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

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What is plastic really?

Polymer + Associated Chemicals

- Plasticisers, antioxidants, UV stabilisers, flame retardants, colorants, antimicrobials & residual chemicals.
- Important these are present in test/ref materials

Primary environmental degradation mechanisms

Despite conventionally being considered an inert material, most thermoplastics can degrade in the natural environment (at varying rates)

CO_2

Sunlight (UV)

Physical/Mechanical

Microbial

Abiotic

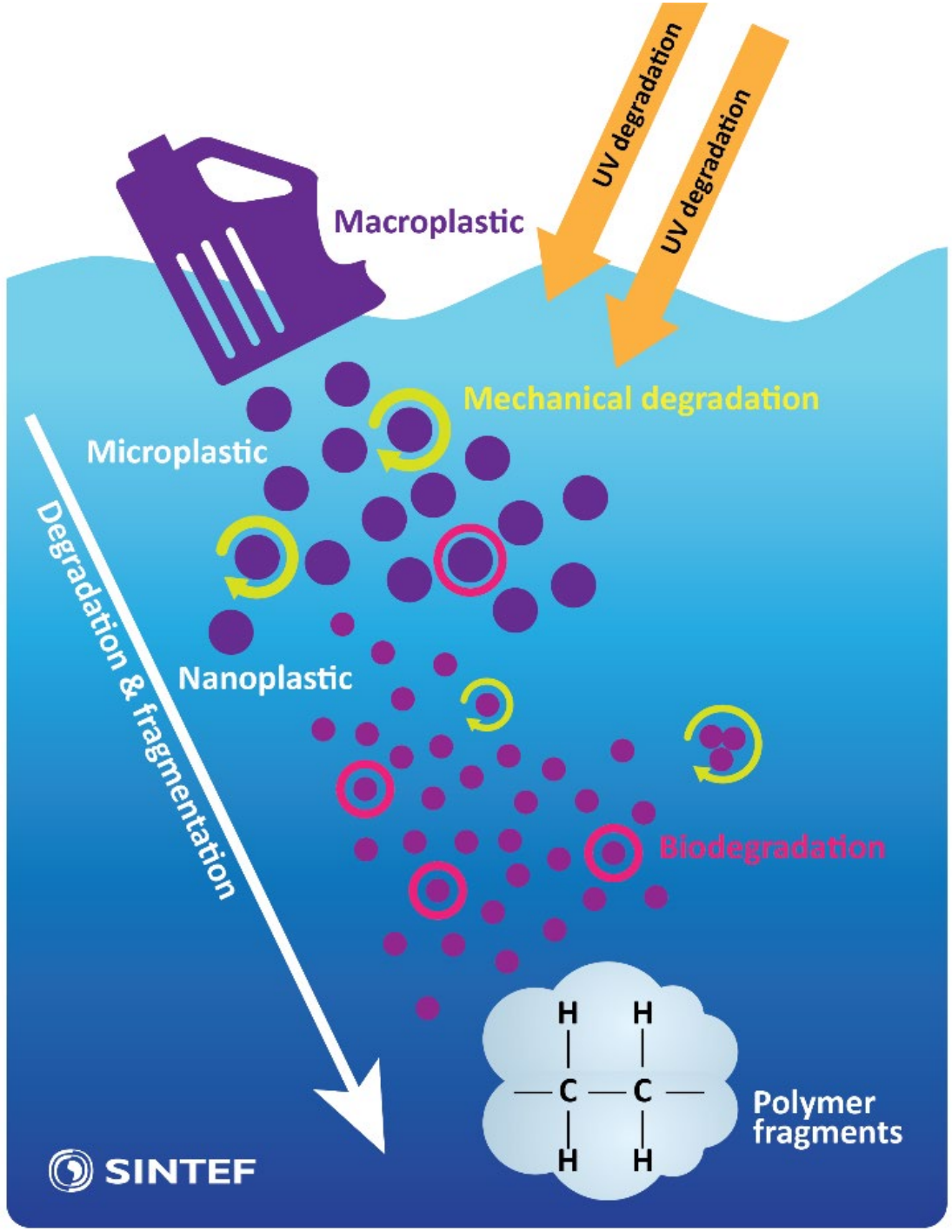
Biotic

Environmental degradation

Irreversible process causing:

- Changes in material properties
- Fragmentation to occur
- Changes to the chemical properties of the material

Process starts mainly at material surface in contact with the environment.

