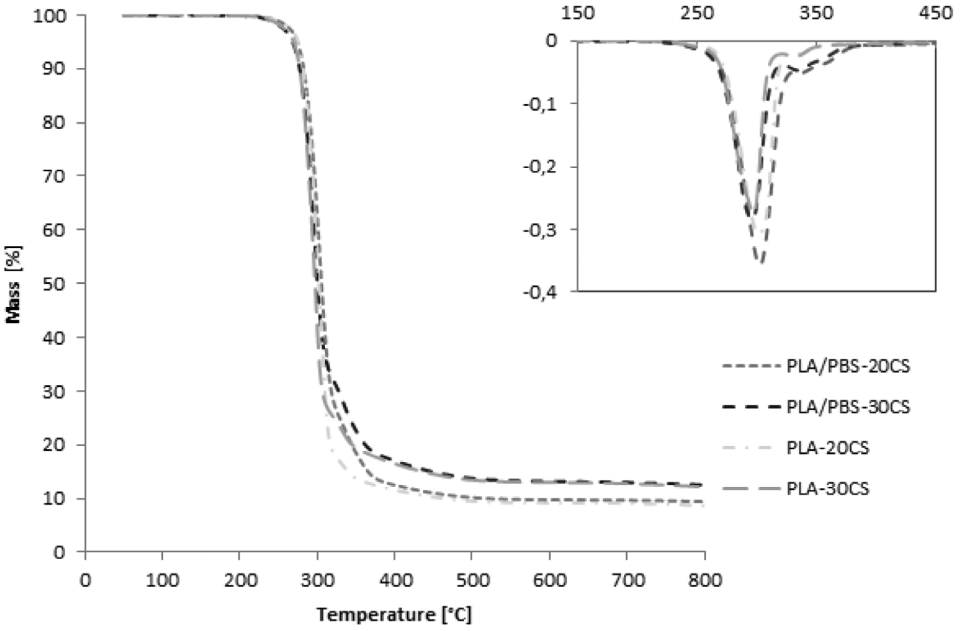

FIGURE 4 TGA curves and their first derivatives for biocomposites. (PLA-20CS = Polylactic acid +20% silverskin; PLA-30CS = Polylactic acid +30% silverskin, PLA/PBS-20CS = blend +20% silverskin; PLA/PBS-30CS = blend +30% silverskin)

Sample	T_{onset} (°C)	T_{max} (°C)	Residue (%)
PLA	350	373	1.3
PLA with 20% coffee silverskin	283	306	8.6
PLA with 30% coffee silverskin	279	298	12.1
PLA/PBS	345	368	4.1
PLA/PBS with 20% coffee silverskin	283	305	9.4
PLA/PBS with 30% coffee silverskin	277	296	12.5

TABLE 2 Decomposition onset temperature, T_{max} and residue of the polymer samples and blends with and without added coffee silverskin

TABLE 3 Mechanical properties of the investigated materials. (all values are expressed as mean values ± standard deviation [SD])

Sample	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
PLA	1967 ± 17^{a}	70.1 ± 0.9^{a}	7.2 ± 0.9^{a}
PLA-20CS	2375 ± 52^{b}	52.8 ± 0.9^{b}	3.2 ± 0.3^{c}
PLA-30CS	2586 ± 55^{c}	$47.3 \pm 5.1^{b,d}$	2.4 ± 0.5^{c}
PLA/PBS	1756 ± 19^{d}	60.3 ± 1.2^{c}	15.7 ± 2.6^{b}
PLA/PBS-20CS	2075 ± 35^{a}	$48.0 \pm 1.3^{b,d}$	3.6 ± 0.3^{c}
PLA/PBS-30CS	2259 ± 21^{e}	42.9 ± 1.1^{d}	2.7 ± 0.2^{c}

[a-e]Values in the same column with different superscripts are signifcantly different ($p \leq 0.05$).

