



Unprecedented high percentage of food waste powder filler in poly lactic acid green composites: synthesis, characterization, and volatile profile

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Abstract

The attractive qualities of plastics lead us, around the world, to an enormous need for plastic goods, which results in their unsustainable overconsumption. Bio-based products are the core concept of circular economy, yet this sector suffers from the high cost of their production. In practice, biopolymers, such as polylactic acid (PLA), are still limitedly used, due to their expensiveness and not outstanding technological properties. A circular and sustainable solution would be to use waste from the food industry as filler that contributes to reduce the cost of PLA-based materials, thereby encouraging their widespread use. At the same time, this would be a circular approach to wisely upgrade food waste and prevent pollution. Ceramic food waste powder fillers from egg shells and from mussel shells were compounded with PLA at 180 °C to obtain composites, which contain an unprecedented high amount of filler, equal to 140 over 100 parts of PLA. We analyzed volatile organic compounds emitted from PLA and, for the very first time, from its composites via headspace-solid phase microextraction-gas chromatography-mass spectrometry (HS-SPME-GC-MS). The molecular fingerprint of the volatiles comprises only three aldehydes, a ketone, and two lactides. Volatiles typical of fossil plastics, that are causative factors of hormone disruption or reproductive dysfunction, are effectively missing. Scanning electron microscopy, used to examine the structure of the composite, indicates that both the egg shells and the mussel shells are suitable fillers, in that they form a sufficiently strong interface with the polymer.

Keywords Waste upcycling · PLA composites · Mussel shells · Egg shells · Volatile profile · SEM surface characterization

Highlights

- Mussel shell powder was used for the first time as PLA filler
- Eggshell powder and mussel shell powder were loaded to the PLA matrix at an unprecedented high percentage
- The volatiles released by these composites were analyzed for the first time
- Composites do not release volatiles that are hormone-disruptors, derived from fossil based plastics
- SEM images confirm eggshell powder and mussel shell powder can be used as fillers
- Eggshell and mussel shell waste upcycling decreases the cost of the bio-based composite

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Introduction

The fossil plastic use poses serious concerns as regards its high “carbon footprint,” the lack of recycling facilities or its expensive recycling, its unsustainable use due to its non-renewability, non-biodegradability, and the risk toxic additives incorporation.

Consumers ask for environmentally sustainable products and effective and sustainable waste disposal. Societal and legislative pressure is stimulating a steady growth in the use of biodegradable plastics (Ahmed et al. 2018; Ghosh et al. 2013) via increased restrictions for the use of polymers with high “carbon footprint.” Industries focus on the development of new bio-based feedstocks. The production of value added items supports the development of a circular and sustainable economy in a thriving bio-based sector via the emergence of food value chains.

Poly lactide or poly(lactic acid) (PLA) is a bio-based linear aliphatic polyester produced by lactic acid polymerization, for example, by direct condensation (Masanobu et al. 1995). Its building block is lactic acid, i.e., 2-hydroxypropionic acid, which is derived in turn from the fermentation of starch sources.

PLA is nowadays the front runner in the emerging bio-based product market (Nagarajan et al. 2016). It is among the most popular bioplastics (Madhavan Nampootheri et al. 2010) and it is therefore increasingly used in applications, including composites (Mohanty et al. 2002), textile, transportation, and packaging sectors, but also for food packaging and biomedical purposes.

Noteworthy, PLA is one of the most nontoxic, biodegradable, and bioabsorbable products for use in the human body in implant devices, tissue scaffolds, and internal sutures. While, in the biomedical sector, the high cost of PLA is not a problem, for short-term usage or disposable items, its expensiveness limits its widespread use. PLA blending technique to achieve suitable properties for different applications has been receiving significant attention (Hamad et al. 2018). Anyhow, the use of low-cost fillers of the PLA matrix and the production of composites could be a feasible solution.

