Production and analysis methods for pristine and degraded microplastic and nanoplastic reference materials

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The wicked challenge of environmentally realistic NP/MP test and reference materials

Microplastic (MP) and nanoplastic (NP) particles are contaminants of emerging concern due to (i) their expected high abundance in various environmental compartments, and (ii) the hypothesized and partially demonstrated deleterious effects on organisms that ingest or otherwise come into contact with them. To date, most environmental fate and hazard assessments have utilised spherical, monodisperse polymer particles that do not represent the **continuum of partially degraded, irregular-shaped MPs found in the natural environment**. The presence and characterization of NPs in the environment is still proving a challenge due to limitations in available methodologies. A such, there is a strong need for environmentally relevant test and reference materials. Unfortunately, these are proving hard to produce and assess, largely due to the same reasons as described above.

Option 1: Bottom up synthesis

Pros: Relatively easy/fast/cheap, controllable
Cons: Lack of sufficient environmental realism, lack of heterogeneity and lack representativeness for environmental samples

Option 2: Top-down production (This study)

Pros: Can be applied to plastic from any stage of the life-cycle, provides heterogenous mixtures of shape and size, creates particles more representative of true secondary MPs/NPs.
Cons: Hard to obtain amounts needed for laboratory testing due to low yields, especially of small MPs and NPs.

Option 2a: Mechanical degradation

- Cryomilling was applied to pristine pellets of polypropylene (PP), polyethylene (PE, HDPE, and LDPE), polyethylene terephthalate (PET), polystyrene (PS) and polytetrafluoroethylene (PTFE).
- The <100 µm size fraction was collected and the particle size distribution analysed by Morphology G3 (Fig. 1).
- By mass, the <10 µm fraction was negligible (<0.05%).

