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High levels of microparticles release from biodegradable polylactic acid paper cups compared with polyethylene-lined cups

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ABSTRACT

Polylactic acid (PLA) is a popular replacement for conventional fossil-fuel based plastics products such as polyethylene (PE) due to its high biodegradability and recyclability. Previous studies confirmed that PLA microplastics (MPs) and PE MPs pose similar toxicity risks due to that MPs' risk is primarily attributed to physical and indirect nutritional effects. Surprisingly, despite the widespread use, there have been very few studies of microparticles released from daily products made of biodegradable materials. We investigated release levels from eight single-use paper cups (SUPCs) lined with PLA and PE film. Under typical hot-beverage preparation conditions, the total number of particles released from PLA SUPCs was 4.2 times higher than that from PE SUPCs, with total numbers of 180,000 ± 31,000 and 43,000 ± 10,000 particles per litre, respectively. 22,000 ± 6,000 MPs were released per litre from PLA, which was 3.6 times the level of MPs released from PE SUPCs. In addition, significant levels of cellulose microfibres were released from PLA SUPCs, with quantities of 38,000 ± 31,000 microfibres per litre, while no such fibres were released from PE SUPCs. It should be noted that the levels of these particles may be underestimated due to the exclusion of nanoparticles (less than 0.8 μm, filter's pore size), unidentified microparticles with high fluorescence backgrounds and attachments between different types of particles. In summary, a proportionately higher level of release of additive microparticles together with the release of cellulose microparticles are the key difference between biodegradable plastics like PLA and conventional plastic such as PE. Cellulose blending in manufacturing is likely related to higher MPs release from PLA cups than PE cups. Therefore, it is highly recommended to re-assess the manufacturing process, potential health and environmental risks of biodegradable plastic products as well as the formulation of related policies.

1. Introduction

Microplastics (MPs) released from single-use plastic products are a concern due to the potential risk of high levels of ingestion by consumers [1,2]. Extremely high levels of MPs and nanoplastics (10^{12} particles per litre, mean size of 30–80 nm) had been reported to be released from polyethylene (PE) lined SUPCs [2]. Conventional SUPCs are comprised of a paperboard substrate with a base weight of 150 to 350 g/m^2 and a plastic liner of 8 to 20 g/m^2 (thickness of around 50 μm) [3]. PE-lined SUPCs are one of the most widely used disposable cups, with daily consumption rates of 136 million, 27.4 million and 7.2 million in the US, China and Germany, respectively [4]. This huge consumption contributes significant plastic pollution to the environment. For instance, in Europe, disposable plastics make up around 70% of marine litter [5]. Currently, there is a significant drive to replace and/or reduce the usage of conventional PE-lined SUPCs. A global survey found that 75% of people across 28 countries agree with the ban on single-use plastics [6]. In the EU, SUPCs made of expanded polystyrene and oxo-degradable plastics will be banned by 2030 [7]. Similarly, the US Secretary of the Interior issued Secretary's Order 3407 in 2022, which aims to identify

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environmentally preferable alternatives to single-use plastic products, such as compostable or biodegradable materials. Clearly, there is a global drive to reduce and replace conventional SUPCs.

Biodegradable plastic (e.g., polylactic acid-PLA) based SUPCs are widely considered to be the solution [3]. It is believed that these biodegradable plastics will undergo decomposition into carbon dioxide (CO_2), biomass and water within a timescale that is short enough for the plastics not to be harmful to marine life and not to lead to an accumulation of plastics in the environment [8]. PLA has become increasingly used in single-use products (e.g., disposable cutleries and paper cups) owing to its variety of advantages, such as being 100% biodegradable and compostable, safe and non-toxic, and good mechanical and physical properties [9]. To date, PLA-lined SUPCs are the most widely used compostable SUPCs [3]. The global market for PLA is expected to grow 26.6% from 2022 to 2030, while the market for PLA-lined SUPCs is growing 8.5% annually [10,11].

However, recent studies have pointed out that biodegradable plastics can release high levels of MPs [12]. The toxicity risk from both conventional PE MPs and PLA MPs is primarily attributed to physical and indirect nutritional effects [13,14]. It was reported that in marine animals MPs released from biodegradable plastics have similar toxicity to conventional MPs [15]. Furthermore, a previous report published by United Nations Environment Programme (UNEP) indicated that the by-products and litters produced during the degradation of biodegradable plastic can cause the similar or even worse risks as conventional plastics in biodiversity and ecosystem functions [16].

It is also well known that the degradation of biodegradable plastics such as PLA is highly temperature dependent. While at lower temperatures and sub-optimal conditions, PLA had no observable degradation even after 120 days [17], at a temperature of 57 °C it can degrade in composting or thermophilic anaerobic conditions in a few weeks [13]. Considering that the most common use of SUPCs is in hot beverage preparation, which involves high temperatures (up to around 100 °C) and repeated mechanical shaking, we hypothesize that PLA SUPCs may release higher levels of MPs compared with conventional SUPCs. To test this hypothesis, three global leading brands of commercial PE-lined SUPCs and five PLA-lined SUPCs were selected to mimic hot beverage preparation and to record the levels of MPs release. Raman Spectroscopy combined with multiple other techniques (e.g., FTIR, SEM and AFM) was used to quantify and characterize the released particles. It was found that there were 22,000 ± 6,000 MPs per litre released from PLA SUPCs, which was 3.6 times higher than that released from PE SUPCs. An in-situ ethanol treatment was also conducted to reveal the presence of additive microparticles and their influences on the physicochemical modification of microplastics. Additionally, significant levels of cellulose microfibres were also released from PLA SUPCs while there was no cellulose released from PE SUPCs. SEM images reveal that the new PLA SUPCs have fibre-like particles attached to the inner surface, while no obvious particles are observed on the surface of PE SUPC. This study underscores the urgent need to re-assess the potential health and environmental risks of biodegradable plastic products and formulate related policies.