Natural fillers would lead to the so-called “green composites,” which represent an emerging area in materials science and sustainable chemistry (La Mantia and Morreale 2011).

Generally speaking, the food industry waste would provide the best options for fillers. Efficient utilization of food waste is of concern to consumers, environmentalists, and policy makers. Food industry waste upcycling to produce new bio-based products has a number of advantages: (1) it avoids the cost of waste disposal; (2) it reduces the high cost of bio-based composites that prevents the takeoff of this sector because filler is waste, which comes at no cost while delivering from the burden of disposal; (3) it avoids taking edible resources as a starting material for bio-based composites; (4) it provides a

waste upgrade that results in an output different from the usual ones (bio-fuels or bio-energy); (5) the bio-based composites are expected not to release volatiles typical of fossil plastics that are known causative factors of hormone disruption or reproductive dysfunction; (6) the obtained composites are biodegradable.

In an attempt to devise new “green composites,” cellulosic materials have been widely used (La Mantia and Morreale 2011; Masmoudi et al. 2016). Since the organized interplay between organic and inorganic phases results in materials with good mechanical performance, we decided to focus on food waste of inorganic nature. It is interesting to note that a number of waste products from agro-food systems are in fact ceramics, most particularly calcium carbonate (CaCO_3). Reinforcement of fossil-based thermoplastic polymer with CaCO_3 fillers to improve their properties and to obtain the best compromise among price, volume, and performance has been well investigated (Jiang et al. 2007; Pukánszky 1995). However, not many studies have been conducted on the usage of this filler in bio-based polymers.

Some attempts of introducing quarry-extracted CaCO_3 to poly(lactic acid) have been also performed for use in biomaterials, attempts which resulted in no brittle behavior and were considered as promising (Kasuga et al. 2003).

Millions of kilograms of waste chicken eggshells and of waste mussel shells are produced yearly and pose a severe challenge to the environment (Walton et al. 1973). They are an interesting source of CaCO_3 with a negative cost; hence, we decided to focus on egg shells and mussel shells as tentative fillers.

As for egg shells, it has been evidenced that the presence of carbonate minerals, with over 95% calcium carbonate, results in a density around 2.53 g/cm^3 (Toro et al. 2007). Also, their limited porosity has the potential to improve the mechanical properties of the polymer matrix in which they are introduced (Tsai et al. 2006). Mussel shells are also mainly composed of calcium carbonate, but they have a slightly higher density (around 2.60 g/cm^3) closer to the nominal density for this salt, especially because they are more compressed as for structure, due to the accumulation of growth rings and the higher thickness. The main application so far as for filler has been in concrete, with effects not dissimilar to those of quarry sand (Barbachi et al. 2017).

While the mussel shell powder was never used as a PLA filler, the eggshell powder was loaded to PLA but only to 5 wt.% (Ashok et al. 2014), 7 wt.% (Somdee and Hasook 2017), or 20 wt.% (Betancourt and Cree 2017). Moreover, percentages of not bio-sourced CaCO_3 higher than 40% have never been explored (Murariu and Dubois 2016). Of course, to obtain good results, the granulometry of ceramics need to be appropriate for introduction into the thermoplastic polymer by obtaining a sufficiently sound and durable interface: this works effectively with nanosized CaCO_3 filler, where the

introduction can be in amounts up to 30 wt.% (Kim et al. 2008). The challenge is to introduce higher amounts of micro-sized bio-sourced filler with positive results, demonstrated by measuring mechanical properties, such as hardness and by scanning electron microscopy (SEM) that is useful for the characterization of the composites.

Actually, we aim at producing a PLA composite with an ultra-high content of CaCO₃ fillers from both eggshell and mussel shell powder in order to dramatically reduce the cost of the final material.