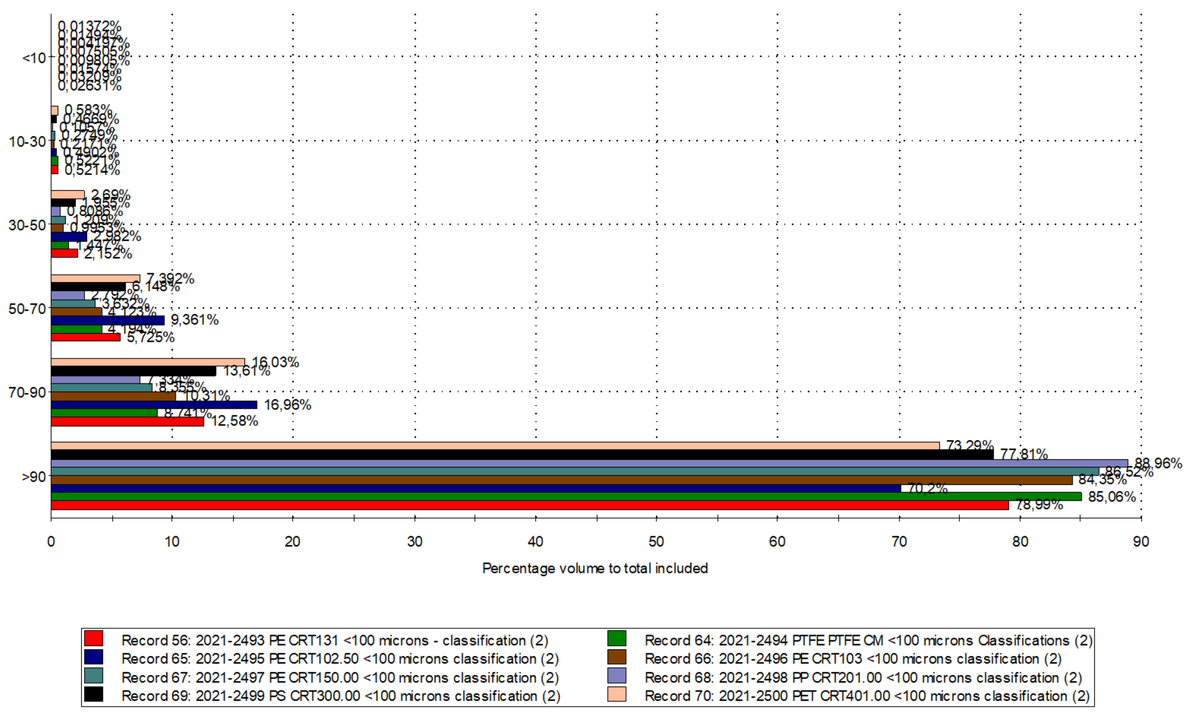

Fig 1: Relative volume distribution of sizes <10 – 100 µm after cryomilling of different polymer plastics by Morphology G3.

Option 2b: Accelerated UV-degradation

- To promote further fragmentation, selected polymers (PE, PS, PET) previously subjected to cryomilling (<100 µm) were subjected to thermal pre-treatment, UV-C ozonation (3 hr) and probe sonication to facilitate fragmentation (Fig. 2). [1]

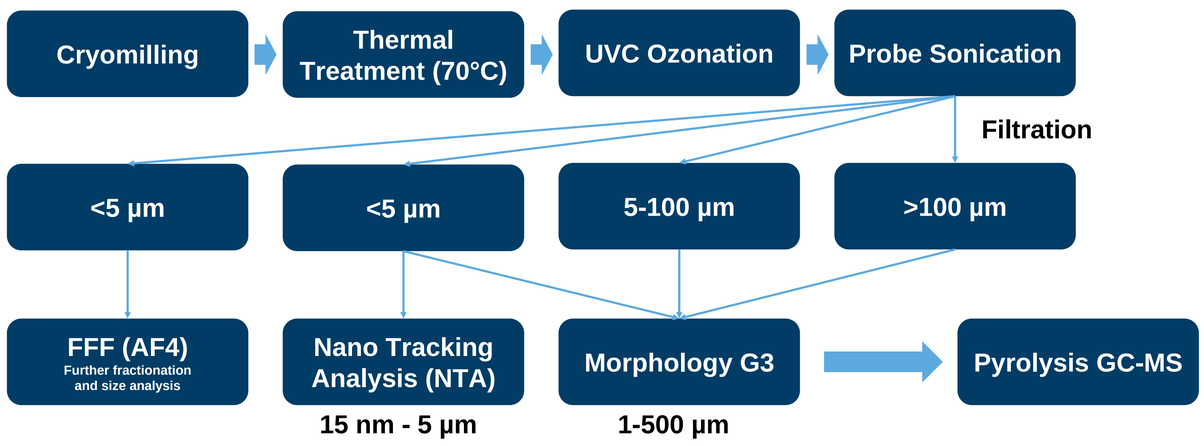

Fig 2: Overview of the degradation protocol and hyphenated fractionation and multi-instrument identification and quantification workflow for sMP and NP characterisation.

- UV-C ozonation increased the relative mass yield of NP (<5 µm) over small MP (5-100 µm) for all three polymers, with particular increase of particles between 1-7 µm (Figs. 3 & 4).