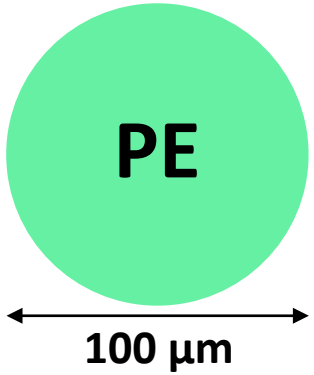


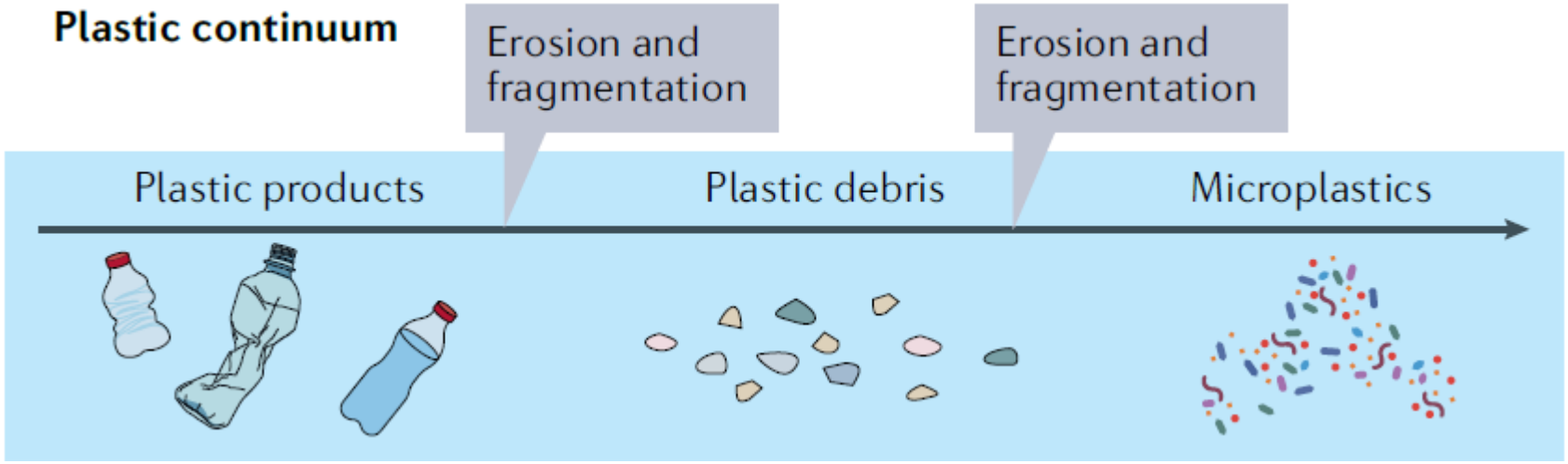
Plastic litter/particles in environmental matrices

- Irregular shaped
- Partially degraded
- A continuum of sizes, shapes and densities
- A wide range of polymer types
- A reservoir of different plastic-associated chemicals.

Currently…….

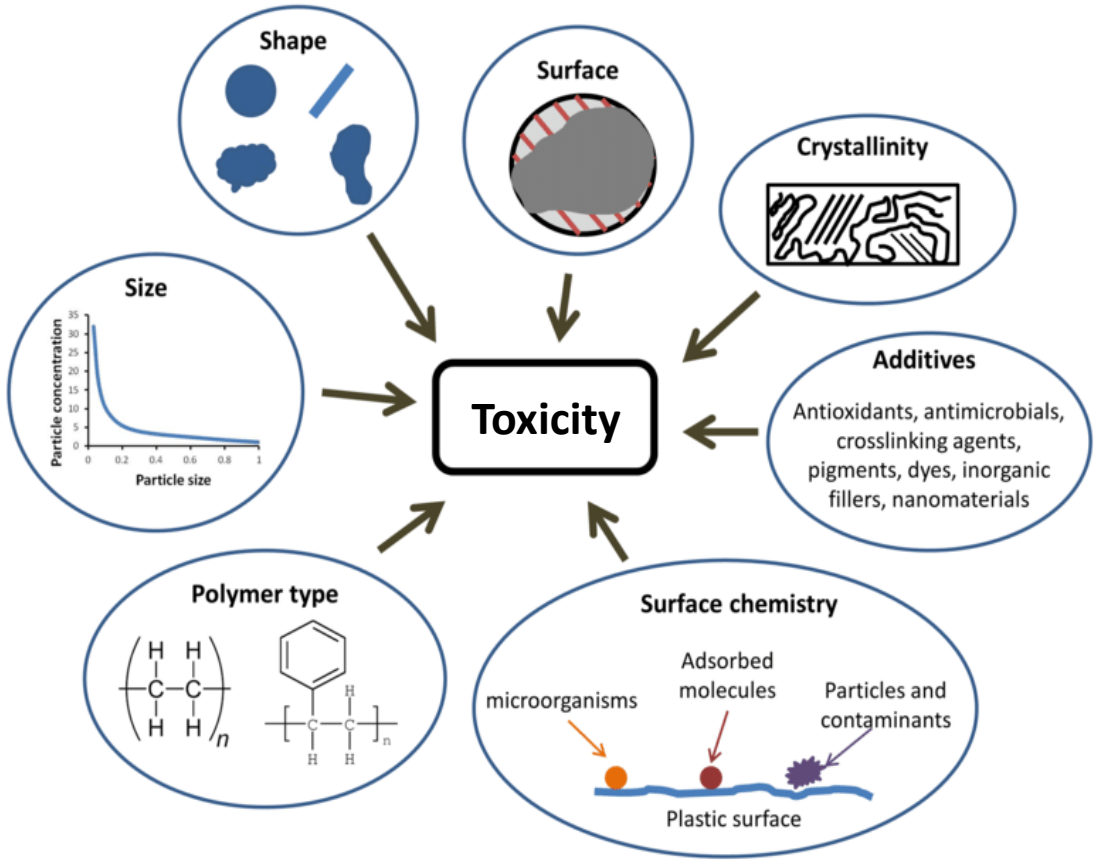
….. many MNP toxicity studies employ spherical particles of a single size or narrow size distribution (monodisperse), comprised of a single polymer type…….