In addition, to possibly apply the obtained composite in a sustainable and not harmful way, it is necessary that the emission of volatile organic compounds (VOCs) from the obtained composite did not pose a concern to the public health. In this respect, there is a dearth in the literature: there is only one study concerning the VOCs emission from raw PLA (Salazar Gonzalez et al. 2017) but no study focused on the volatile fingerprint of PLA composites. For this reason, we aim at characterizing the volatile profile of PLA and, for the very first time, of the bio-sourced composites we produced.

Materials and methods

Synthesis of PLA and PLA composites

PLA was obtained heating (L)-lactic acid (90%, Carlo Erba, Milan) comprising 0.6% stannous chloride as a catalyst for 2 h at 180 °C (Laonud et al. 2010) according to the reaction scheme in Fig. 1. After the reaction was completed, the reaction mixture was cooled down to room temperature.

Mussel shell powder and egg shell powder, used as fillers, were obtained from the grinding of the shells via a coffee mill.

A constant weight percentage of 140 wt.% of each filler (posing 100 the weight of the PLA matrix) was manually added to melted PLA and the mixture was stirred and kept at constant temperature (180 °C) for 15 min before the preparation of testing specimens in order to homogenize the melted mixture.

Volatile profile of PLA and PLA composites

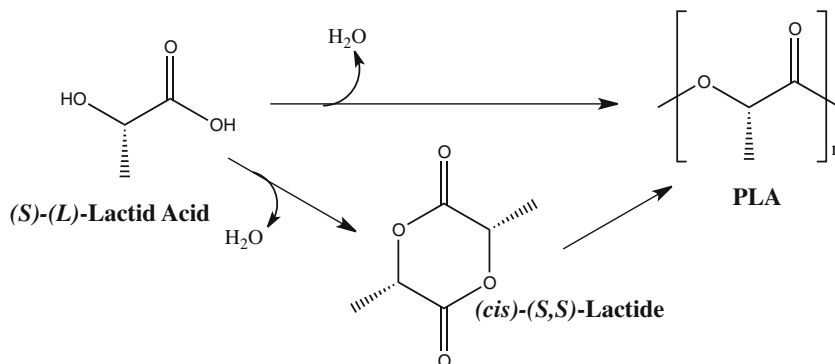
PLA, PLA/mussel shell composites, and PLA/egg shell composite samples were used to seal glass ampoules so that the volatiles are released from the same surface area (0.38 cm²). Ampoules were inserted in 60-ml headspace vials after 4 days from their production, closed through a PTFE/silicone septum. In order to reveal the possible presence of odorants in ambient air, control samples were analyzed (Ripari et al. 2016).

VOCs in the headspace were measured through solid phase microextraction gas chromatography coupled to mass spectrometry (HS-SPME-GC-MS). The experimental design was run in triplicate.

SPME fibers were obtained from the Supelco Company (Bellefonte, PA). The fiber was divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) 50/30 μm and was conditioned before use, as recommended by the manufacturer. Before extraction, the stabilization of the headspace in the vial was reached by equilibration for 30 min at thermostated temperature (20 ± 0.1 °C). Volatiles were then adsorbed for 12 h. After extraction, injections provided the fiber thermal desorption into a Hewlett Packard GC-MS, G1800C GCD Series II (Palo Alto, CA) equipped with a HP-5MS column 30 m × 0.25 mm i.d. × 0.25 μm film thick (Hewlett Packard). The mass spectrometer was tuned before the analyses via a reference gas (perfluorotributylamine) across the full mass range.

