

Supporting Information

Laboratory-Simulated Photoirradiation Reveals Strong Resistance of Primary Macroplastics to Weathering

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Number of pages: 9

Number of texts: 2

Number of figures: 6

High temperature pyrolysis

High temperature pyrolysis was conducted on a Multi-Shot Pyrolyzer (EGA/Py-3030D, Frontier Laboratories Ltd.) coupled with a Shimadzu GC/MS system (GC/MS: GCMS-TQ8040; Ion source: 250°C; MS quadrupole: 250°C; acquisition mode: scan; scanning range: $m/z = 29-650$; MS library: NIST17). The subsampled tabs were pyrolyzed in the reactor furnace at 600°C for 0.3 min. The inlet temperature was set at 300°C and the split ratio was set at 20:1. For measurement of the volatile pyrolyzates generated during pyrolysis, an Ultra ALLOY® Capillary Column UA+-5 (30 m length, 0.25 mm I.D., 0.25 μm film thickness of 95% polydimethylsiloxane and 5% polydiphenyldimethylsiloxane stationary phase, Frontier Laboratories Ltd.) was employed, and helium was used as the carrier gas at a flow rate of 1 mL/min. The GC oven program was set as 30°C (2 min) \rightarrow 20°C min⁻¹ \rightarrow 320°C (14 min). Identification of the pyrolyzate chemical structures was based on the NIST17 library. Three samples for each plastic type were analyzed as triplicates.

Detection of additives from plastic sheets

Through the thermal desorption pyrolysis of plastic samples, several additives were identified (figure S1). Notably, bisphenol A (BPA) was detected in several LDPE samples, butylated hydroxytoluene (BHT) was detected in all HDPE samples, 2,4-di-tert-butylphenol (2,4-DtBP) was detected in several PP samples, and the plasticizer diethyl phthalate (DEP) was found in several PS samples. BHT and 2,4-DtBP are commonly used as stabilizers in commercial plastics¹, functioning as antioxidants to extend their lifespan. BPA is commonly used in the manufacture of PC and epoxy products, also as an additive to increase elasticity of plastic products¹. DEP is frequently employed as a plasticizer in plastic sheets to reduce cracking¹. Additionally, a compound known as (2,3-diphenylcyclopropyl) methyl phenyl sulfoxide was consistently found in every PS sample, despite being rarely reported in relevant studies. Sulfur is not contained in PS backbone chains, but elemental sulfur or organic sulfur compounds are often added to enhance flame retardancy². Thus, in this study, sulfur compounds were confirmed as plastic additives in PS. In PC plastics, 2,4-DtBP and BPA were detected in every sample, albeit in very low but consistent levels. These compounds could also be generated through the thermal decomposition of the PC backbone; thus, they were not considered as separate plastic additives in PC.

References

- (1) Hahladakis, J. N.; Velis, C. A.; Weber, R.; Iacovidou, E.; Purnell, P. An Overview of Chemical Additives Present in Plastics: Migration, Release, Fate and Environmental Impact during Their Use, Disposal and Recycling. *Journal of Hazardous Materials* **2018**, *344* (Supplement C), 179–199. <https://doi.org/10.1016/j.jhazmat.2017.10.014>.
- (2) Jiang, L.; Kong, R.; Yi, Y.; Yang, S.; Mei, Y.; Feng, X.; Yao, Z.; Zhang, J. Direct Introduction of Elemental Sulfur into Polystyrene: A New Method of Preparing Polymeric Materials with Both High Refractive Index and Abbe Number. *Polymer* **2019**, *180*, 121715. <https://doi.org/10.1016/j.polymer.2019.121715>.