2. Materials and methods

2.1. Particles release from conventional and compostable SUPCs

In this study, 3 brands of PE and 5 brands of PLA-lined SUPCs were tested for particle release. These PE and PLA SUPCs were purchased from 3 global leading brand retail shops in Dublin, and 5 different manufacturers, all of which have the PE or PLA liners on the inner side of the paper board. The manufacturers selected to comply with the FSC certification and have plastic laminated lining thicknesses of 15–20 μm. The details of each cup are summarized in Table 1. Referring to established protocols [18,19], our experiments were conducted to mimic hot beverage preparation and to test particle release levels (Fig. 1). To eliminate potential interference of particles in the air, all the tested SUPCs were covered with glass lids. For each sample, a brand-new paper SUPC was directly filled with 250 ml deionized (DI) water with the temperature of 95 °C (typical brewing temperature is 92 °C-96 °C [20]). After covering the cup with a glass lid, it was placed on a shaker and slightly shaken for 15 min at a speed of 50 r.p.m to mimic the shaking actions during holding, moving, and drinking activities of the user. The water samples were then allowed to naturally cool to room temperature (~30 mins) followed by filtering through a gold-coated polycarbonate membrane (APC, Germany Ltd) with a pore size of 0.8 μm using a vacuum pump. This filter membrane can effectively capture micro-sized particles that are large enough to avoid background spectra during Raman testing. The filter membrane was placed on a dry, clean glass petri dish to await further testing. Raman spectroscopy and AFM were used respectively to determine the type and morphology of the particles released from PE and PLA paper SUPCs. Finally, ImageJ 1.53 t software was used to quantitatively determine the total number of released particles (PMPs) and the size distribution of the PLA SUPCs. Firstly, the function “Set scale” was applied in ImageJ to set the known distance of the image based on the screen size of Raman microscope (110 μm *86 μm). Subsequently, the particle number can be counted manually and the length and width of particles can be obtained with the function “Straight”. The experiment was repeated 5 times for each sample to obtain the average result (n = 5). After the total number of released particles was determined, the filter membrane was exposed to 20 ml of ethanol to eliminate additive microparticles aggregated by small molecules. The filtrate was collected and drop casted onto aluminium foil and allowed to dry to analyze the dissolved additive particles using FTIR. After ethanol treatment, the filter membrane was dried naturally and the remaining insoluble particles were analyzed using Raman, SEM and AFM. The ethanol treatment can improve the accuracy of Raman detection of the MPs and cellulose microparticles by eliminating the additive particles. The additive-attached MPs and cellulose particles can be better detected. The filtration method and membrane selection in this study are beneficial to avoid potential contaminants and to facilitate Raman detection.

Table 1
Summary of paper SUPCs used in this study.

No	Lining Material	Colour	Volume	Weight (g)
1	PE	White	12 oz	14
2	PE	Red	12 oz	17
3	PE	Red	12 oz	23
1	PLA	White	12 oz	10
2	PLA	Brown	12 oz	14
3	PLA	Green	8 oz	13
4	PLA	Orange	8 oz	13
5	PLA	Brown	12 oz	16

2.2. Control experiments and contamination prevention

Glass beakers and DI water were used in control experiments following the same protocol (Fig. 1). The DI water was sourced from a Veolia UltraPure water system, which includes a Thermo Scientific™ Barnstead™ Nanopure unit with a 0.2 μm absolute final filter for dispensing and monitoring water quality. The DI water used in this study had a resistivity of 18.2 MΩ and a conductivity of 1.5 μs/cm. No PLA MPs were found in the control samples, while there were only 300 particles per litre detected from the control samples. These control sample levels were 2–3 orders of magnitude lower than that detected in PE and PLA SUPCs, confirming the reliability of our methods (Fig. 2a). In addition, the control experiment was repeated using room temperature (around 25 °C) DI water instead of 95 °C DI water to investigate the influence of water temperature on particle release. Particle release levels from PE and PLA SUPCs under room temperature conditions were similar to the control sample (Fig. S1). To prevent potential

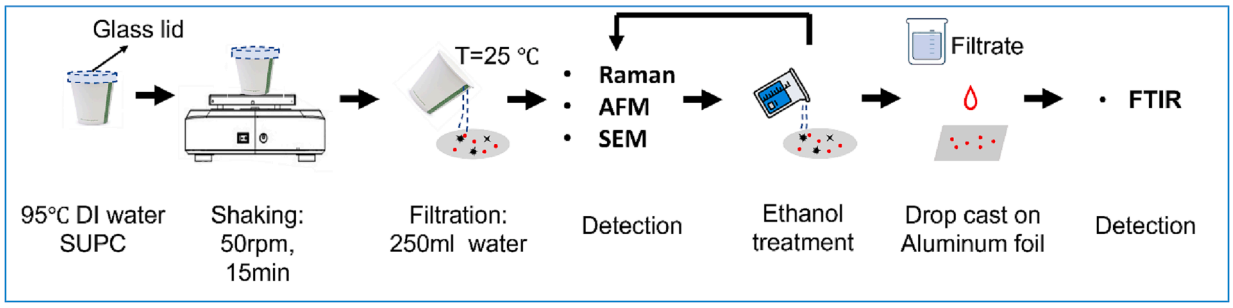

Fig. 1. The experiment protocol for preparing SUPC samples.

contamination, all glassware was cleaned using an ultrasonic bath for 30 mins before each experiment. Lab coats and gloves were worn throughout, consistent with our reported protocol [19].

2.3. Microplastic identification

Multiple techniques were used to characterize the particles released from PE and PLA SUPCs. Gold-coated membrane filters that captured released particles were analyzed using Raman spectroscopy (Renishaw InVia Raman spectrometer) equipped with a 532 nm laser (Coherent), a cooled charge-coupled device and a microscope (NT-MDT) with a 100 × objective (Mitutoyo, M Plan Apo; numerical aperture = 7.0). The whole Raman system is controlled by the WiRE 3.4 (Renishaw) software. For each sample, four areas were randomly selected for detection at the top, bottom, left, and right sides of the filter membrane. Ten images (40 images in total) with the size of 110 μm *86 μm were captured in each area. The particles in each image were characterized using Raman spectroscopy to obtain the Raman spectra, followed by comparing them with the Raman spectra of standard materials (e.g., PE, PLA and cellulose). Referring to previous studies [18,21,22], the hit quality index (HQI) value of 0.70 was set as the minimum threshold for identifying particle composition.