The fiber was left in the injection port (equipped with a 0.75 mm i.d. inlet liner) for 4 min. The injector was set at 270 °C and operated in the splitless mode for 1 min. Before sampling, the fiber was reconditioned for 5 min at 270 °C and blank runs were done periodically during the study to reveal possible carryover. The carrier gas was helium; constant flow 1 ml/min; and the oven temperature was held isothermal at 30 °C for 15 min, then programmed from 30 to 200 °C at 10 °C/min. Mass spectra were acquired in the electron impact mode (70 eV), using full scan with mass analysis in the range 30–300 amu. The detector temperature was set at 270 °C. As the SPME technique is a solventless one, no solvent delay was

Fig. 1 Polymerization reaction scheme



needed and in this way, we could detect also the earliest eluting analytes. The identification of the constituents was based on the comparison of the retention times with those of authentic samples obtained from Sigma Aldrich (Milan, Italy). The identification was also based on computer matching against commercial (<http://webbook.nist.gov/chemistry/>) libraries: the identity of the spectra at 98% was needed for identification of compounds (Cecchi and Alfei 2013). Volatile compounds were also identified by comparison of their linear retention indices relative to n-alkanes, calculated using straight-chain alkanes mixture C6-C19, with the averaged values reported in the bibliography for chromatographic columns similar to that used (Van Den Dool and Kratz 1963).

In order to ground the possible presence of odorants in ambient air, control samples of the laboratory were analyzed.

Absolute peak areas were recorded in area counts (Vincenzetti et al. 2018). Only compounds with a signal to noise ratio higher than 3 were considered.

Mechanical properties

Shore D hardness tests according to ASTM D2240 (ISO 7619-1) standard were performed using a PCE durometer. Density measurements were performed according to DIN 53479 (Method A) standard. Both hardness and density were measured on five samples per category.

Scanning electron microscopy

To characterize morphology of PLA and its composites and the quality of the interface, a SEM Hitachi S-2500 scanning electron microscope was used. Prior to observation, the specimens were sputter-coated (Edwards S150B) with gold.

Results and discussion

Molecular fingerprint of PLA and its composites

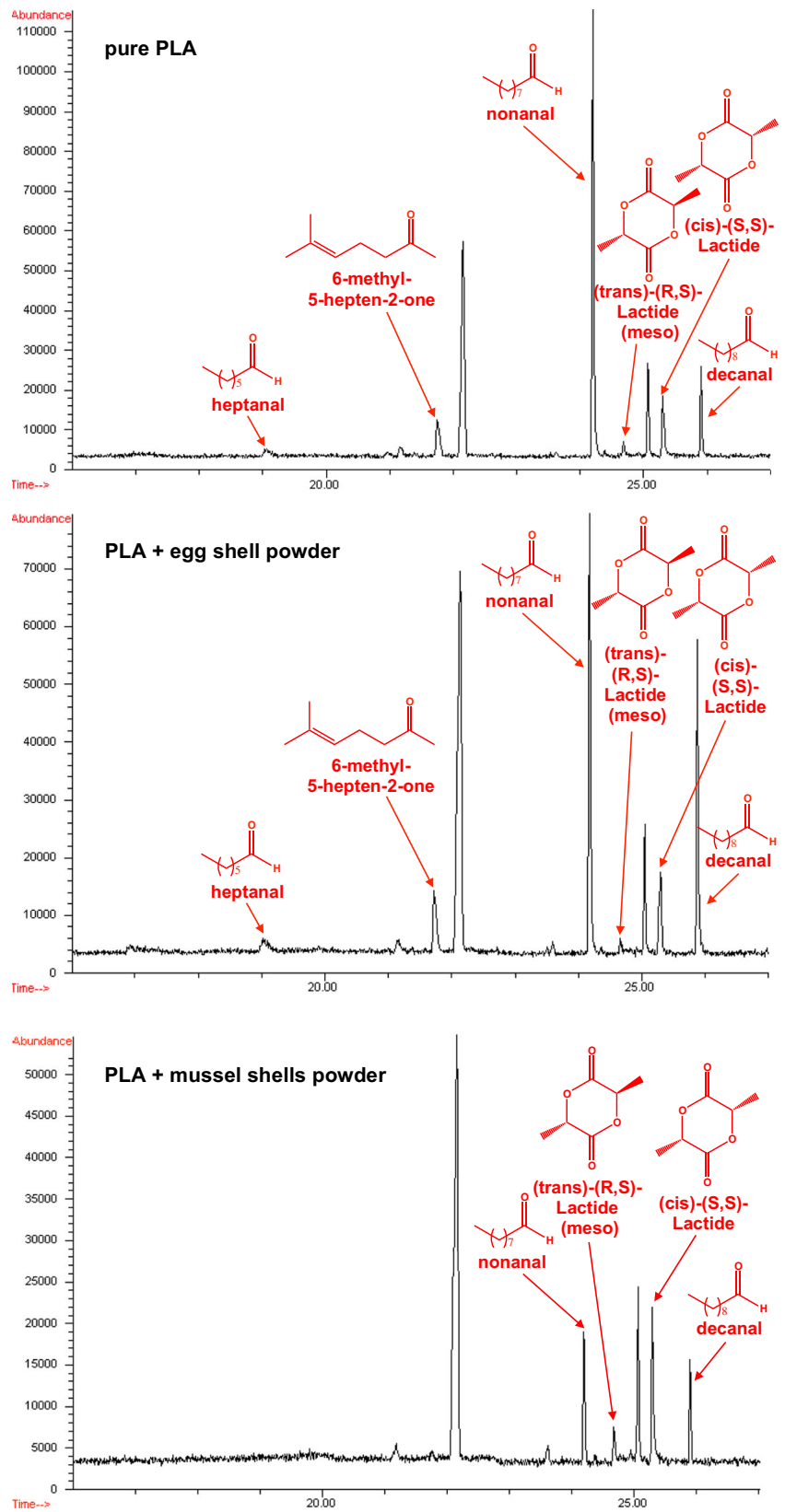
VOCs are defined as “any organic compound having an initial boiling point less than or equal to 250 °C measured at a standard atmospheric pressure of 101.3 kPa.” (Directive 2004/42/CE of the European Parliament and the Council EUR-Lex) (European Union Publications Office). We decided to sample them via HS-SPME SPME because of the ease of use, low cost of the technique, and the absence of solvents. This environmentally and user friendly technique allows for integrating analyte extraction from the sample matrix, enrichment, and transfer to the gaschromatograph.