comparison to the base PLA/PBS blend. Therefore, increased levels of silverskin in the PLA/PBS blend offset the reduction caused by the PBS addition. The increase in Youngs modulus can be partially related to the previously described increase in crystallinity promoted by the presence of silverskin but mainly to the composition of the filler that contains approximately 18% of cellulose and 2% of lignin.[55]

The stress–strain curves (Figures 5 and 6) demonstrate a progressive decrease in the values of the tensile strength, by increment in the silverskin content. This reduction in the values of tensile strength shows that increasing the amount of silverskin leads to a poor stress transfer capability and results in easier fracture. It is however to be underlined that this detrimental effect is lower than the one found in other composites where different agro-wastes have been used. For example, potato pulp powder produced a 30% decrease in tensile strength when used at 20 wt% as a filler in poly(3-hydroxybutyrate-co-3-hydroxyvalerate).[56] A 30%wt addition of coffee grounds to PBAT more than halved the original tensile strength[57] and the addition of wood flour at 30 wt% to a blend of

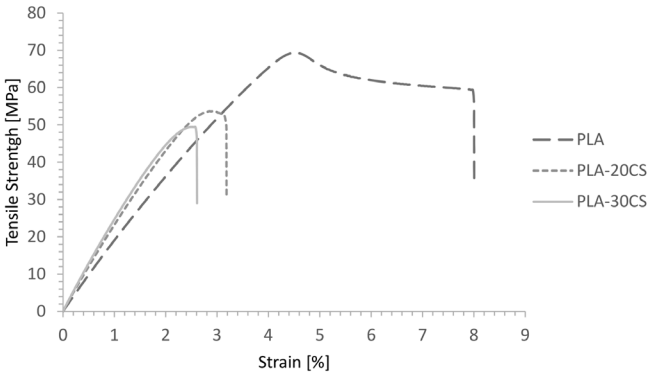

FIGURE 5 Representative stress–strain curves for the base PLA, PLA with 20% silverskin (PLA-20CS), and PLA with 30% silverskin (PLA-30CS) samples

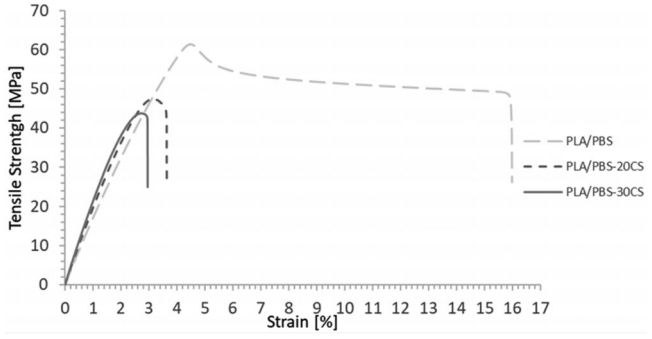

FIGURE 6 Representative stress–strain curves for the base PLA/PBS blend, PLA/PBS with 20% silverskin (PLA/PBS-20CS), and PLA/PBS with 30% silverskin (PLA/PBS-30CS) samples

PLA/PBS reduced the tensile strength to about one third of the original one[19] In the case of silverskin, there seems to be a better interaction with the surrounding matrix probably deriving from a similar hydrophobicity. When these figures are compared those of the current study with 24% and 20% reduction at 20% silverskin and 32% and 28.5% reduction at 30% silverskin for PLA and PLA/PBS respectively then it can be seen that the silverskin containing samples perform favorably.

Elongation at break is decreased by addition of the silverskin with higher proportions of silverskin having a greater effect. This is a common trend in thermoplastic composite properties as reported in literature,[42,43,58,59] that is, a decrease in the deformation at break as the concentration of filler increases. Blending PBS with PLA leads to a significant increase in the ductility of the blend,[13] although a comparison between silverskin loading cancels this effect (Figures 5 and 6) and results in a decrease in the extent of elongation at break of up to 80% for PLA/PBS-30CS.

The data shows that by changing the type and level of additive the mechanical properties of the base PLA can be changed. For example, for the highest ductility then PBS without silverskin would be the best additive whilst if higher Young modulus is required then PLA with added silverskin, but no PBS might be a solution.

