Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

Electronic Supporting Information

Characterizing Microplastic Size and Morphology of Photodegraded Polymers Placed in Simulated Moving Water Conditions

Tayler S. Hebner and Melissa A. Maurer-Jones*

Department of Chemistry and Biochemistry, University of Minnesota Duluth, Duluth MN USA

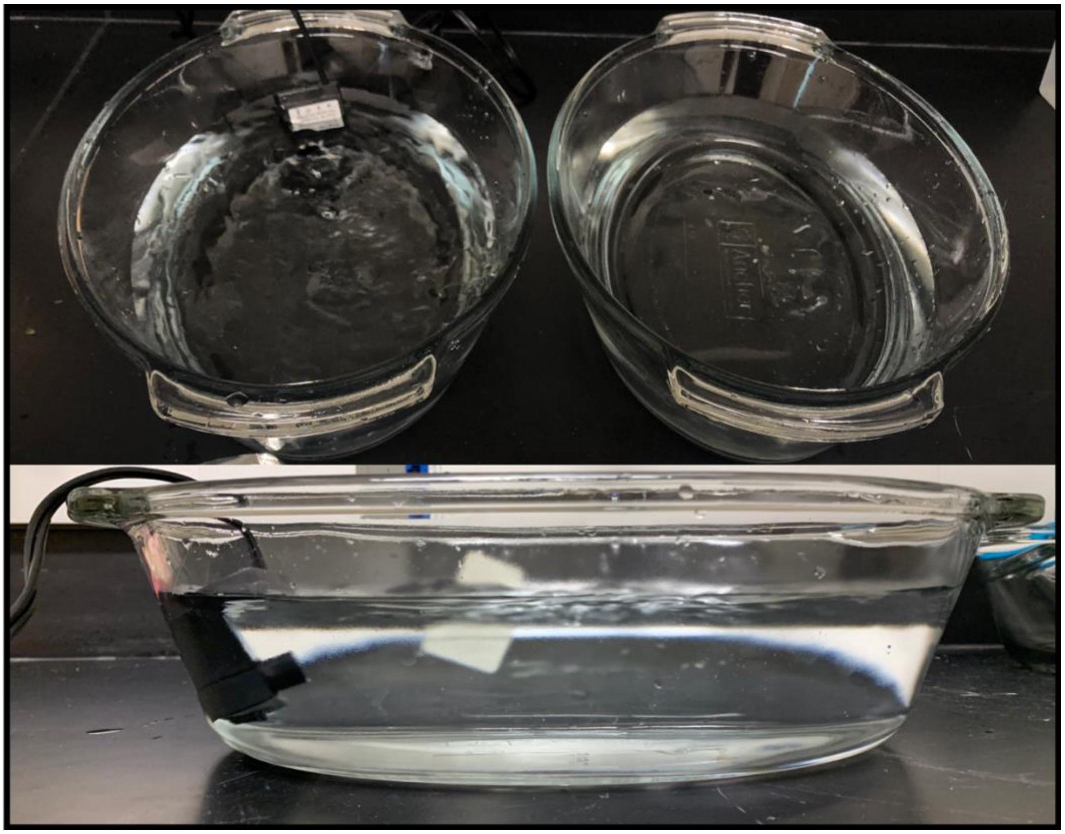
1. Characteristics of Polymers Used in Study and Aquatic Microcosms

Polymer thin films manufactured with blown extrusion were purchased from Goodfellow USA (Coroaopolis, PA). Manufacturer supplied characteristics[1] of the materials are reported in Table S1. Polypropylene sheet was injection molded and characterized previously.[2]

Table S1. Polymer sample characteristics[1, 2]

Polymer	Thickness	Tensile Strength (MPa)	Elongation at Break (%)	Comments
Polypropylene	0.025 mm or 0.050 mm	130-300	150	Biaxially oriented blown film
Polyethylene	0.030 mm	5-25	400	Biaxially oriented blown film
Polyethylene Terephthalate	0.023 mm	190-260	NA	Biaxially oriented blown film
Polypropylene	3.1 mm	30	NA	Injection molded sheet from Sigma Aldrich pellets (M_w ~340,000) in type IV dogbone shape

Images of the aquatic microcosms set-ups:



2. Ambient Control Studies

To account for particles that might occur in the samples as a result of atmospheric deposition, Petri dishes with deionized water were placed uncovered in the working environment anytime aqueous microcosms were uncovered and manipulated. Control plates were filtered on a 200 mesh filter (i.e., 74 µm openings, smallest size used for experiments) and counted under the stereo microscope. Control microplastics were differentiated based on their morphology and the results are shown in Table S2.

Table S2. The number of particles counted in the ambient controls .

	Fragments	Fibers	Clusters	Total
Day 1	0	4	0	4
Day 2	0	0	0	0
Day 3	0	1	0	1
Day 4	0	3	0	3
Day 5	0	5	0	5

3. Pump Control Microcosm

To account for particles that might have been the result of breakdown of the plastic components of the pump in addition to any microplastics that may have entered the microcosms over the course of the 7 day incubation, a pump was placed in 1800 mL of deionized water and after 7 days, the water was filtered on 200 mesh (~74 µm openings). Microplastics were counted under a microscope and the results are shown in Table S3.