The molecular fingerprint of VOCs from PLA and from its composites is outlined in Table 1. It details the odor type (Dunkel et al. 2009) and the chemical class of each VOC, its experimental and literature retention indices (Van Den Dool

Table 1 Odor type experimental and literature retention indices (RI), average GC peak areas and standard deviation (triplicate experimental design), and chemical class of VOCs analyzed by HS-SPME-GC-MS

Analyte	Odor type	RI literature	RT experimental	PLA average area count	Standard deviation	PLA/mussel shell average area count	Standard deviation	PLA/egg shell average area count	Standard deviation	Chemical class
Heptanal	Green	902	906	1.98E+05	2.96E+04	ND	ND	4.14E+05	1.04E+05	Aldehyde
6-Methyl-5-hepten-2-one	Citrus	999	1009	3.86E+05	6.38E+04	ND	ND	3.96E+05	1.02E+05	Ketone
Nonanal	Aldehydic	1115	1126	2.18E+06	1.94E+05	2.15E+05	1.12E+05	3.69E+06	1.82E+06	Aldehyde
Trans (R,S) lactide (meso)	NA	NA	1168	9.64E+04	2.68E+04	7.42E+04	4.46E+04	7.22E+04	1.98E+04	Ester
Cis (S,S) lactide	NA	NA	1199	5.26E+05	9.29E+04	3.39E+05	1.21E+05	6.39E+05	2.13E+05	Ester
Decanal	Aldehydic	1214	1225	7.30E+05	2.60E+05	2.24E+05	3.16E+04	2.28E+06	1.10E+06	Aldehyde

Fig. 2 Chromatograms of pure PLA, PLA/egg shell powder composite, and PLA/mussel shell powder composite



and Kratz 1963) as well as its abundance. These data are particularly interesting since there is no research about the emission from PLA composites and there is only one study concerning the VOC emission from raw PLA (Salazar Gonzalez et al. 2017).