3.4 | Scanning electron microscopy

Scanning electron micrographs (250×) of the fracture surface after tensile test, for unloaded samples as well as the different composites are shown in Figure 7. The fracture surface of pure PLA is featureless flat, smooth, and discloses a brittle fracture (Figure 7a). However, for the PLA/PBS sample we can observe evidence of increased ductility (Figure 7d). The distribution of coffee silverskin in all the samples are nearly homogeneous, and no clustering of silverskin was found. This feature underlines an efficient mixing during the compounding process. From the micrographs, it is noticeable that the fracture surface of the samples gets rougher by increasing addition of the amount of coffee silverskin. Pores of low dimension (2–6 microns) can be seen in the matrix consequently contributing to the tensile strength reduction observed during tensile tests.

3.5 | Contact angle analysis

The surface wettability of the samples, evaluated in this study as water contact angle measurement, is important since it helps gain an understanding of the interaction between these materials and the environment, particularly when it comes to packaging materials. The mean

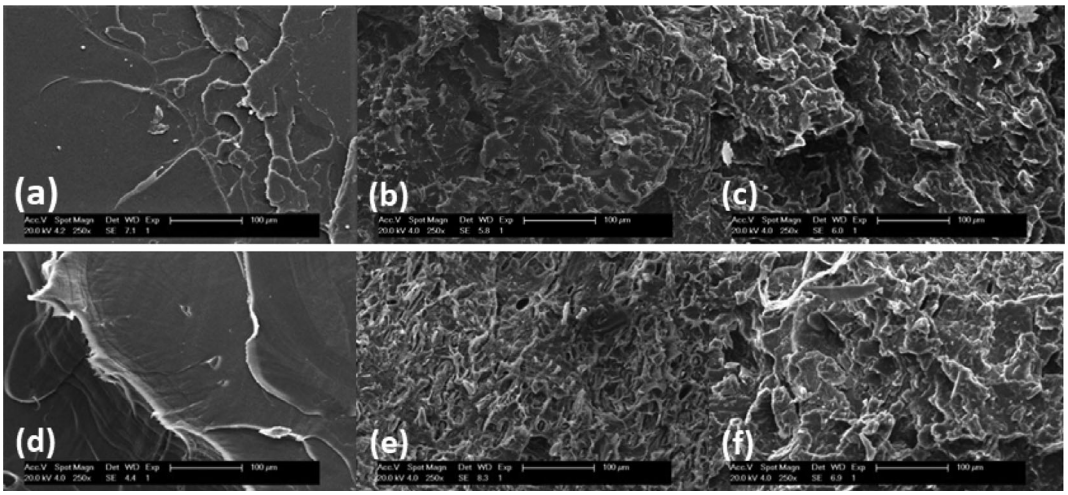

FIGURE 7 SEM images of the tensile fracture surface of: (a) PLA, (b) PLA with 20% silverskin (PLA-20CS), (c) PLA with 30% silverskin (PLA-30CS), (d) PLA/PBS, (e) PLA/PBS with 20% silverskin (PLA/PBS-20CS) (f) PLA/PBS with 30% silverskin (PLA/PBS-30CS)

TABLE 4 Values of contact angle for different samples. (all values are expressed as mean values ± standard deviation [SD])

Sample	Contact angle (*)
PLA	94.2 ± 3.77^{a}
PLA with 20% silverskin	$88.2 \pm 3.83^{a,b}$
PLAwith 30% silverskin	87.2 ± 4.23^{b}
PLA/PBS	84.8 ± 2.58^{b}
PLA/PBSwith 20% silverskin	85.6 ± 3.87^{b}
PLA/PBSwith 30% silverskin	86.5 ± 2.02^{b}

[a,b]Values with different superscripts are significantly different ($p \leq 0.05$).

value of contact angle for pure PLA is 94.2 deg, whereas this value for the PLA/PBS is 84.4 deg (Table 4). The decrease of about 10 ° in this property can be explained by the effect of PBS increasing the wettability and inducing water permeation channels in PLA.[42,60] In contrast adding silverskin to the PLA does reduce contact angle but not to as great an extent as by adding PBS. Conversely, in PLA/PBS blends silverskin addition has a negligible effect on the contact angle value. The differences are however rather limited, a feature that seems to support the observation previously made for explaining the effects on the mechanical properties, that is, the close hydrophobic characteristics of filler and matrix. However, by changing the additives used in the PLA the moisture sorption properties of the polymer blend can be changed.

