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Electronic Supporting Information

Chemical heterogeneity observed in the development of photo-oxidized PET micro- and nanoparticle weathered controls

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ATR-FTIR and OPTIR measurement summary. Because the generation of the infrared spectra from absorbance and scattering methods are different, a brief discussion was included for the two infrared spectroscopy methods implemented in this work. Differences in the spectra for the films were observed for the two different measurements used in both the pristine and PO films. Comparison of ATR-FTIR, Raman and OPTIR spectra of bulk and microplastic samples has been previously reported.[1] ATR-FTIR measurements represent the absorbance spectra resulting from the evanescent wave probing the top (1 to 2) µm of the surface. The OPTIR spectra are derived from the thermal properties of the sample using a pump-probe instrumental configuration and estimation of the sample expansion interrogated deeper than (1 to 2) µm. The OPTIR spectra for (*n* > 100) sub-10 µm cryomilled PET particles was shown (Fig. S5) for comparison to the weathered samples. Most notably for the pristine PET films, the λ_{max} for the ν_{as}(CO) peak was shifted from 1710 cm^{-1} to 1723 cm^{-1} and the differences in the intensities from (1200-1325) cm^{-1} that comprise (C=O)-C stretching of the ester, in plane ring-ester modes, and ring and O-C stretching modes were observed. The vibrational modes associated with the benzene ring were unshifted (1017 cm^{-1}, 1100 cm^{-1}, 1410 cm^{-1}, 1577 cm^{-1}, etc.), indicating differences in the mode of interrogation affect sample response or sample stability. This was most notable in the photo-oxidized (PO) spectral comparisons, where the oxidation products were marked by a blue shift from 1710 cm^{-1} and the red shifted products from 1240 cm^{-1} and 1100 cm^{-1} with low signal intensity likely result from instability. Work on the instability of products probed with OPTIR are currently ongoing. Although there were slight differences in the pristine spectra, both techniques were capable of monitoring chemical changes after exposure.

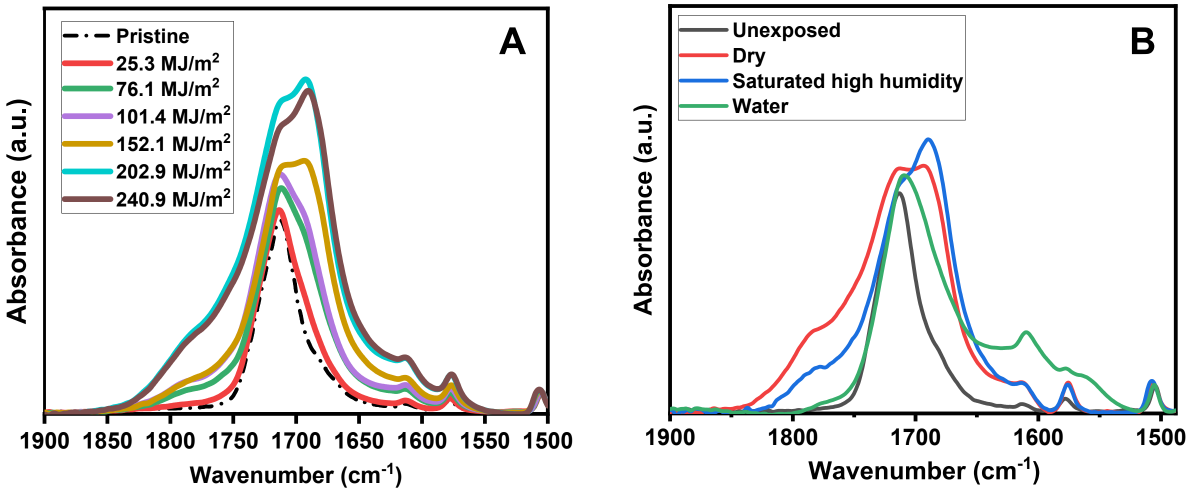

Fig. S1. Representative ATR-FTIR spectra (A/A_0) for a PET film as function of exposure inside of the SPHERE (left panel). Comparison of carboxylic region in the presence and absence of water during exposure (right panel). All spectra were normalized to the benzene ring vibration at 1410 cm^{-1}. "Water" in panel B represented submerged films in the reaction cell during exposure.