……..this does not represent the complex mixture of polydisperse, partially degraded particles and associated chemicals found in the environment.

This poses a problem for risk assessment



We need environmentally relevant MP and NP for assessing fate and effects – what options?

Lambert et al., 2017. Ecotoxicity testing of microplastics: considering the heterogeneity of physico-chemical properties. *Integrated Environmental Assessment and Management*. 13 (3). 470-475.

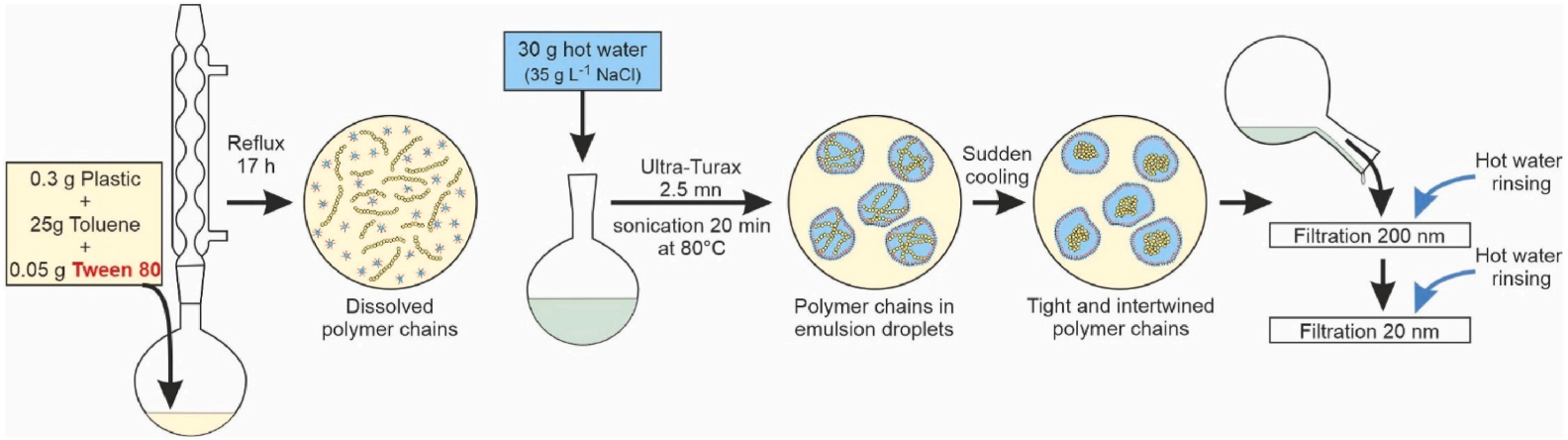
Top-down vs bottom-up

Most studies have used PS – not the most relevant plastic!