None of the volatiles detailed in Table 1 were found in the ambient air. Interestingly, priority air pollutants released by fossil plastics that pose a significant public health threat (such as phenylalkanes, phthalates, and bis-phenol A) are missing from the volatile profile of PLA and its composites. It is rewarding to observe that VOCs known to be causative factors of hormone disruption or reproductive dysfunction are similarly missing.

The volatile profile is very simple. In Fig. 2, the chromatographic profiles for raw PLA, PLA compounded with eggshell powder, and PLA compounded with mussel shell powder are detailed, respectively. *Cis*-(S,S)-lactide and *trans*-(R,S)-lactide are easily predicted to be released from the PLA matrix. The presence of *cis*-(S,S)-lactide can be taken for granted, since it is the dimer of the (S)-(L)-lactic acid used to obtain PLA; anyhow, at high temperature, an inversion of configuration may occur. This explains the presence of smaller amounts of *trans*-(R,S)-lactide. Surprisingly, these lactides were not previously found in the volatile profile of raw PLA (Salazar Gonzalez et al. 2017). Heptanal, nonanal, and decanal are typical food odorants that do not pose a concern to the public health: they were actually found also in the volatile fraction of both fillers. Compounding PLA with mussel shells seems to reduce the VOC emission, since the chromatographic volatile profile of the filler is almost flat and the presence of the filler reduces the surface of PLA available for emission of its volatiles. In this respect, the filler behaves as a kind of PLA matrix diluent, decreasing its emissions.

It cannot be excluded, anyhow, that at higher temperature, PLA and its composites are not exempt from other emissions; it was however demonstrated that PLA is one of the lowest emitters if used as a 3D printer filament (Azimi et al. 2016).

Mechanical properties

The two fillers introduced in the PLA matrix had a dimension around $300 \pm 80 \mu\text{m}$ for egg shell powder and $420 \pm 100 \mu\text{m}$ for mussel shell powder, respectively, as from observation under low magnification. The large variations of granulometry are not only due to the limited precision of the grinding process, yet also to the fact that the particles appear elongated, especially in the case of mussel shell powder.

Shore D hardness results for pure PLA was 39 ± 1 , while for PLA with egg shell powder was 75 ± 2 and for PLA with mussel shells powder was 59 ± 2 on the empirical Shore D scale. These data for pure PLA are largely inferior to industrially produced PLA, as reported by De Rosa et al. (2011), which measured a Shore D value in the region of 80. However, it is promising to observe that the introduction of this amount of food waste–obtained ceramic filler allowed considerably recovering over the value of pure PLA. The hardest composite is the PLA/egg shell one.

Density results were $1.275 \pm 0.015 \text{ g/cm}^3$ for pure PLA, $1.637 \pm 0.012 \text{ g/cm}^3$ for PLA with egg shell powder, and $1.774 \pm 0.013 \text{ g/cm}^3$ for PLA with mussel shells. This is compatible with the amounts of fillers in the polymers and their respective absolute densities, as from data from literature provided in the “Introduction” section.