AFM system combined with Raman spectroscopy was also used to study the morphology of representative particles. After characterizing the released particles by Raman spectroscopy, the AFM system was used to generate surface morphology images of representative particles from which their shape and size were determined. Gwyddion 2.61 software was used to analyze the AFM image and 3D topographic images. To further investigate the topography of plastic lining and microparticles, scanning electron microscope (SEM) tests were performed. Before the test, small pieces (around 0.5 cm^2) of PE and PLA cups were cut and cleaned using DI water. After drying, each sample was fixed onto a double-sided adhesive tab on an aluminium SEM stub. The fixed samples were sputter coated with a 10-nm Pt layer (Cressington 208HR) and analyzed using SEM (Zeiss Ultra Plus) with an acceleration voltage of 5 kV and magnifications ranging from 50 × to 10,000 ×. Using the same method, microparticles on the filter surface were also analyzed.

2.4. In-situ test of PLA microplastics and additive microparticles

A previous study reported the ability of chemical additives to become leached from plastics and absorb onto MPs, and their potential implications for human health [23]. In a recent report we showed that additive microparticles can be dissolved by ethanol treatment [24,25]. Therefore, an in-situ test was conducted to identify additive microparticles using this ethanol treatment in combination with Raman spectroscopy and AFM analysis. Selected particles were first identified by Raman spectroscopy and imaged by AFM. Subsequently, three drops of alcohol were sequentially dropped onto the filter membrane and the corresponding changes in the Raman spectra and morphology of the particles were recorded. Raman spectra and AFM images acquired after each drop of ethanol tracked the compositional and morphological changes of the selected particles.

3. Results

3.1. Total microparticles and additive microparticles released from PLA and PE SUPCs

Following the hot beverage protocol described in Fig. 1 and the Method section, the total number of plastic-released microparticles (PMPs) captured on the filter membrane from PE and PLA SUPCs was determined without ethanol treatment. Fig. 2a shows the total PMPs levels from PE samples 1–3 and PLA samples 1–5, respectively. On average, the total number of PMPs released from PLA SUPCs was 4.2 times higher than that of PE SUPCs, 180,000 ± 31,000 PMPs/L and 43,000 ± 10,000 PMPs/L, respectively. Fig. 2B shows that types of released PMPs, include MPs, additive microparticles, cellulose microparticles and unidentified particles.

To identify the levels of released additive microparticles, the filter membrane was then placed onto a glass holder and rinsed using 20 ml ethanol. Of the 180,000 ± 31,000 particles released per litre, 20,000 ± 6,000 were removed by ethanol and therefore identified as additive microparticles [24], accounting for around 11.1% of the total particles released from the SUPCs. Fig. 2c-d shows two different locations randomly selected on the filter membrane of a PLA sample before and after ethanol treatment under an optical microscope (dark mode). By reviewing 10 random images captured using the microscope, the calculation result shows that 10.8%±5.2% of the total particles are removed following the ethanol treatment, consistent with our statistical analysis.

Following the same protocol, a large quantity of additive microparticles was also released from PE SUPCs. The total number of particles released was 43,000 ± 10,000 PMPs/L, while the additive microparticles comprised 13,000 ± 6,000 particles/L, accounting for 29.9% of the total.

The filtrate containing the dissolved additive microparticles was then drop casted onto an aluminium (Al) foil and allowed to air dry. Raman testing found that the additive microparticles released from PE and PLA cups showed near identical spectra to that of PE, with HQIs of 0.94–0.96 compared with standard PE polymer (Fig. 2e). In contrast to PE, the additive microparticles were ethanol soluble and are again attributed to the precipitation of small molecular additives incorporated into the polymer. FTIR analysis showed significant peaks around 1742 cm^{-1} and 2930 cm^{-1} (Fig. 2f), which are associated with carbonyl groups (C = O) and hydrocarbon groups (C-H) [26]. Library fitting indicates that they are fatty acid mixtures, which are widely used to facilitate plastic processing and modify plastic properties [27].

An in-situ test was conducted to reveal the details of the process whereby ethanol dissolves and separates additives microparticles from MPs. Fig. 3a shows a representative AFM image of micron-sized particles released from a PLA SUPC captured on the surface of the filter membrane. There are large irregular-shaped particles (green circles in Fig. 3a) released from the PLA SUPC. The particles were then