Macroplastic **Mesoplastic** **Microplastic** **sMP (<50 µm)** **Nanoplastic**

Top-down

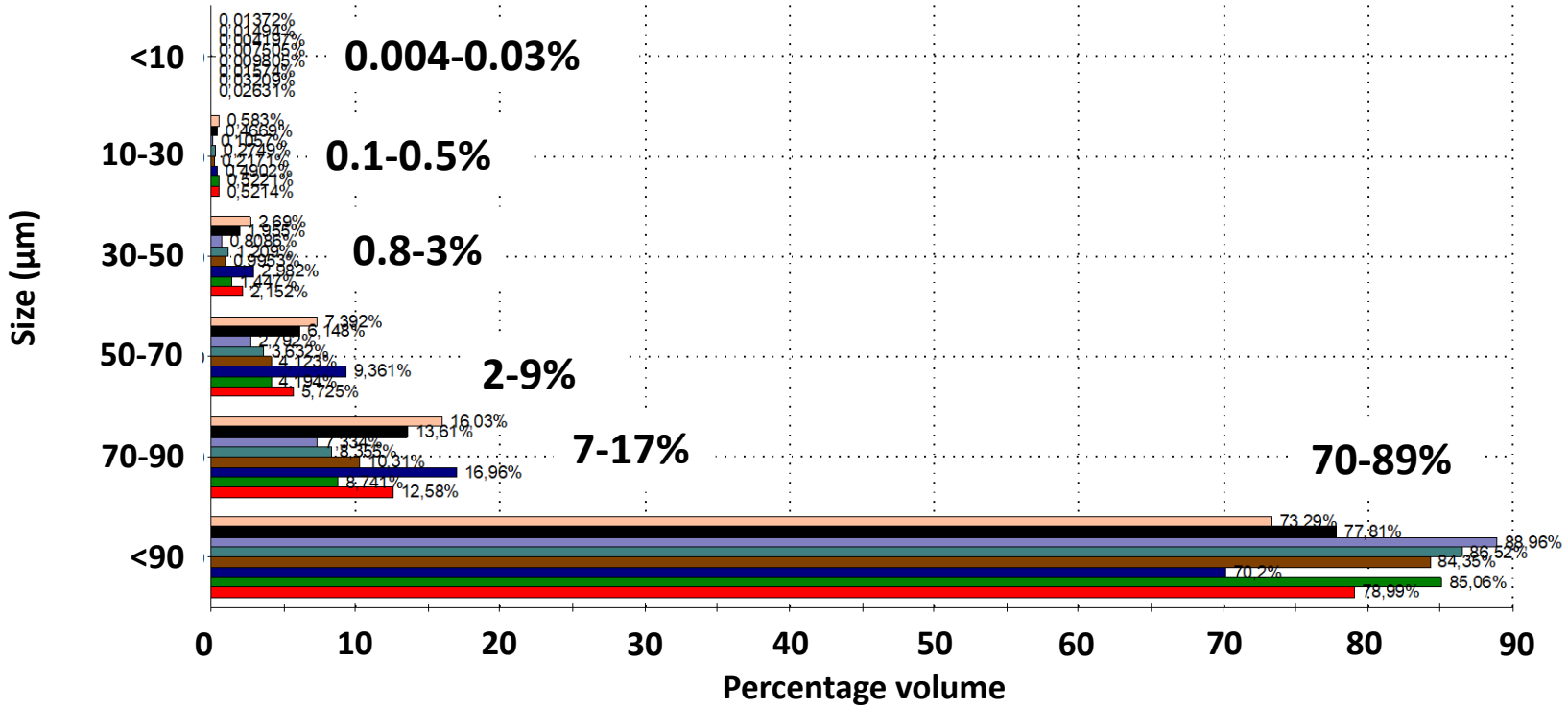
Bottom-up

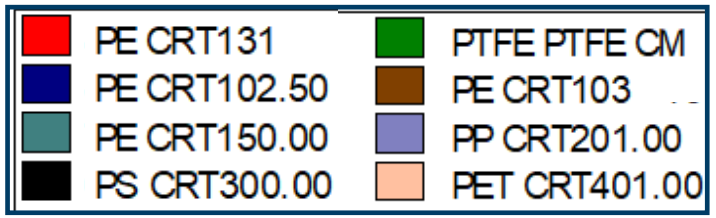


Merdy, P., F. Delpy, A. Bonneau, S. Villain, L. Iordachescu, J. Vollertsen and Y. Lucas (2023). "Nanoplastic production procedure for scientific purposes: PP, PVC, PE-LD, PE-HD, and PS." Heliyon **9**(8): e18387.

Cryomilling most commonly used top-down method

- Achieves irregular shapes
- Difficult to produce significant yields <10 µm





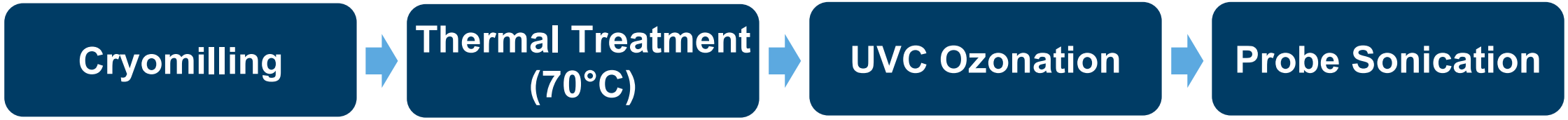
Need alternative approaches for sMP and NP

Testing and optimization of 3 strategies from literature:

- #1: Thermal degradation + UVC degradation + probe sonication (Sarkar et al., 2021)
- #2: Multiple mechanical processes: Sonication vs ‘wet grinding’
- #3: Partial solubilization with a long chain alkane (Peller et al., 2022)

