Microplastic Research Should Embrace the Complexity of Secondary Particles

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Research identifying the ubiquitous presence of microplastics in the environment has accelerated further research to investigate their environmental behavior and fate. Whether a primary microplastic (manufactured microbeads, fibers, pellets) or secondary microplastic (larger plastic debris breaking into smaller fragments), their fate in the environment is influenced significantly by the extent and nature of chemical and physical alteration under environmental conditions. Investigating and quantifying the nature and extent of this chemical and physical change is fundamental to more accurately describe the ultimate environmental fate and behavior of microplastics in the environment. However, this is an area that is often overlooked in microplastics research, or it is approached in a nonstandardized way. For example, a Web of Science search of the term "microplastic*" in 2019 returned 291 papers from three journals publishing the highest number of microplastics papers. Of these 291 papers, 77 described experiments performed in the laboratory with microplastics produced, purchased, or collected by the authors, and only five papers (approximately 6.5%) compared degraded and non-degraded samples to assess the effect of weathering on experimental outcomes.

Degradation, weathering, and aging are used interchangeably to describe the transformation of flexible, hydrophobic, and transparent plastics into brittle, hydrophilic, and opaque plastics (Figure 1). The degree to which weathering occurs, affecting plastic properties, is related to the chemistry of the plastic and the intensity, time, and manner of exposure to environmental agents. Different environments include air, water, soil, inside biological systems, and sunlight as key contributors to weathering and breakdown, leading to conformational changes in primary and secondary microplastics. Different microplastic properties undergo modifications in different environmental situations, and can include the following.

**Leaching of Plastic Additives.** Plastic polymers have chemical additives included to enhance their properties, for example, to last longer, to burn slowly, to be more flexible, or to degrade slower or faster. Certain additives are of environmental concern. The additives are slowly released by the plastics during their useful life and this continues once discarded to the environment. The chemicals diffuse through

![Figure 1. Diagram depicting the main expected differences between degraded and non-degraded polymers.](https://dx.doi.org/10.1021/acs.est.0c02194)
the plastic chains by a variety of mechanisms, most importantly via diffusion through spaces called free volume. The amount of the free volume is affected by polymer chain size (the smaller the polymer chain, the larger the free volume); and, thus, by the polymer chain being broken during degradation, decreasing its size, and increasing the free volume, this might further facilitate the leaching of chemicals.

Wettability. The majority of newly manufactured plastic polyolefins, like polypropylene or polyethylene, are hydrophobic and not wettable by water. This can be moderated either by the presence of additives (e.g., for antifogging) or by environmental degradation, which can lead to the production of polar groups on the plastic surface. For a pristine, fully hydrophobic polyolefin, contact and interaction with water will be minimized compared to a degraded one, because the latter will be more wettable than the former. This can affect all study outcomes that are influenced by such interactions with water, like the formation of biofilm on the plastics in soil or water.

Sorption/Desorption. The degree of polarization of a plastic surface through chemical additives and weathering will also impact the sorption properties of the plastic in the environment. Therefore, characterizing the nature and extent of surface polarization is important to more accurately understand the sorption capacity of the plastic. Working only with primary microplastics may cause misleading sorption/desorption behavior.

RECOMMENDATIONS

Our recommendations are (1) to include weathering and aging studies on primary and secondary microplastics in laboratory studies as an essential part of investigating microplastics in the environment, and (2) for a more standardized approach to assess the extent of weathering and environmental effects on plastics in influencing their environmental behavior and fate.

To address point (1), the production of secondary microplastics and weathered primary and secondary plastics in the laboratory, photodegradation is typically performed using UV-A or UV-C lamps. The former simulates natural sunlight more effectively but takes several months to induce changes in properties; UV-C is faster (a few weeks) but reflects the natural aging process less effectively. However, both can be performed in a low-cost, self-made aging chamber, or systems emulating specific environments. Additionally, since degradation is more intense on the surface, sampling microplastics from an already degraded piece, by milling layers in different depths using a computer numerical control (CNC) machine, also allows samples of the same polymer to be obtained, with the same original formulation, but different levels of degradation.

To address point (2), a more standardized characterization of the extent of physical and chemical weathering and degradation should also be included to allow interlaboratory comparisons and good reproducibility. For example, carbonyl, hydroxyl, or vinyl indices calculated from Fourier transform infrared (FTIR) can quantify the amount of chemical degradation in polyethylene and polypropylene. The number of terminal groups in the plastic can be determined by titration and indicates the decrease of molecular weight for polyesters and polyamides. Contact angle measurements using a goniometer indicates wettability, which varies as a function of the level of degradation. Finally, the melt flow index can indicate changes in molecular weight for all thermoplastics. All these techniques are commonly used in polymer science, and there is abundant literature providing standard protocols.

Using only primary microplastics in toxicity assessments will provide insights into effects at environmental settings close to the source of the microplastics, for example in the vicinity of production and distribution sites. However, due to regulatory measures against single-use plastics and promotion of the circular economy, we do expect a trend more toward a predominance of secondary microplastics because of the effects of degradation of the macro- and microplastics in the environment. This facet of reality includes considering mixtures of microplastic particles at various stages of degradation, which would be challenging to reproduce through laboratory experiments alone. Progress in the laboratory can still be made by initially considering just the effects of aging for certain particle types as described above. What we learn about this could subsequently also be applied to understanding effects of degradation in complex mixtures present in real environmental samples.

In summary, the proposed approaches to characterize and quantify the nature and extent of microplastic weathering will help move microplastic research closer to realism and environmental relevance.

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Notes
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