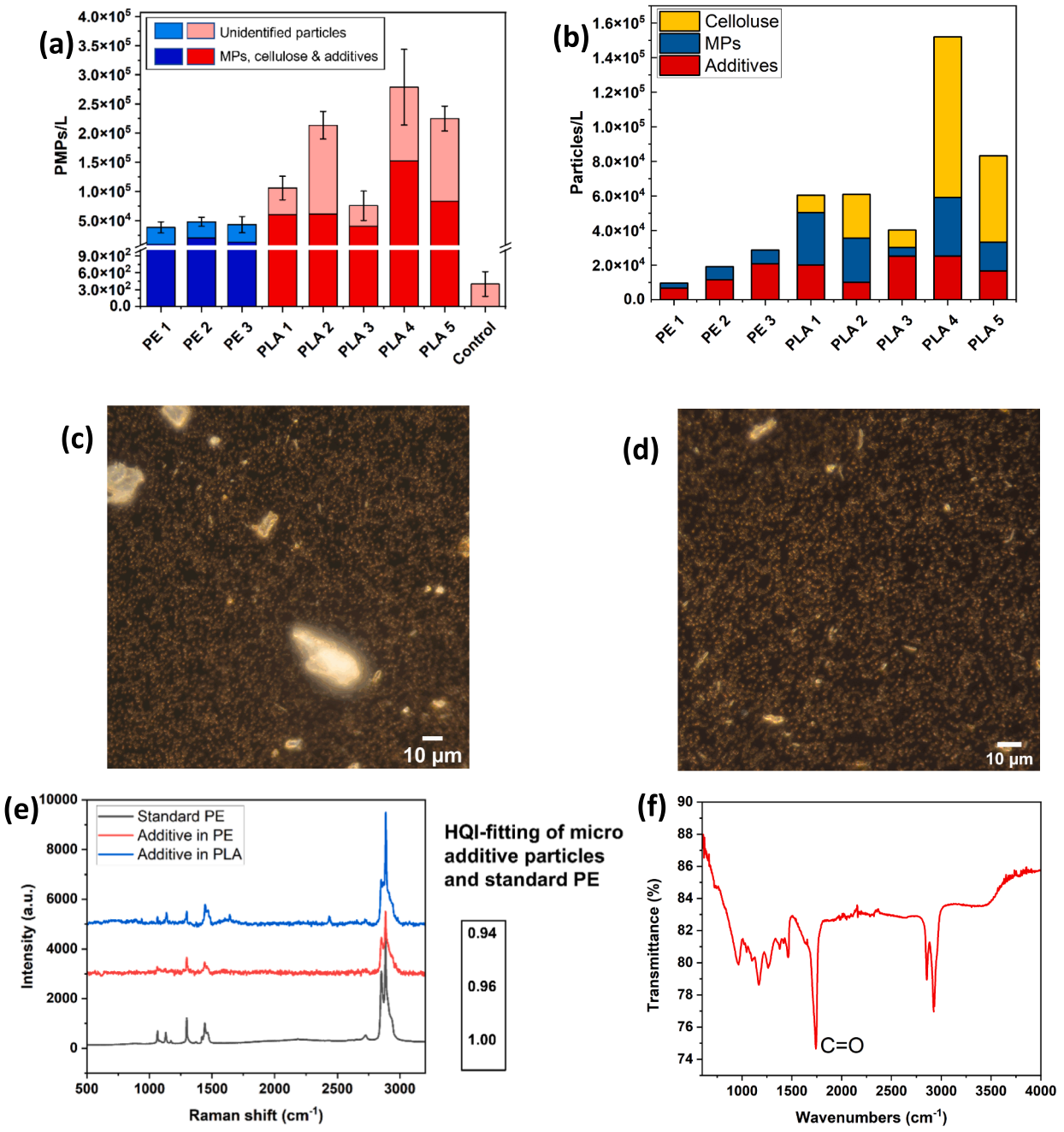

Fig. 2. Total particle numbers, types and characterizations from PE and PLA SUPCs before and after ethanol treatment, as well as filtration identification. (a) PMPs released from different brands of PE SUPCs (1–3) and PLA SUPCs (1–5) with DI water background. (b) Particle type and proportion released from PE and PLA SUPCs. Optical microscope image of PLA sample on a gold membrane (c) before and (d) after ethanol treatment (dark mode). (e) Raman spectrum of standard PE and additive microparticles released from PE and PLA SUPCs. (f) FTIR spectrum of filtrate from PLA sample on the aluminum foil.

sequentially exposed to ethanol to further investigate their composition. After exposure to 1 drop of ethanol (Fig. 3a-c), the particles' topography was substantially changed.

The bottom and right regions of the particles in Fig. 3B disappeared after 1 drop of ethanol treatment (green circle regions in Fig. 3c). Further ethanol treatment resulted in no significant change in the particle shape (Fig. 3d). Raman analysis showed that the major spectral peaks associated with this green circle region originally located around 2880 cm^{-1} are shifted to around 2944 cm^{-1}, the latter being attributable to the asymmetric stretching of CH_3 of PLA polymer [28]. Meanwhile, the peak intensity at low wavelength regions around 1200–1500 cm^{-1} substantially decreased while the peak at 1600 cm^{-1} disappeared. Consistent with this topography change, further ethanol treatment resulted in no significant change in the Raman spectra (Fig. 3d). HQI of the tested particles compared to standard PLA polymer increased from the original level of 0.27 to 0.84 and then 0.95 after 1 and 3 drops of ethanol treatment, respectively. Comparing the spectra changes of the PLA-MPs in the selected areas, it is reasonable to attribute the peak shift of around 2900 cm^{-1} and high intensity of peaks between 1200 and 1500 cm^{-1} to the attached additives, which showed strong signals at 2880 and 1200–1500 cm^{-1}. A validation test using standard PLA particles confirmed that ethanol does not dissolve or damage PLA polymer (Fig. S2a-b). Evidently, additive microparticles can be released alone or can attach to the surfaces of PLA MPs. Ethanol treatment can