3.6 | Biodegradation

Following the short biodegradation test, all specimens remained intact when removed from the soil and there were no obvious signs of biodegradation such as holes or major color change. There were visible signs of growth of microorganisms at the soil level and above although these were not identified. Some differences in final moisture content and mass loss of the samples were observed as shown in Table 5. The amount of weight loss after 42 days at low temperature is remarkable for all samples when compared with other biopolymers tested in more demanding conditions.[61] The PLA samples showed low moisture and very low mass loss, with mass loss increasing with the addition of PBS. In general, addition of silverskin was shown to increase both final moisture content and mass loss. The PLA/PBS-20CS sample however, had a lower final moisture content and a corresponding lower mass loss than the other sample types containing silverskin. This could be due to the slightly higher tendency towards crystallization of this sample compared with the one formulated with just PLA and 20 wt% of silverskin. However, at an addition rate of 30% the highest mass loss of all the sample types was observed, thus indicating that the extra addition of the silverskin improved biodegradability, with results affected by other concomitant effects, such as increased porosity.

The rate of decomposition for polyester biopolymers depends, apart from the test conditions[62] (temperature, relative humidity, and so on) on structural and microstructural features such as crystallinity, porosity, and hydrophobicity. It has been proved (Figure 2) that silver skin promotes crystallinity development and decreases the contact angle with water (Table 4). At the same time, according to the decrease in mechanical properties, the imperfect transition interface between the matrix and filler can create preferential paths for the water diffusion as well as it is promoted by the formation of porosities as evidenced by microscopy. At high amounts of CS, the

TABLE 5 Moisture content and mass loss of composites after 42 days (mean value ±standard deviation. (refer to Table 1 for sample codes)

Sample	Moisture content after exposure (%)	Mass loss (%)
PLA	1.04 ± 0.53^{a}	0.48 ± 0.52^{a}
PLA/PBS	2.55 ± 1.85^{a}	3.07 ± 4.97^{b}
PLA with 20% silverskin	21.65 ± 2.86^{c}	4.19 ± 0.51^{c}
PLA- with 30% silverskin	28.97 ± 4.59^{d}	5.33 ± 0.78^{d}
PLA/PBS - with 20% silverskin	15.30 ± 3.20^{b}	3.02 ± 0.60^{b}
PLA/PBS - with 30% silverskin	$26.47 \pm 6.60^{c,d}$	5.93 ± 0.45^{d}

[a-d]Indicate groups separated significantly at $p = 0.05$.

porosity effect becomes predominant thus leading to increased water penetration leading to a faster decomposition. This simple test shows that the silverskin addition leads to increased microbial breakdown of the materials. Further testing to determine the specific levels of biodegradation or composting are still required, however.

4 | CONCLUSIONS

Coffee silverskin, obtained as a by-product from coffee production, has been successfully dispersed in PLA and PLA/PBS formulations in amounts up to 30 wt% thus reducing the overall quantity of biopolymer matrix. Elastic modulus of all the resulting biopolymer blends was increased although there was a concurrent modest lowering (max 32%) of the tensile strength of the materials. A contribution to this enhancement derives from the nucleating effect of the silverskin that promoted higher crystallinity. Although the filler addition tends to level the plasticity of the blend, when compared with pure PLA, PLA/PBS composites still maintain a higher deformation at break. Preliminary tests on biodegradation suggest that, despite the increase in crystallinity, on account of the low values of the contact angles of the specimens, significant mass loss was measured in ambient conditions after a relatively short time. Overall, the material possesses acceptable mechanical properties which can be selected to give differing characteristics based on the additives used. The materials also show promise for further trials aimed at determining the composting and disposal profile with an aim to provide an acceptable environmental impact.