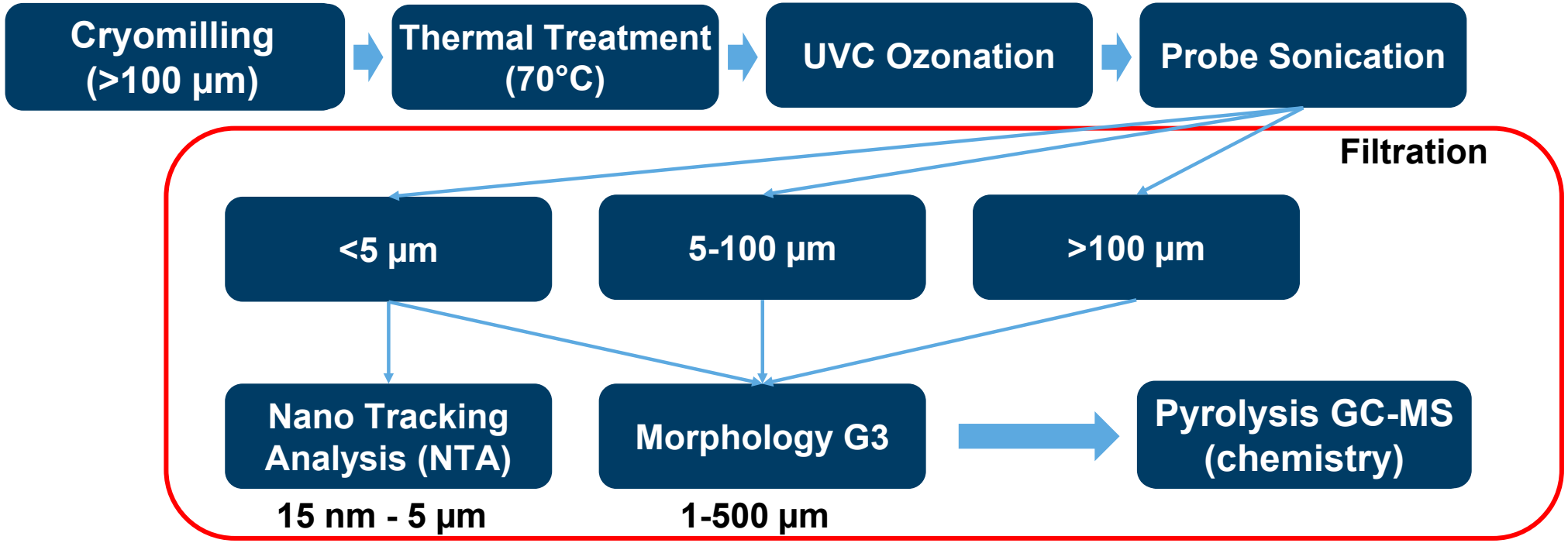
Sarkar, A. K., A. E. Rubin and I. Zucker (2021). "Engineered Polystyrene-Based Microplastics of High Environmental Relevance." Environmental Science & Technology **55**(15): 10491-10501.
Peller, J. R., S. P. Mezyk, S. Shidler, J. Castleman, S. Kaiser, R. F. Faulkner, C. D. Pilgrim, A. Wilson, S. Martens and G. P. Horne (2022). "Facile nanoplastics formation from macro and microplastics in aqueous media." Environmental Pollution 313: 120171.

Strategy #1



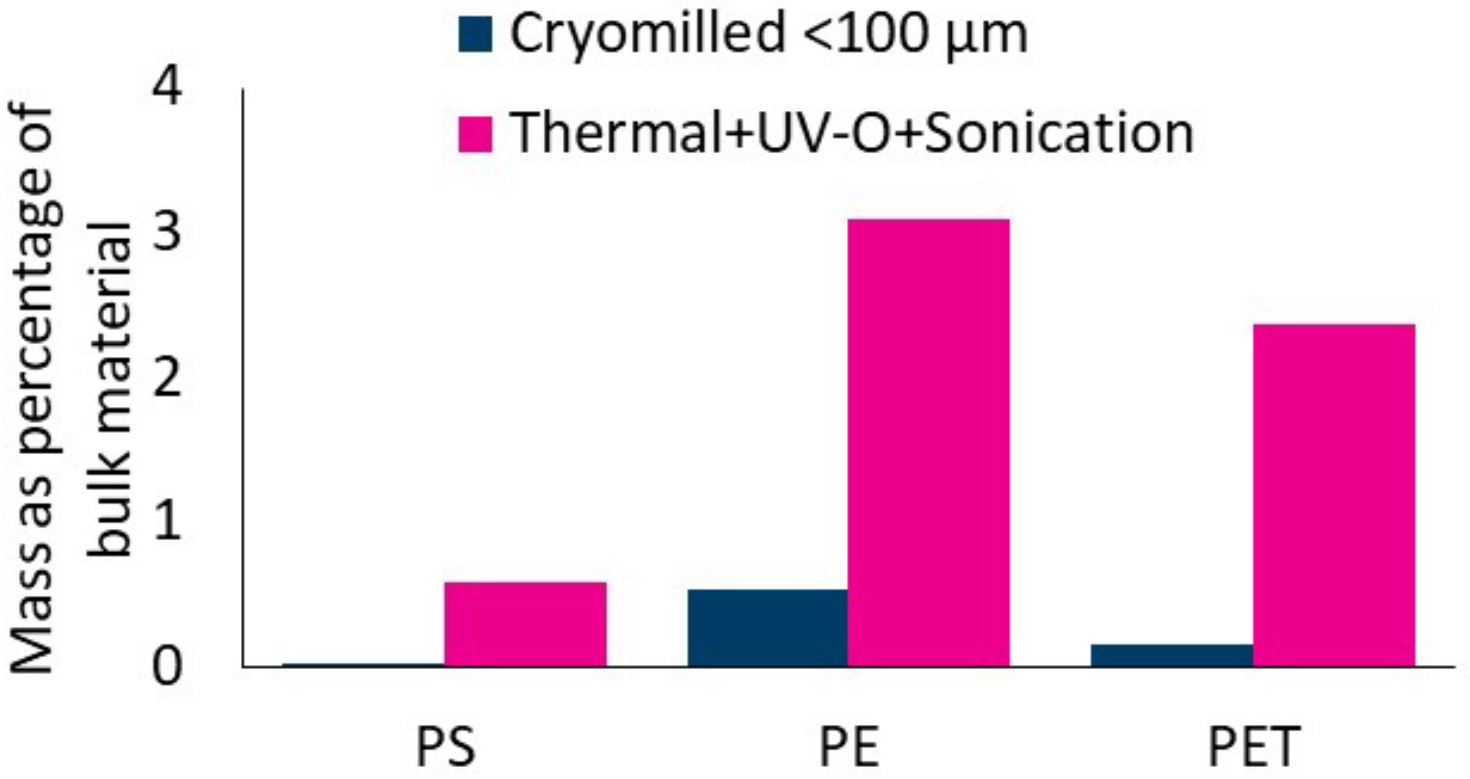
Sarkar et al., (2021) tested method for PS and found that it reduced particle size to 1 µm, but did not quantify the NP fraction and no yields presented.