Fig. 3 SEM images of pure PLA

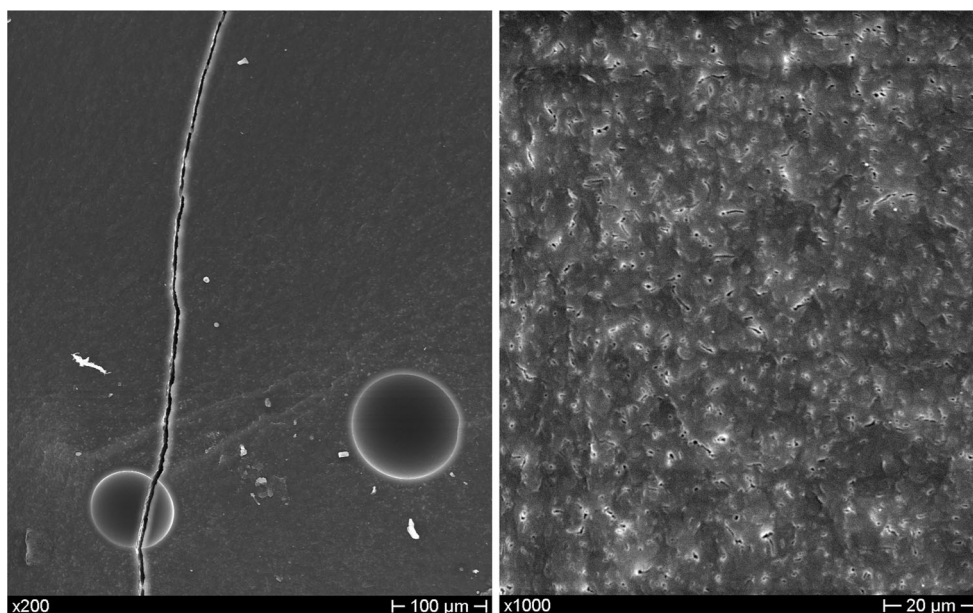
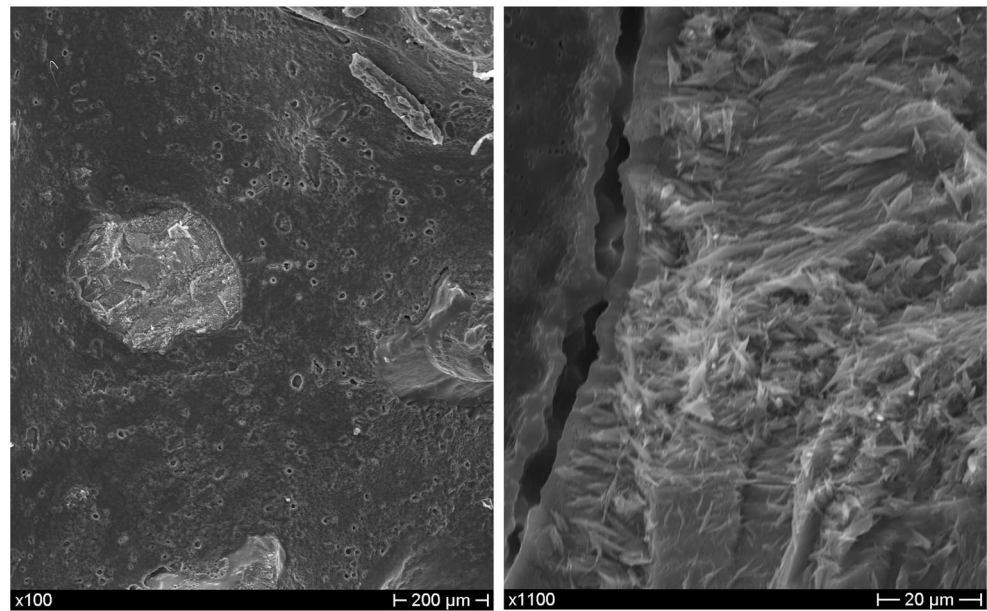