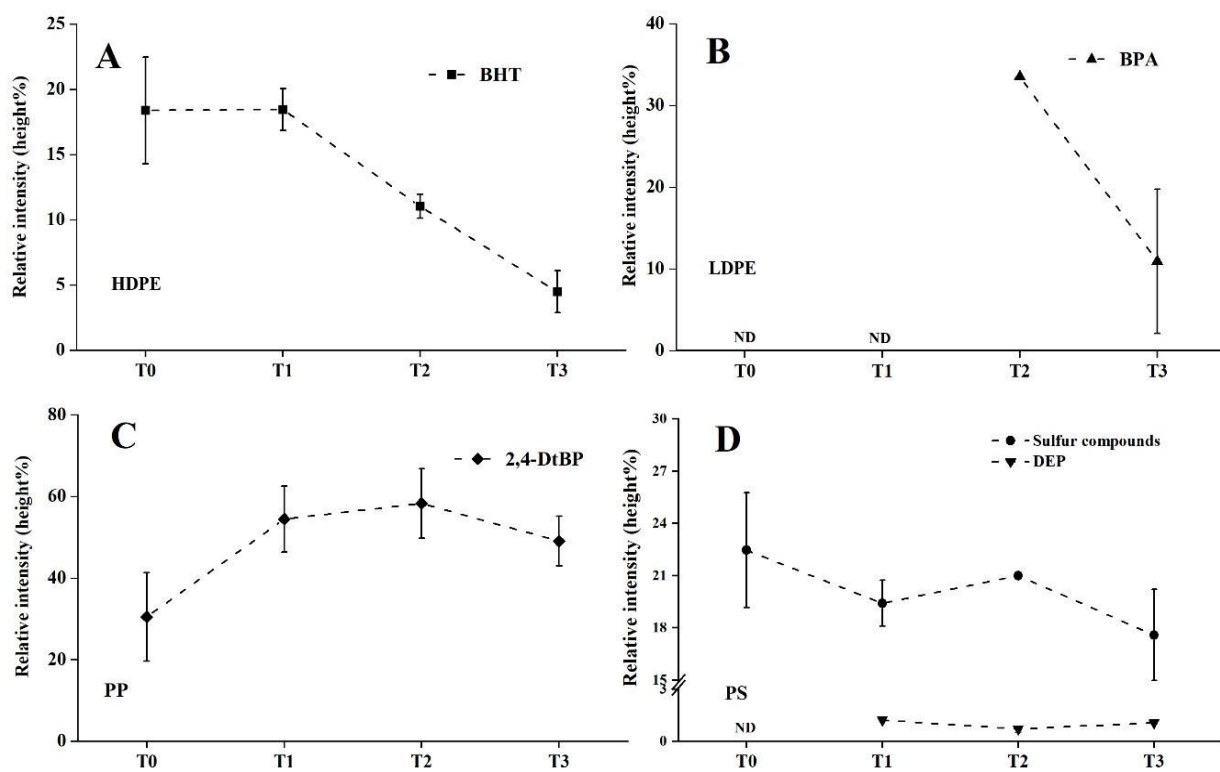


Figure S1. Plastic additives identified through flash evaporation of butylated hydroxytoluene (BHT) from HDPE (A), bisphenol A (BPA) from LDPE (B), 2,4-di-tert-butylphenol (2,4-DtBP) from PP (C), and diethyl phthalate (DEP) from PS (D) from laboratory weathering experiments.