Strategy #1



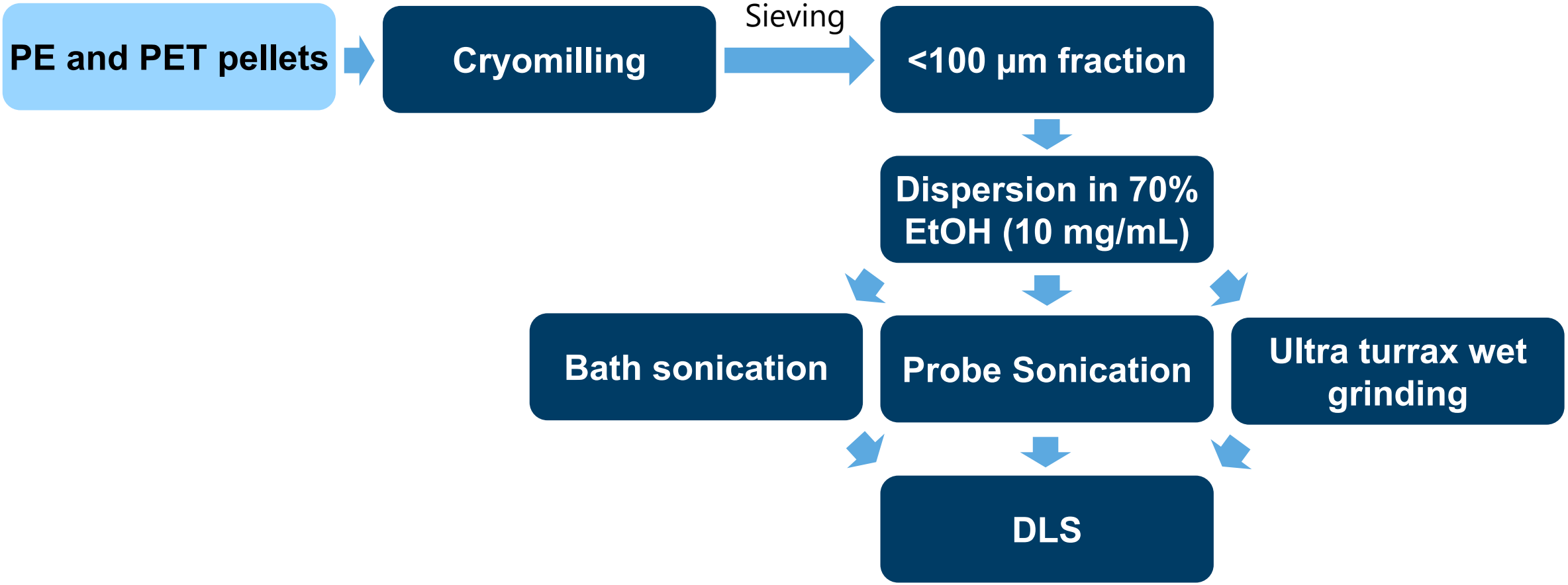
- Checked reproducibility with PS
- Also tested with PE and PET
- Quantified sMP and NP fractions