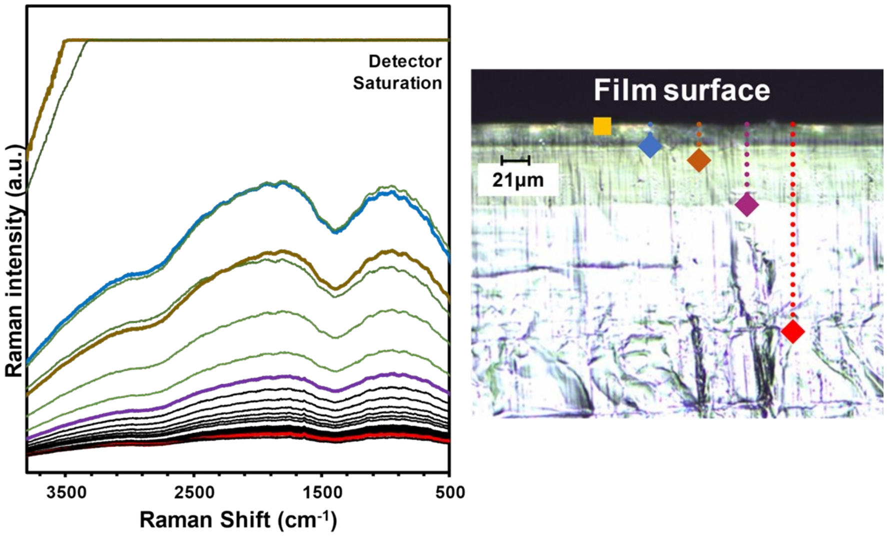

Fig. S2. Raman intensity spectra for cross-section of photo-oxidized PET film. The color of the Raman spectra (left panel) corresponded to the denoted location on the optical image (right panel). The signal intensity in the first 20 μm from the film surface resulted in detector saturation.

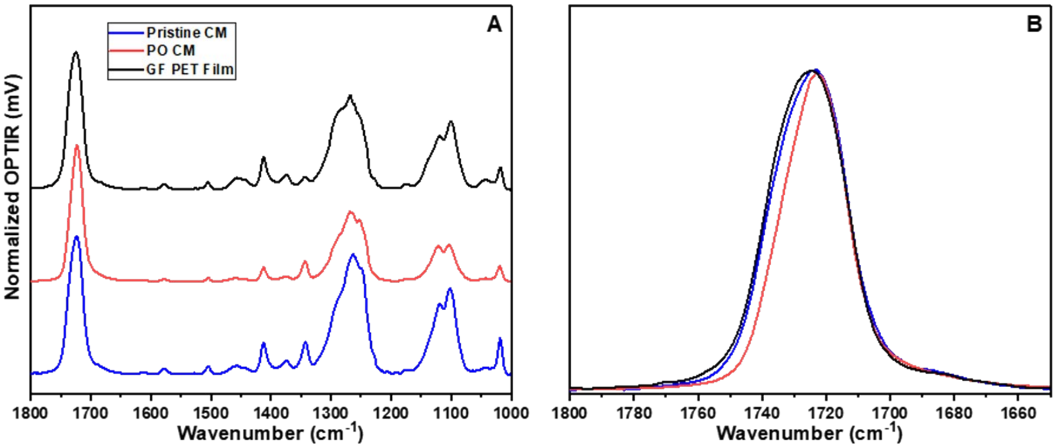

Fig. S3 Summarized OPTIR comparison spectra of the original PET film (black trace), cryomilled, unexposed MNP (blue trace), and weathered MNP (red trace) in Panel A. Panel B is the normalized spectra for all three spectra in the carboxylic region for comparison. See Figure S5 for representative pristine CM spectra.