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CONFLICT OF INTEREST

The authors declare no potential conflict of interest.

AUTHOR CONTRIBUTIONS

Amir Kia Aghaye Ghazvini: Data curation (lead); investigation (lead); writing – original draft (lead). **Simon Curling:** Formal analysis (equal); methodology (equal); writing – review and editing (equal). **Graham Ormondroyd:** Conceptualization (equal); supervision (equal); validation (equal). **Andrea Saccani:** Methodology (equal); validation (equal); writing – review and editing (equal). **Laura Sisti:** Conceptualization (equal); resources (lead); supervision (equal).

DATA AVAILABILITY STATEMENT

Data available on request from the authors

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REFERENCES

[1] K. Amulya, R. Katakojwala, S. Ramakrishna, S. Venkata Mohan, *Composites, Part C* **2021**, *4*, 100111.
[2] A. Pellis, E. Herrero Acero, V. Ferrario, D. Ribitish, G. M. Guebitz, L. Gardossi, *Trends Biotechnol.* **2016**, *34*, 316.
[3] V. Shanmugam, R. A. Mensah, M. Försth, G. Sas, Á. Restás, C. Addy, Q. Xu, L. Jiang, R. Esmaeely, N. Shuvr, S. G. George, T. Jose, F. Berto, M. S. Hedenqvist, O. Das, S. Ramakrishna, *Composites, Part C* **2021**, *5*, 100138.
[4] R. Muthuraj, M. Misra, A. K. Mohanty, *J. Appl. Polym. Sci.* **2018**, *135*, 24.
[5] N. Peelman, P. Ragaert, K. Ragaert, B. De Meulenaer, F. Devlieghere, L. Cardon, *J. Appl. Polym. Sci.* **2015**, *132*, 132.
[6] K. Khatami, M. Perez-Zabaleta, I. Owusu-Agyeman, Z. Cetecioglu, *Waste Manage.* **2021**, *119*, 119.
[7] S. Milovanovic, J. Pajnik, I. Lukic, *J. Appl. Polym. Sci.* **2022**, *2021*, 51839.
[8] E. Balla, V. Daniilidis, G. Karlioti, T. Kalamas, M. Stefanidou, D. N. Bikiaris, A. Vlachopulos, I. Koumentakou, D. N. Bikiaris, *Polymer* **1822**, *2021*, 13.
[9] U. Sonchaeng, F. Iñiguez-Franco, R. Auras, S. Selke, M. Rubino, L. T. Lim, *Prog. Polym. Sci.* **2018**, *86*, 86.
[10] S. Su, R. Kopitzky, S. Tolga, S. Kabasci, *Polymer* **2019**, *11*, 11.
[11] M. Shibata, Y. Inoue, M. Miyoshi, *Polymer* **2006**, *47*, 47.
[12] S. Y. Hwang, E. S. Yoo, S. S. Im, *Polym. J.* **2012**, *44*, 44.
[13] Y. Deng, N. L. Thomas, *Eur. Polym. J.* **2015**, *71*, 71.
[14] W. Pivsa-Art, K. Fujii, K. Nomura, Y. Aso, H. Ohara, H. Yamane, *J. Appl. Polym. Sci.* **2016**, *133*, 133.