Improvement & potential

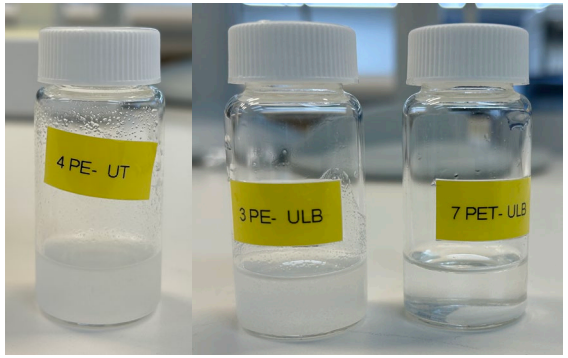


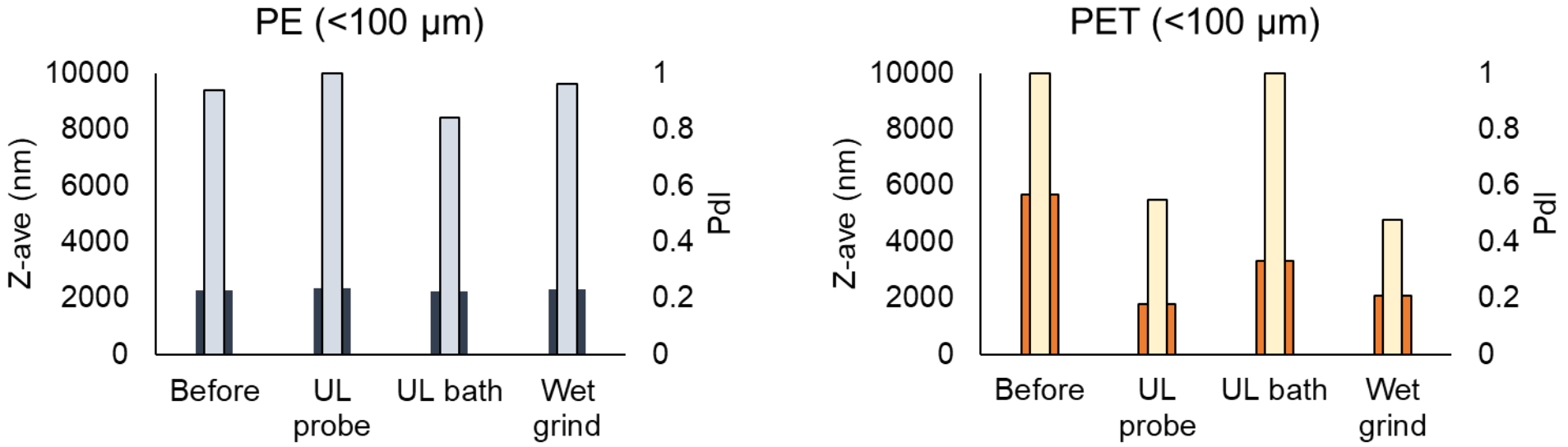
- Percentage increase in no. particles and mass in size range 1-7 µm for all materials
- No measurable increase in the NP yields

Strategy #2


PE and PET pellets
Cryomilling
Sieving
<100 µm fraction
Dispersion in 70% EtOH (10 mg/mL)
Bath sonication
Probe Sonication
Ultra turrax wet grinding
DLS