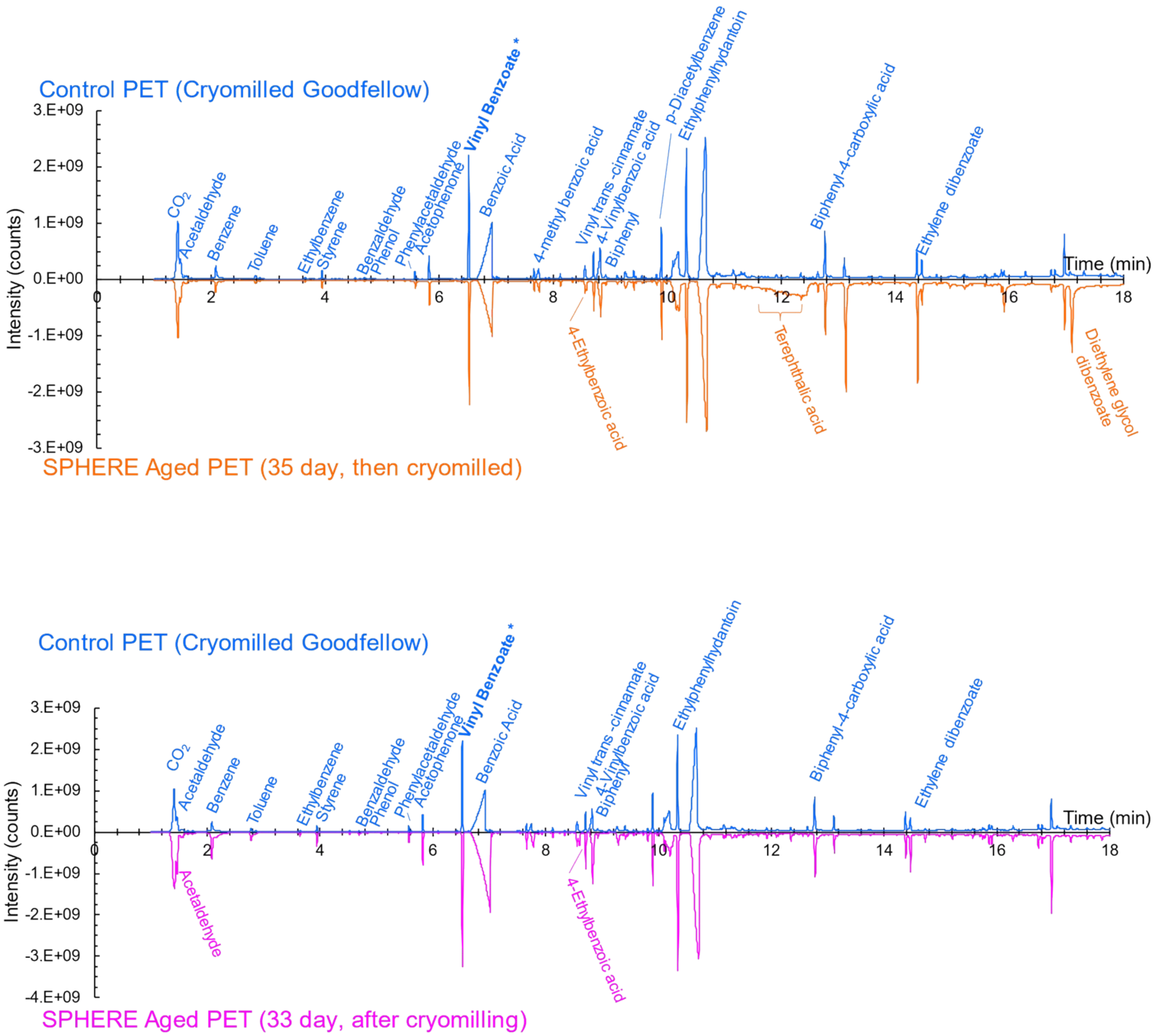

Fig. S4. Representative single shot py-GC-MS chromatograms of pristine and PET samples exposed in the SPHERE for ≥35 d. (Top panel) comparison of the pristine, CM PET powder to PO film that was cryomilled after exposure. (Bottom panel) comparison of the pristine, CM PET powder to pristine film that was cryomilled prior to similar PO exposures in the sphere.