[15] E. A. Hassan, S. E. Elarabi, Y. Wei, M. Yu, *Text. Res. J.* **2018**, *88*, 88.
[16] J. Ostrowska, W. Sadurski, M. Paluch, P. Tyński, J. Bogusz, *Polym. Int.* **2019**, *68*, 68.
[17] C. Aversa, M. Barletta, M. Puopolo, S. Vesco, *Polym.-Plast. Technol. Mater.* **2020**, *59*, 59.
[18] V. Gigante, M. B. Coltelli, A. Vannozzi, L. Panariello, A. Fusco, L. Trombi, G. Donnarumma, S. Danti, A. Lazzeri, *Polymer* **2019**, *11*, 11.
[19] S. Chuayjuljit, C. Wongwaiwattanakul, P. Chaiwutthinan, P. Prasassarakich, *Polym. Compos.* **2017**, *38*, 38.
[20] J. Ludwiczak, S. Frackowiak, K. Leluk, B. Hanus-Lorenz, *Cellul. Chem. Technol.* **2019**, *53*, 53.
[21] Z. Cao, Y. Lu, C. Zhang, Q. Zhang, A. Zhou, Y. Hu, D. Wu, G. Tao, F. Gong, W. Ma, C. Liu, *J. Appl. Polym. Sci.* **2017**, *134*, 134.
[22] F. Luzi, E. Fortunati, A. Jiménez, D. Puglia, D. Pezzolla, G. Gigliotti, J. M. Kenny, A. Chiralt, L. Torre, *Ind. Crops Prod.* **2016**, *93*, 93.
[23] M. Ferri, M. Vannini, M. Ehrnell, L. Eliasson, E. Xanthakis, S. Monari, L. Sisti, P. Marchese, A. Celli, A. Tassoni, *J. Adv. Res.* **2020**, *24*, 24.
[24] G. David, M. Vannini, L. Sisti, P. Marchese, A. Celli, N. Gontard, H. Angellier-Coussy, *Polymer* **2020**, *12*, 12.
[25] P. Toro, R. Quijada, M. Yazdani-Pedram, J. L. Arias, *Mater. Lett.* **2007**, *61*, 61.
[26] A. Dönmez Çavdar, H. Kalaycioğlu, F. Mengeloğlu, *J. Reinf. Plast. Compos.* **2011**, *30*, 833.
[27] H. Y. Li, Y. Q. Tan, L. Zhang, Y. X. Zhang, Y. H. Song, Y. Ye, M. S. Xia, *J. Hazard. Mater.* **2012**, *217*, 256.
[28] J. Fehlberg, C. Lee, L. M. Matuana, E. Almenar, *J. Appl. Polym. Sci.* **2020**, *137*, 137.
[29] H. Sharma, I. Singh, J. P. Misra, *Polym. Polym. Compos.* **2019**, *27*, 527.
[30] J. D. Hernandez-Varela, J. J. Chanona Perez, P. Resendis-Hernandez, L. Gonzales Viscoriano, J. V. Mendez-Mendez, S. Cardenas-Peres, H. A. Calderon Benavides, *Food Hydrocolloids* **2022**, *124*, 107252.
[31] C. V. Garcia, Y. T. Kim, *J. Polym. Environ.* **2021**, *29*, 2372.
[32] D. Pujol, C. Liu, J. Gominho, M. À. Olivella, N. Fiol, I. Villaescusa, H. Pereira, *Ind. Crops Prod.* **2013**, *50*, 50.
[33] P. Esquivel, V. M. Jiménez, *Food Res. Int.* **2012**, *46*, 46.
[34] Y. Narita, K. Inouye, *Food Res. Int.* **2014**, *61*, 61.
[35] C. Coelho, M. Ribeiro, A. Cruz, M. Rosário, M. Domingues, M. A. Coimbra, M. Bunzel, F. M. Nunes, *J. Agric. Food Chem.* **2014**, *62*, 7843.
[36] Y. F. Tsang, V. Kumar, P. Samadar, Y. Yang, J. Lee, Y. S. Ok, H. Song, K. H. Kim, E. E. Kwon, Y. J. Jeon, *Environ. Int.* **2019**, *127*, 127.
[37] N. J. Chitra, R. Vasanthakumari, S. Amanulla, *Int. J. Eng. Res. Technol.* **2014**, *7*, 9.
[38] M. Y. Tan, H. T. Nicholas Kuan, M. C. Lee, *Int. J. Polym. Sci.* **2017**, *2017*, 1.