Strategy #2

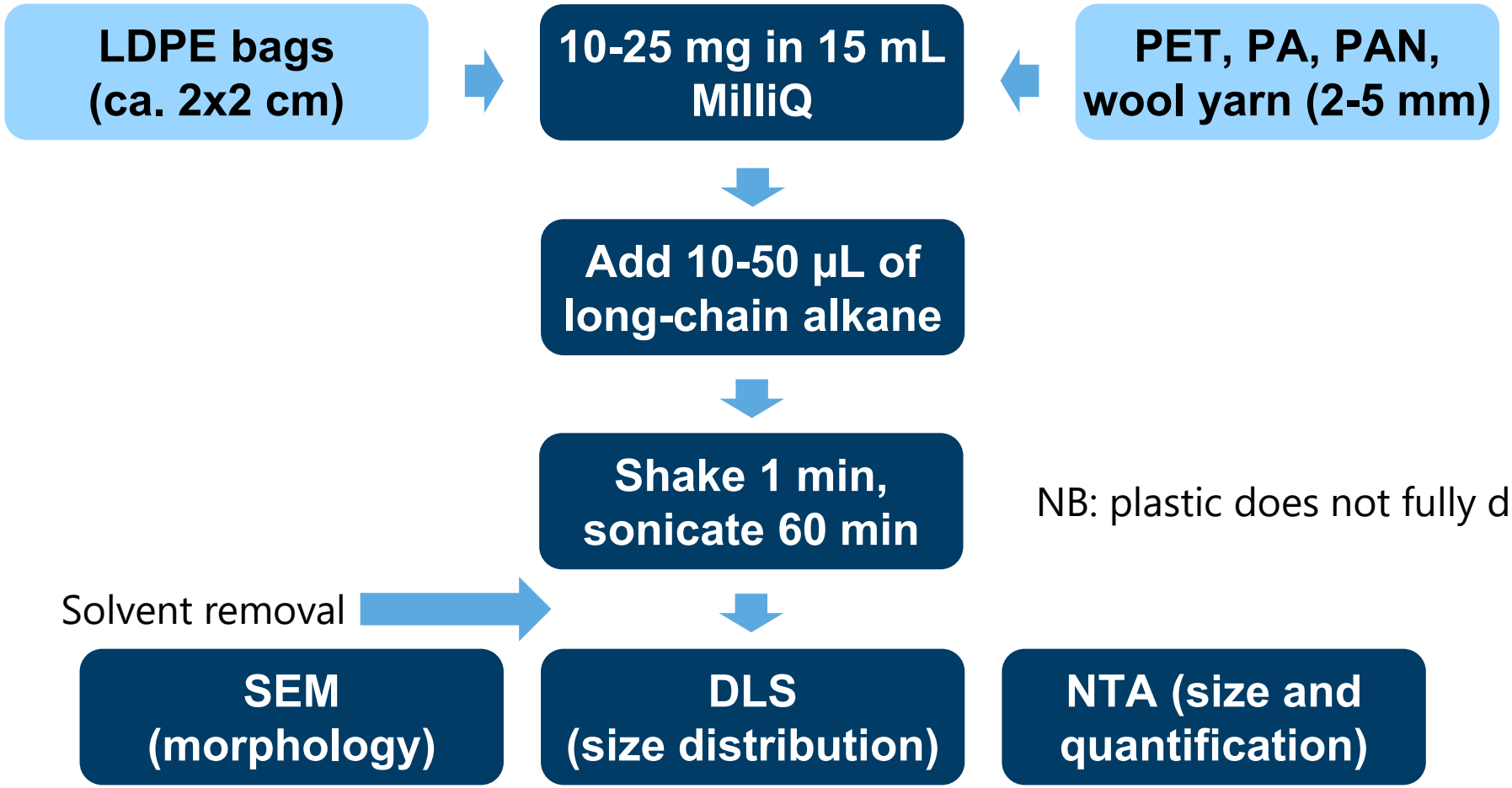




Dark colour is the z-average and light colour is the PDI

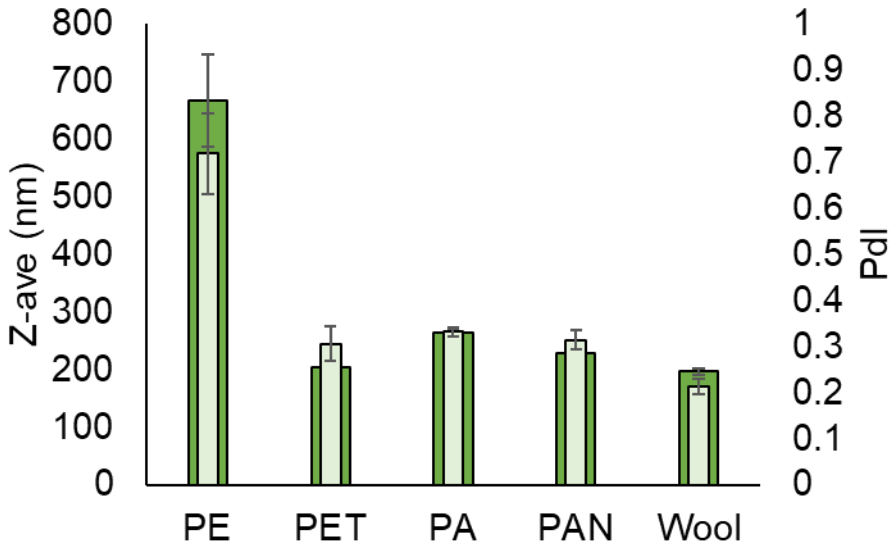
- PE - no change in size with any treatment and large PDI, sizes beyond the range of DLS
- PET - Some reduction in mean size with all methods, but not into the nano-range. Still large PDI.

Strategy #3



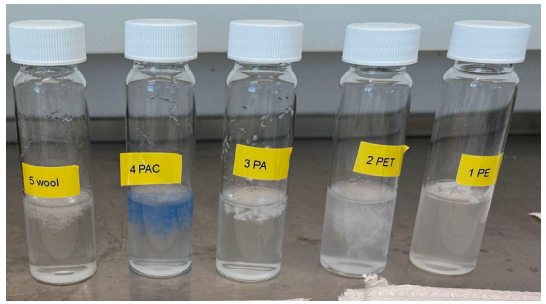
NB: plastic does not fully dissolve

Strategy #3: Hot off the press

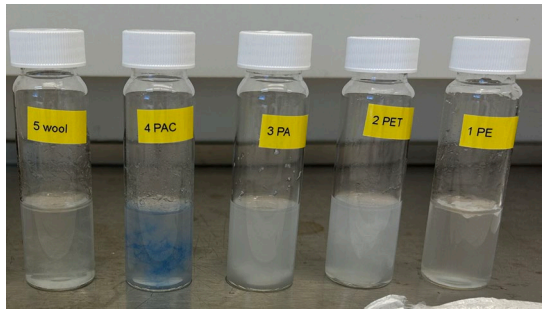


Dark green is the z-average and light green is the PDI

Before



After



Next Steps

- **Mass balance/yield**
- **SEM imaging (morphology)**
- **NTA (size and concentration)**
- **pyGC-MS (chemical profile)**

- PE nano-scale particles formed, z-ave ca. 650 nm, relatively high PDI
- PET, PA, PAN and wool smaller z-ave (ca. 200-300 nm), reduced PDI
- Full physicochemical characterisation to be done, working on improvements to PE method

Peller, J. R.; Mezyk, S. P.; Shidler, S.; Castleman, J.; Kaiser, S.; Faulkner, R. F.; Pilgrim, C. D.; Wilson, A.; Martens, S.; Horne, G. P. Facile Nanoplastics Formation from Macro and Microplastics in Aqueous Media. *Environmental Pollution* **2022**, *313*, 120171. https://doi.org/10.1016/j.envpol.2022.120171.

Summary

- Need for environmentally relevant test/reference sMPs and NPs for fate and effects assessment.
- Cryomilling used for larger MPs produces very low yields of sMP and NP (<50 µm).
- Alternative top-down methods are needed, with some showing promise.
- Methods have different levels of success for different polymer types/materials.

THANKS!

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Thanks!