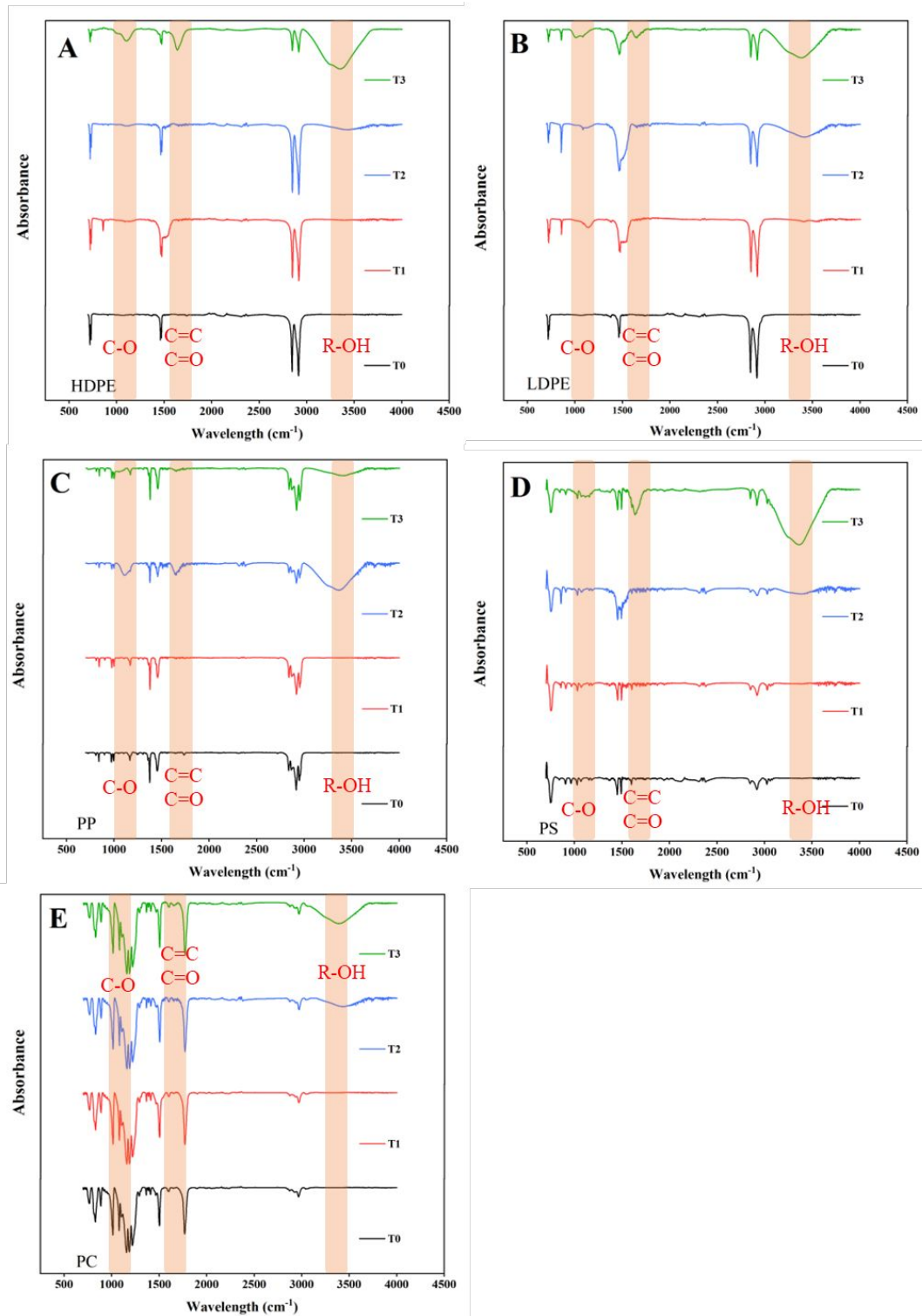


Figure S2. Fourier Transform Infrared Spectroscopy (FTIR) spectra of HDPE (A), LDPE (B), PP (C), PS (D), and PC (E) from laboratory weathering experiments.