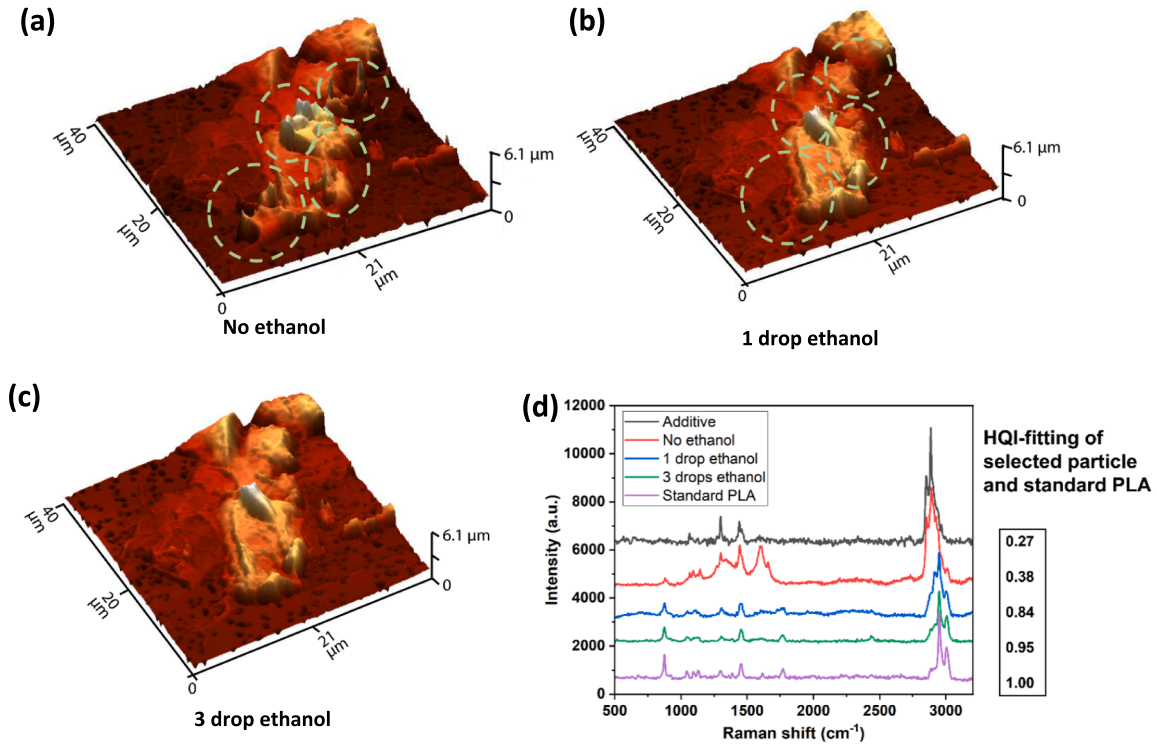

Fig. 3. In-situ AFM images and Raman spectra of ethanol treatment on selected particles. (a-c) AFM 3D in-situ images of additive microparticles attached on a PLA MP before and after 1 drop and 3 drops of ethanol. (d) Raman spectra of an in-situ particle before and after 1 drop and 3 drops of ethanol.

substantially benefit the separation and accurate identification of additive microparticles, enabling an accurate determination of the composition, shape and size of MPs. On the other hand, the ethanol rinse may reduce the size of the mixed particles containing polymers and additives, following some of the MPs captured on membrane filter, which will lead to an underestimation of MPs levels. In addition, the size distribution will be affected so that the true MPs distribution has been shifted to large values due to attached additives.

3.2. Microplastics and cellulose microparticles release from PLA and PE SUPCs

After ethanol treatment to eliminate additive microparticles, the remaining particles are counted and further analysed. Particles identified as MPs released from PLA ranged from 5,000 to 34,000 particles per litre depending on the brand of PLA SUPCs, with an average value of 22,000 ± 6,000 MPs per litre. Representative AFM and SEM images (Fig. 4a, 4c) reveal that around 79% of MPs are flake-like with a coarse surface and an average thickness of around one-tenth of the lateral dimensions. The surfaces of the particles are rich in bumps and valleys after ethanol treatment, so that MPs have a high capacity to adsorb and attach other pollutants, such as chemical additives and persistent organic pollutants (POPs). Fig. 4e shows the Raman spectrum of a PLA MP had a HQI index of 0.94 compared with that of standard PLA material. The Raman peaks at around 1773 cm^{-1} and 2944 cm^{-1} are attributed to the stretching vibrations of C = O bond and CH_3 bond, respectively, which closely match the Raman spectrum of standard PLA material [28,29].

The level of MPs released from PLA SUPCs was 2.6 times higher than that of PE SUPCs. The PE MPs released from PE SUPCs ranged from 3,000 to 8,000 particles per litre, depending on brand, with an average value of 6,000 ± 2,000 PE MPs per litre. Fig. 4g shows the Raman spectra of a detected PE MP with a HQI value of around 0.97 compared with standard PE material.

Surprisingly, a significant quantity of cellulose microparticles/fibres were released from PLA SUPCs, ranging from 10,000 to 93,000 particles per litre, depending on the product brand. Fig. 4b, 4d present AFM and SEM images of some representative cellulose microparticles with a width of 2–4 µm, a length of 14–20 µm and a thickness of 2–4 µm. Clearly, these cellulose microparticles are elongated, irregular strips, with coarse surfaces similar to that of MPs, making them also a potential carrier of chemical additives and other contaminants. Fig. 4f shows the Raman spectra of a cellulose microparticle and cellulose bulk material (fibre). The spectrum comprises two major groups of peaks at 1337 cm^{-1} and 2900 cm^{-1}, which are associated with HCO, HCC and HOC bending, and CH and CH_2 stretching, respectively, both recognised as signature features of the Raman spectrum of cellulose bulk material [30]. The release of cellulose microparticles/fibres was unique to the PLA SUPCs, no such fibres were released from PE SUPCs.

3.3. Size distribution of MPs and cellulose microparticles from PE and PLA SUPCs

The size distribution of the particles released from PLA SUPCs following ethanol treatment was determined by optical microscopy (Fig. 5a, obtained from 418 particles). It was found that 42.9% of the PLA MPs were 3–5 µm in size while 17.9% were in the 5–7 µm range. MPs over 15 µm accounted for less than 5% of the total MPs (Fig. 5a). On the other hand, the size distribution of cellulose microparticles shows that particles between 3 and 5 µm account for the highest (36.4%) proportion of particles (Fig. 5b). Particles in the 9–13 µm range accounted for the second largest number with 36.2%, slightly lower than that of 3–5 µm particles. No cellulose microparticles in the 1–3 µm range were detected (Fig. 5b). However, it is important to note that due to the pore diameter of the membrane, particles with dimensions less than 1 µm are not detected in the present protocol.