Fig. 4 SEM images of PLA/egg shell powder composite

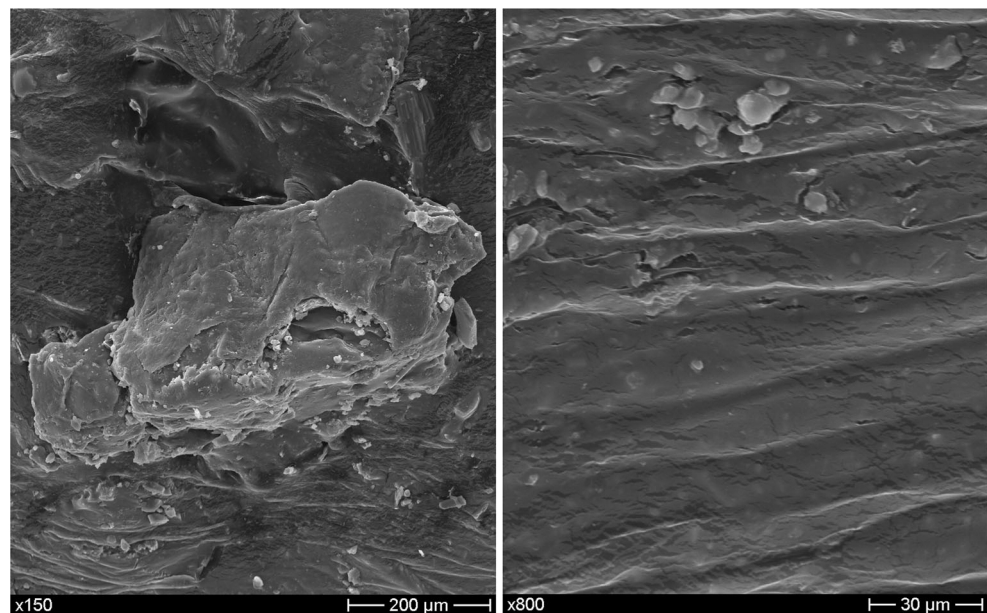


Scanning electron microscopy

The limited hardness of pure PLA can be partially justified, as observed in Fig. 3, as possibly due to its brittleness and heterogeneous erosion and presence of voids, which results in an uneven surface, leading to loss of particles from the surface: this is a well-known occurrence, which normally suggests blending PLA with plasticizers, such as tributyl citrate (Ljungberg and Wesslén 2005). In Figs. 4 and 5, it is observable that the addition with egg shell powder or mussel shell powder created a sufficiently strong interface. Most porosities, which do not exceed as a whole 5% of the total weight of the samples, are in effect attributed to defect in PLA polymerization. In

effect, the images to the left at lower magnification indicate the adhesion between the fillers and the polymer. In contrast, in the images to the right, which concentrate on the filler characteristics, differences are visible, in the sense that egg shell powder has a more even surface with some kind of fibrous structure (Fig. 4), whilst in contrast in mussel shell powder, the effect of growth rings is still clearly perceivable in the step-like structure revealed under microscopic observation (Fig. 5). It may be suggested therefore that the two fillers may both have application for polymer filling, although the polymer needs to be possibly treated in a different way to provide a smoother and less porous surface, especially by adapting its plastic behavior to the microscopic aspect of the filler.

Fig. 5 SEM images of PLA/mussel shell powder composite



Conclusions

We addressed a dearth in the literature about the use of food waste as filler in bio-based polymers, thereby suggesting food industry a way to become more efficient in handling of its waste.

A smart upcycling of food industry waste is to use them as safe filler of bio-based products. Inorganic powders obtained from eggshell and mussel shell waste were compounded with PLA at an unprecedented ultra-high percentage to dramatically lower the cost of PLA-based materials and possibly enabling its widespread. The composites are thermoplastic, biodegradable, and have a low carbon footprint. For the very first time, the molecular fingerprint of VOCs in PLA and in its composites was analyzed using a green approach. It was thus demonstrated that, at variance with fossil plastics, the bio-based composites do not release hormone-disruptors or priority air pollutants that pose a significant public health threat. SEM imaging, on the other side, demonstrated the obtainment of a sound and strong interface between the filler and the polymer. The use of food waste as filler avoids taking edible resources as a starting material for bio-based composites and provides a waste upgrade that results in an output different from the usual ones (bio-fuels or bio-energy).

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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