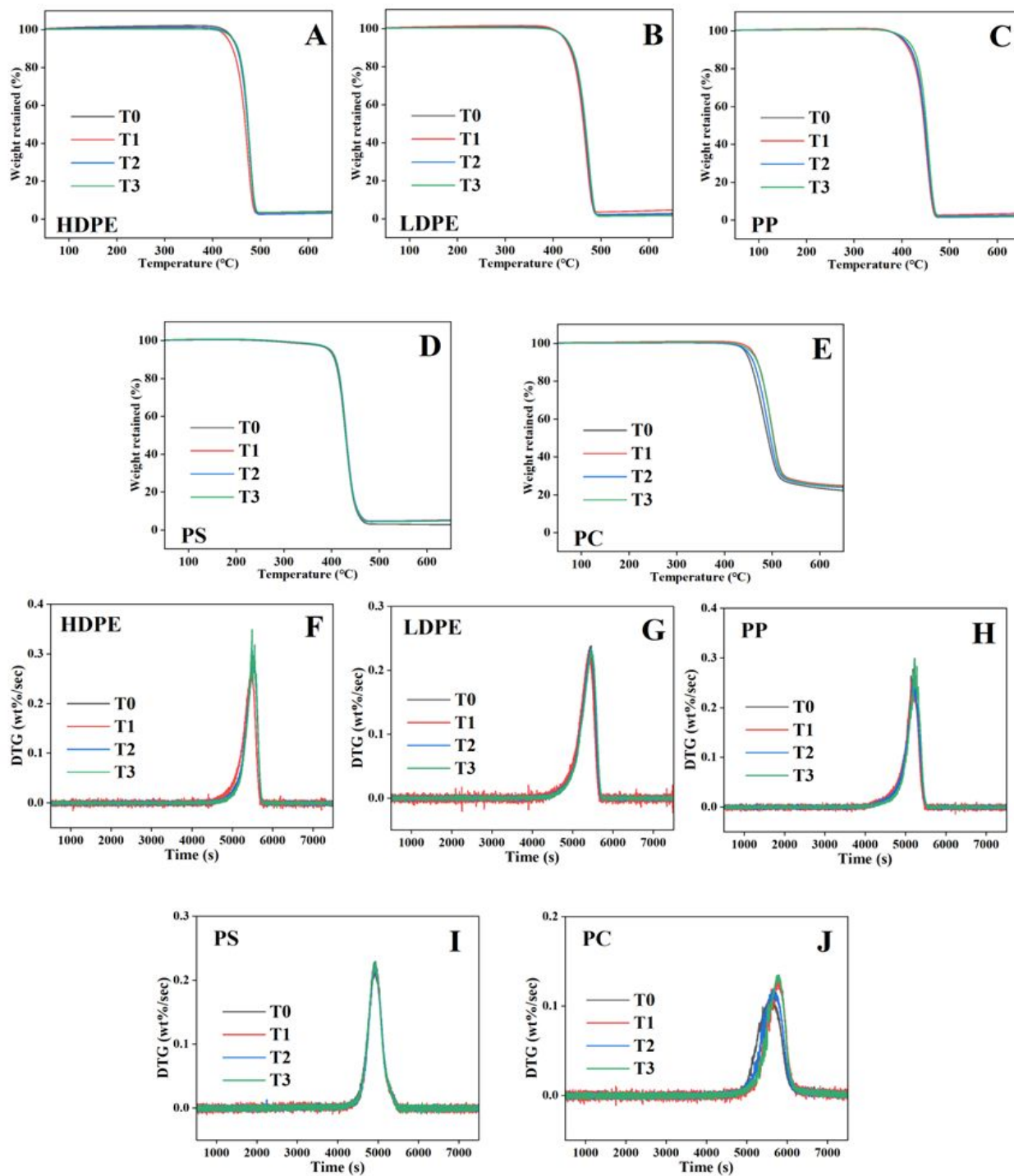


Figure S3. TG curves of HDPE (A), LDPE (B), PP (C), PS (D), and PC (E) and DTG curves of HDPE (F), LDPE (G), PP (H), PS (I), and PC (J) from laboratory weathering experiments.