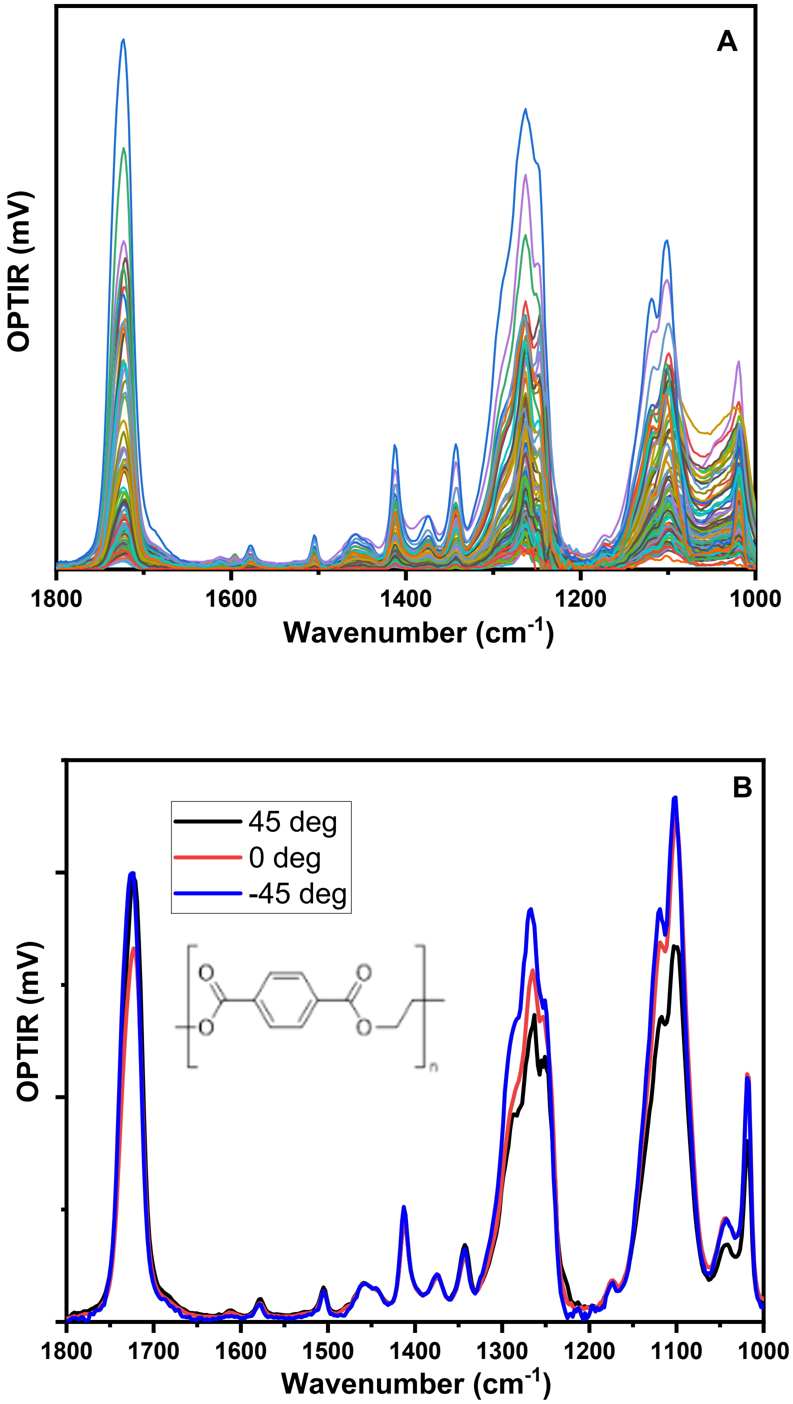

Figure S5. Representative spectra for PET cryomilled particles with largest dimension less than 10 µm (panel A). Relative intensities for the bands centered near 1723 cm^{-1}, 1265 cm^{-1}, and 1101 cm^{-1} demonstrated polarization dependence based on orientation for a sub-10 µm particle (panel B), which were consistent with amorphous film properties. The inset in Panel B represents the repeat unit structure for PET and the characteristic vibrational modes have been summarized previously.[2-4] The polarization measurements demonstrate anisotropy in the small microplastic particle generated from both the exposure and grinding processes. The appearance of anisotropy indicates that spectral signatures for PET MNP require averaging of the spectra to remove bias and provide more representative band intensity ratios, which can improve identification of unknown PET samples.

References

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