Influence of additives on long-term weathering of microplastic

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Abstract

The accumulation of microplastic in environmental compartments poses inestimable ecological risks. Additives and their degradation products might increase environmental effects despite being added to mass polymers in small proportions. While additives improve the polymer functionality and stability during service life, little is known about their long-term effects during weathering. Particularly, migration and leaching are important questions. Thus, a comprehensive analysis of abiotic polymer degradation as function of additive proportions is required to aid risk assessment. The necessity of samples with well-defined plastic compositions and weathering states as well as the small proportions of additives and polymer defects, introduced by photooxidation, make such analysis challenging.

We performed accelerated weathering studies on commercial polypropylene samples before and after removal of the incorporated additives via soxhlet extraction and monitored polymer degradation via particle size measurements, gel-permeation chromatography and NMR spectroscopy. The phosphite processing stabilizer Irgafos 168 was identified as main additive component. As expected, the stabilizer's presence resulted in an induction period. However, afterwards, degradation was accelerated by a factor of four meaning that Irgafos strongly enhances long-term weathering.

To gain insights into this surprising observation on a molecular level, we conducted a model study with pristine and additivated (5 wt% Irgafos 168) polystyrene. The higher additive proportions ease mechanistic investigations using NMR spectroscopy. While solid-state 13C multiCP NMR enables quantification of polymer defects such as peroxides and alcohols, 31P NMR spectroscopy is used to selectively analyze additive degradation. For instance, oxidation of Irgafos to the corresponding phosphates and phosphonates could be observed. Additionally, liquid-state NMR spectroscopy provides insights into the leaching behavior. Surprisingly, even after 3200 h, representing approximately two years of outdoor weathering, large amounts of additive degradation products remain in the polymer. The small extent of leaching might be caused by interaction of polar polymer defects with additive degradation products.

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