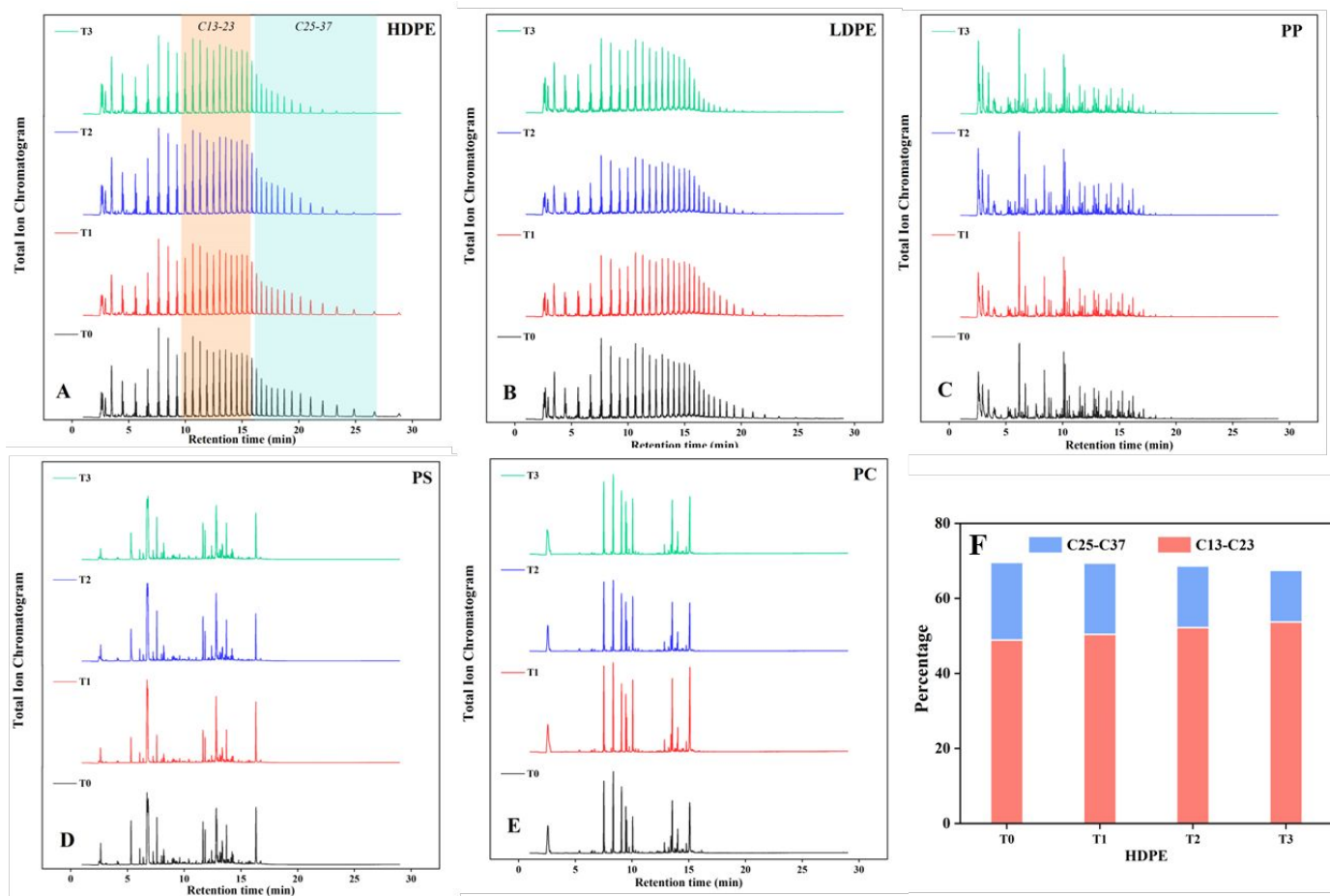


Figure S4. High temperature pyrolysis total ion intensity spectra of HDPE (A), LDPE (B), PP (C), PS (D), and PC (E) from laboratory weathering experiments, and composition of specific pyrolyzates from HDPE (F).