The reported dimensions of the particles are based on the length of their longest axis. In general, the average size of the cellulose

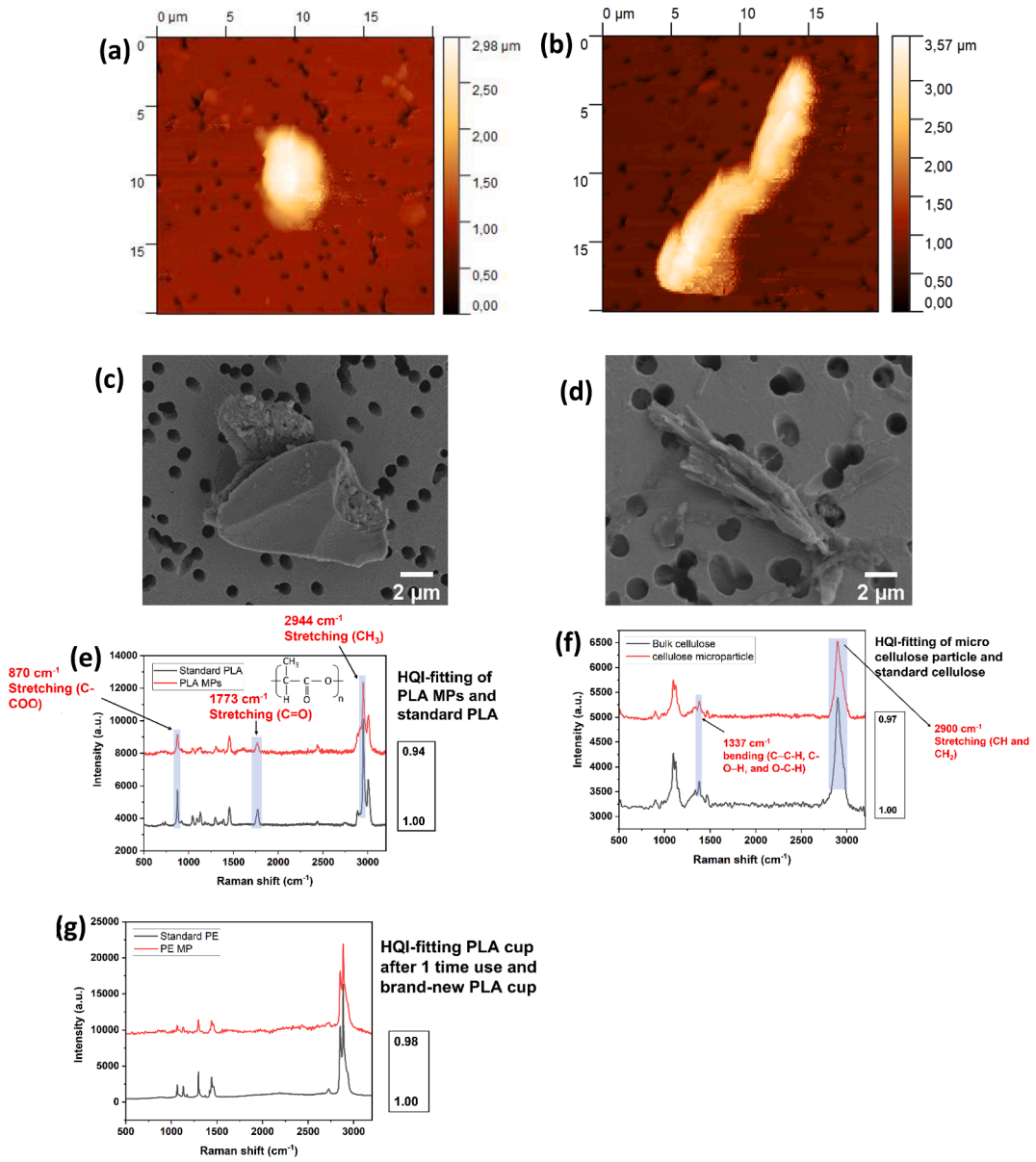

Fig. 4. Representative MPs and cellulose microparticles topographic images and Raman spectra. AFM image of (a) PLA MP and (b) cellulose microparticle on the gold filter membrane from PLA sample. SEM images of (c) PLA MP and (d) cellulose microparticles after ethanol treatment. (e) Raman spectra of standard PLA and PLA MPs released from PLA cup. (f) Raman spectra of bulk cellulose material (fibre) and cellulose microparticles released from PLA cup. (g) Raman spectra of standard PE (sheet) and PE MPs released from PE SUPC.

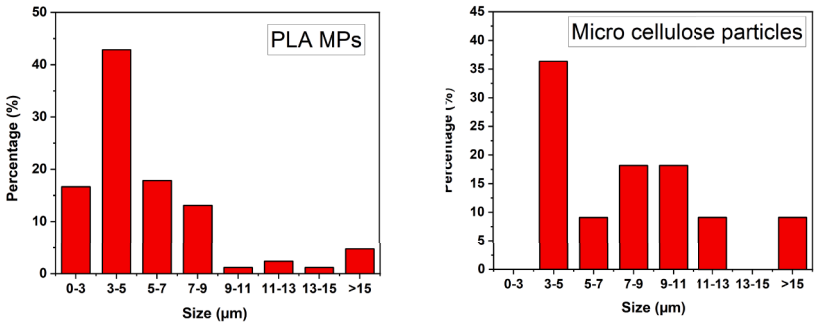

Fig. 5. Size distribution. Size distribution of (a) PLA MPs and (b) cellulose microfibres from PLA SUPC.

microparticles was twice than that of PLA MPs. This is in part due to shape anisotropy of cellulose microparticles that have length-to-width ratios of about 4 to 1 or even higher, while the PLA MPs were irregular ellipsoids with a smaller length-to-width ratio. The PE MPs have a similar size distribution as the PLA MPs, most of them are smaller than 20 μm (Fig. S3), which is consistent with the previous report [31].

3.4. Lining morphology change of PLA and PE SUPCs

It is well known that micro- and nano-sized cellulose particles cannot be digested by humans but could still be a health risk [32–34]. For this reason, SEM testing was used to study the lining of SUPCs and identified the presence of large quantities of fibres attached or buried on/in the inner surface of PLA SUPCs (Fig. 6a). Although it is difficult to perform in-situ chemical identification of fibers on PLA lining, the size and shape of these fibres perfectly match that of cellulose fibres released and captured on filter membrane, indicating that they are the source of microfibers. (Fig. 4b). In contrast, there were no similar fibres observed on the surfaces of PE linings (Fig. 6b). AFM images also confirmed these differences, with fibres protruding about 120 nm on the lining surface. After exposure to hot water many fibres were removed, and significant valleys approximately 90 nm in depth were observed. In contrast, only minor changes in surface roughness were observed in the case of PE. The manufacturing and compositional differences between PE and PLA linings are likely to be one of the reasons for the levels of cellulose microfibres released from PLA cups. Another potential source of cellulose fibres is added cellulose as additives or fillers in the bulk PLA materials, which is a common method to enhance the physiochemical properties of biodegradable plastics [35,36].