[39] S. P. Cestari, L. C. Mendes, D. F. da Silva, J. P. Chimanowsky, V. Altstädt, V. Demchuk, A. Lang, R. G. Leonhardt, J.-H. Keller, *Polím. Ciên. Technol.* **2013**, *23*, 23.
[40] B. S. Baek, J. W. Park, B. H. Lee, H. J. Kim, *J. Polym. Environ.* **2013**, *21*, 21.
[41] C. S. Wu, *Polym. Degrad. Stab.* **2015**, *121*, 51.
[42] G. Totaro, L. Sisti, M. Fiorini, I. Lancellotti, F. N. Andreola, A. Saccani, *J. Polym. Environ.* **2019**, *27*, 27.
[43] F. Sarasini, J. Tirillò, A. Zuorro, G. Maffei, R. Lavecchia, D. Puglia, F. Dominici, F. Luzi, T. Valente, L. Torre, *Ind. Crops Prod.* **2018**, *118*, 118.
[44] S. M. K. Yorseng, K. N. R. Siengchin, S. Ayrilmis, *Process Saf. Environ. Prot.* **2019**, *124*, 187.
[45] S. F. Curling, C. A. Clausen, J. E. Winandy, *Int. Biodeterior. Biodegrad.* **2002**, *49*, 49.
[46] References British Standards Institute Wood Preservatives: Determination of the Effectiveness Against Soft Rotting Micro-Fungi and Other Soil Inhabiting Micro-Organisms, British Standards Institute, London **2001**.
[47] S. Saeidlou, M. A. Huneault, H. Li, C. B. Park, *Prog. Polym. Sci.* **2012**, *37*, 37.
[48] L. Zhang, H. Tian, J. Chen, Y. Sun, H. Duan, *J. Appl. Polym. Sci.* **2022**, *139*, 51797.
[49] W. Wu, G. Wu, H. Zhang, *Polym. Adv. Technol.* **2017**, *28*, 28.
[50] K. P. Cresnar, P. A. Klonos, A. Zamboulis, Z. Terzopoulou, E. Xanthopoulou, L. Papadopoulos, A. Kyritsis, K. Kuzmic, L. F. Zemlji, D. N. Bikiaris, *Thermochim. Acta* **2021**, *703*, 178998.
[51] R. Arrigo, E. Morici, N. T. Dintcheva, *J. Appl. Biomater. Funct. Mater.* **2016**, *14*, 455.
[52] X. Zhang, J. Shi, H. Ye, Y. Dong, Q. Zhou, *Carbohydr. Polym.* **2018**, *179*, 179.
[53] N. S. Q. S. Amorin, G. Rosa, J. F. Alves, S. P. C. Gonçalves, S. M. M. Franchetti, G. J. M. Fechine, *J. Appl. Polym. Sci.* **2014**, *131*, 131.
[54] Z. N. Azwa, B. F. Yousif, *Polym. Degrad. Stab.* **2013**, *98*, 98.
[55] J. Massaya, A. Prates Pereira, B. Mills-Lamptey, J. Benjamin, C. J. Chuck, *Food Bioprod. Process.* **2019**, *118*, 149.
[56] M. C. Righetti, P. Cinelli, N. Mallegni, A. Stäbler, A. Lazzeri, *Polymer* **2019**, *11*, 11.
[57] H. Moustafa, C. Guizani, A. Dufresne, *J. Appl. Polym. Sci.* **2017**, *134*, 134.
[58] Y. Gao, W. Qu, Y. Liu, H. Hu, E. Cochran, X. Bai, *J. Appl. Polym. Sci.* **2019**, *136*, 136.
[59] M. J. Le Guen, V. Thoury-Monbrun, J. M. Castellano Roldán, S. J. Hill, *J. Polym. Environ.* **2017**, *25*, 419.
[60] Y. Wang, Y. Xiao, J. Duan, J. Yang, Y. Wang, C. Zhang, *Polym. Bull.* **2016**, *73*, 73.
[61] M. Rapisarda, F. P. La Mantia, M. Ceraulo, M. C. Mistretta, C. Giuffrè, R. Pellegrino, G. Valenti, P. Rizzarelli, *Polymer* **2019**, *11*, 11.
[62] M. Karamanlioglu, R. Preziosi, G. D. Robson, *Polym. Degrad. Stab.* **2017**, *137*, 137.

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