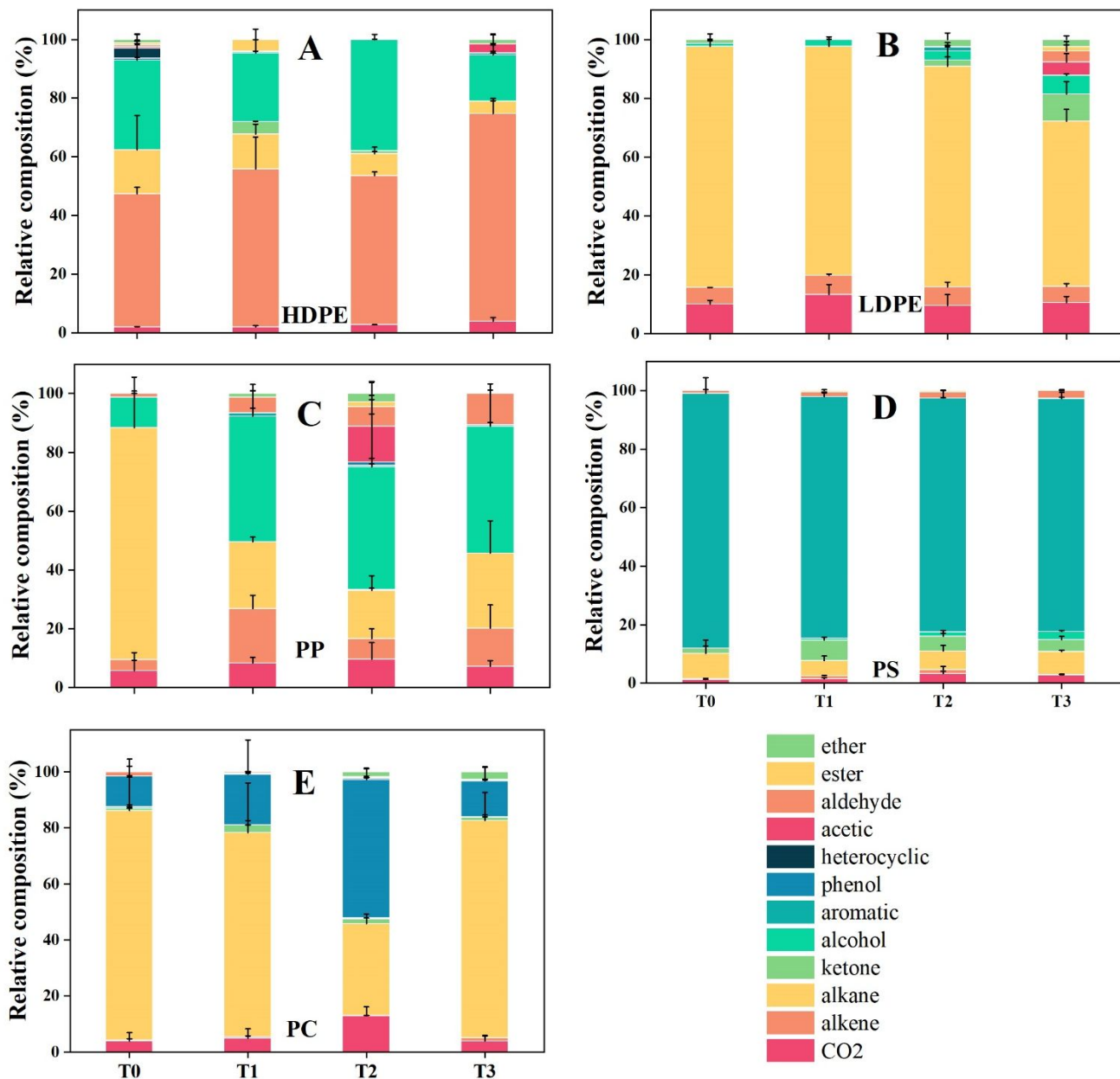


Figure S5. Relative composition of pyrolysis product groups identified through low temperature pyrolysis of HDPE (A), LDPE (B), PP (C), PS (D), and PC (E) from laboratory weathering experiments.