4. Discussion

4.1. Evaluation of MPs and cellulose exposure

Human exposure to MPs and cellulose release from SUPCs depends on consumption levels and future policies on single-use plastics. It is projected that the demand and consumption of disposable coffee cups will continuously increase after the Covid pandemic [37]. The market share of the PLA SUPCs in 2021 was 3.0%, which will grow by 8.5% per year, assuming that the remaining SUPC market is PE SUPCs [38]. Based on this projection, MP exposure per capita will increase steadily, primarily due to the increased market share of PLA SUPCs and the higher levels of MPs released from PLA SUPCs compared to PE SUPCs. The emergence of new policies that prohibit the sale of PE SUPCs will, in the

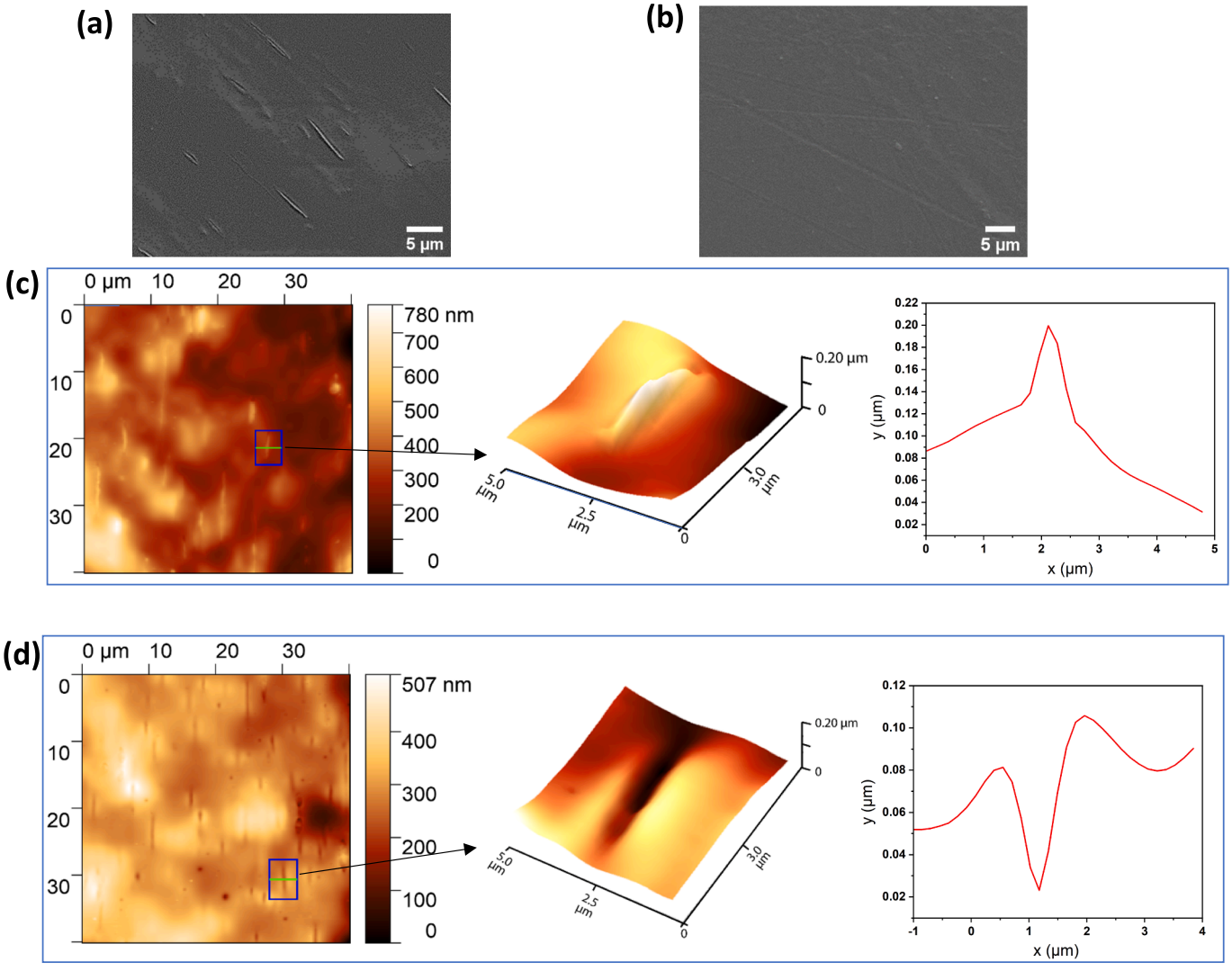

Fig. 6. Topographic images of the inner surface of PE and PLA SUPCs. SEM images of the inner surface of new (a) PLA and (b) PE SUPC. 2D AFM images, 3D images in blue box (~5 × magnification of 2D image) and cross-section graphs of the inner surface of PLA SUPC (c) before and (d) after exposure to hot water. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

absence of innovative packaging technologies, result in increased per capita exposure to MPs. The increased human exposure may be a health threat given the widely reported adverse biological effects caused by PLA MPs [39–41] and micro- and nano-sized cellulose [32–34].