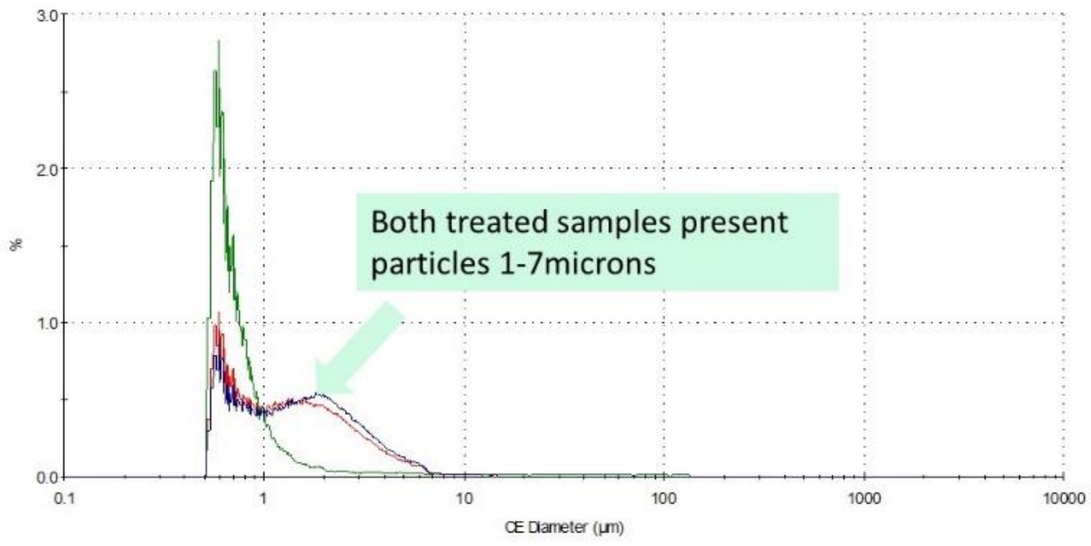

Fig 3: Percentage of PS particles (by number) of specific sizes in the UV-C-ozonated samples (with and without thermal treatment (red and blue) compared to non-UV-treated samples (green).

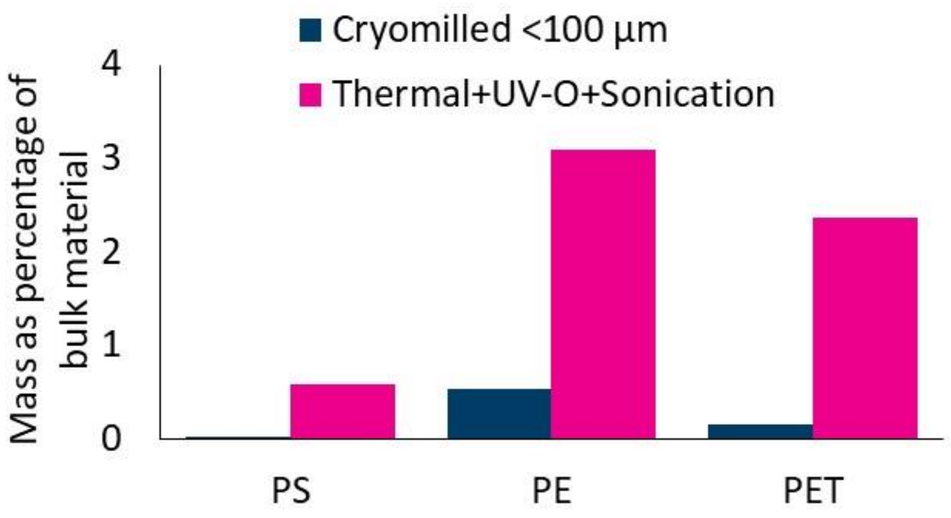

Fig 4: Percentage mass of PS, PE and PET particles <5 µm with (pink) and without (blue) thermal, UV-C ozonation and sonication treatment.

Conclusions

- Cryomilling alone is insufficient to produce reasonable yields of MPs/NPs from larger materials.
- Post cryomilling treatment with a combination of thermal exposure, UV-C ozonation and probe sonication in aqueous dispersion yielded significant increases in the number of particles <5 µm.

Future prospects

- UV treatment at some point in the top-down MP/NP production process is important for creating environmentally relevant reference materials.
- Need a focus on methods that increase the yield of particles <10 µm, especially those <1 µm.
- Assessment of UV-C vs UV-B as an accelerated aging method for producing environmentally degraded NP/MP test materials.

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[1] Amit Kumar Sarkar, Andrey Ethan Rubin, and Ines Zucker. Environmental Science & Technology 2021 55 (15), 10491-10501.