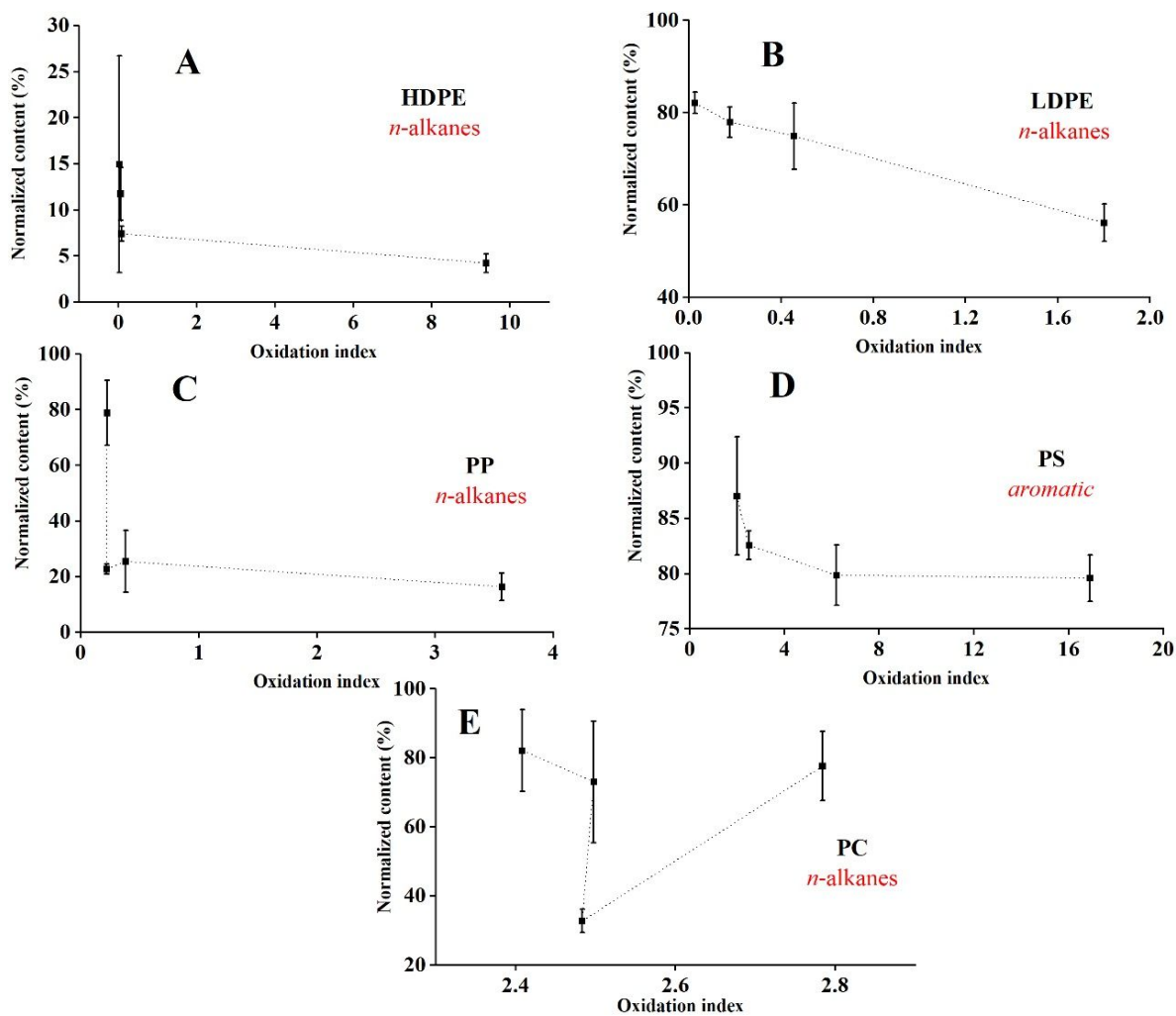


Figure S6. Normalized content of major chemical classes of pyrolyzates identified through low temperature pyrolysis depicted by oxidation index of HDPE (A), LDPE (B), PP (C), PS (D), and PC (E) from laboratory weathering experiments.