4.2. MPs release mechanism and mitigation

To date, little is known about the release mechanism of PLA MPs during daily use scenarios. Previous studies pointed out that PLA polymer has poor heat resistance. It tends to become soft and deforms at temperatures above 55–80°C [42]. Given the high temperature (up to 95 °C) and mechanical shaking during tea/coffee brewing and the drinking process, it is understandable that the damage to the inner film results in a high release level of PLA MPs. In addition, the blending of PLA with additional materials may also contribute to the high release. Pure PLA polymer is very brittle with poor thermal resistance and low ductility, which together do not meet the requirement for SUPCs. Generally, materials such as bio-oils are blended to improve the polymer properties [43,44]. The addition of certain additives or fillers to PLA material can affect its morphology, which refers to the arrangement of the polymer chains in the material. For example, the addition of plasticizers can affect the crystallization bahaviour of the polymer, thereby promoting the formation of amorphous regions and changing the morphology of the material. The more heterogeneous or porous morphology could create more opportunities for MPs to be released as the material degrades or is subjected to abrasion. SEM images clearly showed the presence of blended cellulose fibers in the bulk inner lining of PLA SUPCs and from which cellulose particles/fibres were detected in PLA water samples (Fig. 6a). In contrast, there were no cellulose microparticles released from PE SUPCs (Fig. 6b). From this point of view, based on the different material properties, the manufacturing method used for PE lining of SUPCs if applicable to PLA lining may avoid the excessive release of cellulose fibers.

To reduce the level of MPs released from paper SUPCs, it has been suggested to rinse the SUPC with hot water before use. The industry has also suggested a hot-water pre-treatment of these SUPCs before shipment to the consumers [45]. During the daily use of disposable coffee cups, some users may pre-wash them for hygiene reasons or for repeated use based on environmental and/or personal motivations. However, based on our results involving repeat use experiments, pre-wash and reuse of PLA SUPCs have little impact on the levels of MPs release (Fig. S4a-b). A similar trend in MP release from reused PE SUPCs was observed in previous research [46]. Alternatively, reusable coffee cups (usually PP based) are recommended in coffee stores to reduce environmental impact. Life cycle assessment found that reusable coffee cups have to be used 150 times to reach a break-even point from the perspective of climate change and non-renewable energy [47]. Additionally, reusable plastic cups need repeated rinsing, disinfection and transport during travelling and represent a real exposure to MPs and additives due to the well-known degradation of the PP in presence of hot water [48]. A separate study compared different materials and types of cups and concluded that ceramic mugs have the lowest environmental impacts [49]. Clearly, the optimal mitigation method has yet to be identified and will likely require novel and cost-effective materials and product design.

4.3. Uncertainty of PLA SUPCs and MPs release

The methods of assessment and detection employed in this work have some limitations. In the assessment, the SUPCs market was split into two groups (i.e., PE and PLA-lined SUPCs), similar to the current market situation. However, it can be substantially changed if there is a market breakthrough material in the future. In addition, ethanol treatment can effectively remove interference from the additives. Due to technical limitations, some additive-attached MPs were regarded as single particles in the counting process. This could lead to an underestimation of the total particle numbers. The potential interference from other additives is also expected, given that over 400 additives are used in plastic processing [50]. Based on our previous study, there is potential for an unintentional overestimation of MPs release levels in the previous research due to the similarity of the Raman spectra of PE MPs and chemical additives [24]. In addition, the filtration method in this study is unable to provide any information on the numbers of nanoparticles smaller than 0.8 μm, while previous studies using the drop cast method can capture all the particles in the water sample [51], but compositional characterization is very challenging. Consequently, differences in detection and testing methods could cause quantitative differences between the results of present and previous studies. In addition, the unidentified particles detected in PE and PLA samples exhibited Raman spectra (Fig. S5) with high fluorescence background, so that their composition could not be determined, but they had a similar size distribution to that of PE and PLA MPs, ranging in size from 3 μm to 15 μm.

It also should be noted that the PMPs release levels obtained using ultrapure DI water in this study may be different from the real beverages. For instance, the pH of DI water used in this study was 6.8–7, which is slightly higher than the actual hot drink (e.g. pH of coffee is around 5, pH of black tea is 4.9–5.5). A previous study has shown that additives particles are more likely to be released from plastics with low pH levels [52]. Additionally, the acidic condition can weaken the bonds between the microplastics and the product surface, making it easier for the microplastics to detach and be released [53]. On the contrary, impurities in hot beverages (organic compounds, caffeine and tannins) may attach to the surface of inner lining, preventing the direct contact between hot liquid and plastic lining and resulting in a slower speed of PMP release. Crucially, ultrapure DI water is an effective tool widely used in previous studies investigating microplastic release from daily use plastic products, such as PE-lined cups [2,31], disposable plastic food containers [54,55] and teabags [1,56]. These studies using DI water provide valuable information on MPs and additives released from our daily plastic products and the potential human exposure.

5. Conclusion

This study takes the biodegradable PLA SUPC as an example, compared with the traditional plastic PE SUPCs, investigating the total particle release level of biodegradable and conventional plastic products by mimicking hot beverage preparation and drinking protocol. When exposed to 95°C water, PLA SUPCs can release up to 4.2 times as many microparticles compared to traditional SUPCs, including a large proportion of additive microparticles. Ethanol treatment was verified as an effective method to separate MPs and additive microparticles. It should be noted that the wide existence of additive-attached MPs and cellulose microparticles could lead to an underestimation of the total particle numbers. Additionally, since 0.8-μm pore size membrane filter was used in the study, nano-sized particles are not captured in our measurement, which substantially contributes to the underestimation of the total particle numbers. Crucially, the approach described here can be used to investigate MPs and additives released from other biodegradable plastic products and assess the potential MPs exposure trends.

This paper has provided an in-depth investigation of biodegradable plastics with an investigative insight on their candidature to be the best alternative to traditional plastics and the future in terms of new environmentally friendly materials. Clearly, it is too early to conclude that biodegradable SUPCs are a better alternative than conventional SUPCs from both human and environmental health perspectives. Taken together, there is still a large research gap on the potential harm of biodegradable MPs and additives to human health, which should be an important research direction in the future.

CRediT authorship contribution statement

J.J.W., J.J.B., and L.X. conceptualized and supervised the study and

reviewed and edited the manuscript; L.Y. performed the experiment, analyzed the data, and wrote the original manuscript; D.L. and Y.S. prepared samples and performed the experiment (Raman spectroscopy, FTIR and SEM); C.H., R.P. and L.P. performed the experiment, and all authors provided comments on the manuscript.

Declaration of Competing Interest

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2023.143620.

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