Table S3. The number of particles counted in the pump controls.

Fragments	Fibers	Clusters	Total
1	10	0	11

It should be noted that 2 of the counted fibers observed were clearly black or dark blue , which were intentionally excluded from the polymer sample microplastic counts because all polymer samples were transparent or opaque. Therefore, these counts are substantially lower than those observed from the microcosms, and the pump and incubation/microplastic isolation procedure do not contribute substantially to the overall microplastic counts.

4. Microplastic Data Tables

Data tables for all the microplastic experiments incorporated in the main manuscript.

Table S4. Average number of microplastics formed from **polypropylene (PP)** irradiated with 254 nm light for 72 h per side as designated by morphology (fragment, fiber, or cluster) in ***turbulent*** *water*.

Size Range [µm]	Fragments	Fibers	Clusters	Size Range Total
841+	23	0	0	23
240-841	27	7	1	36
177-240	27	97	16	140
74-177	18	210	66	293
Total	**95**	**314**	**83**	**492**

Table S5. Average number of microplastics formed from **PP** irradiated with 254 nm light for 72 h per side as designated by morphology (fragment, fiber, or cluster) in ***stagnant*** *water*.

Size Range [µm]	Fragments	Fibers	Clusters	Size Range Total
841+	9	0	0	9
240-841	14	4	1	19
177-240	28	37	11	75
74-177	18	66	23	106
Total	**67**	**107**	**34**	**208**

Table S6. Number of microplastics formed from **50 µm thick blown-extruded PP film** irradiated with 254 nm light for 72 h per side as designated by morphology (fragment, fiber, or cluster) in ***turbulent*** *water*.

Size Range [µm]	Fragments	Fibers	Clusters	Size Range Total
841+	9	14	0	23
240-841	8	16	1	25
177-240	13	76	2	91
74-177	12	80	5	97
Total	**42**	**186**	**8**	**236**

Table S7. Number of microplastics formed from **50 µm thick blown-extruded PP film** irradiated with 254 nm light for 72 h per side as designated by morphology (fragment, fiber, or cluster) in ***stagnant*** *water.*

Size Range [µm]	Fragments	Fibers	Clusters	Size Range Total
841+	6	10	0	16
240-841	0	15	0	15
177-240	2	42	3	47
74-177	1	36	2	39
Total	**9**	**103**	**5**	**117**

Table S8. Number of microplastics formed from **3.1 thick injection molded PP sheet** irradiated with 254 nm light for 72 h per side as designated by morphology (fragment, fiber, or cluster) in ***turbulent*** *water.*

Size Range [µm]	Fragments	Fibers	Clusters	Size Range Total
841+	0	6	0	6
240-841	1	35	1	37
177-240	5	57	6	68
74-177	7	45	7	59
Total	**13**	**143**	**14**	**170**

Table S9. Number of microplastics formed from **3.1 thick injection molded PP sheet** irradiated with 254 nm light for 72 h per side as designated by morphology (fragment, fiber, or cluster) in ***stagnant*** *water.*

Size Range [µm]	Fragments	Fibers	Clusters	Size Range Total
841+	0	5	0	5
240-841	1	14	1	16
177-240	5	44	3	52
74-177	9	34	6	49
Total	**15**	**97**	**10**	**122**

Table S10. Number of microplastics formed from **polyethylene (PE)** irradiated with 254 nm light for 72 h per side as designated by morphology (fragment, fiber, or cluster) in ***turbulent*** *water.*

Size Range [µm]	Fragments	Fibers	Clusters	Size Range Total
841+	1	0	0	1
240-841	5	2	1	8
177-240	10	94	28	132
74-177	6	114	39	159
Total	**22**	**210**	**68**	**300**

Table S11. Number of microplastics formed from **PE** irradiated with 254 nm light for 72 h per side as designated by morphology (fragment, fiber, or cluster) in ***stagnant*** *water*.

Size Range [µm]	Fragments	Fibers	Clusters	Size Range Total
841+	1	0	0	1
240-841	4	2	3	9
177-240	2	22	4	28
74-177	10	41	10	61
Total	**17**	**65**	**17**	**99**

Table S12. Number of microplastics formed from **polyethylene terephthalate** (PET) irradiated with 254 nm light for 72 h per side as designated by morphology (fragment, fiber, or cluster) in ***turbulent*** *water.*

Size Range [µm]	Fragments	Fibers	Clusters	Size Range Total
841+	0	0	0	0
240-841	5	12	0	17
177-240	7	39	5	51
74-177	4	73	11	88
Total	**16**	**124**	**16**	**156**

Table S13. Number of microplastics formed from **PET** irradiated with 254 nm light for 72 h per side as designated by morphology (fragment, fiber, or cluster) in ***stagnant*** *water.*

Size Range [µm]	Fragments	Fibers	Clusters	Size Range Total
841+	0	0	0	0
240-841	0	3	1	4
177-240	3	25	3	31
74-177	6	25	3	34
Total	**9**	**53**	**7**	**69**

Table S14. Total number of microplastics formed from irradiation of **PP with different times** of irradiation and placed into ***turbulent*** *water*.

Size Range [µm]	0 h	24 h	48 h
841+	0	0	2
240-841	0	0	5
177-240	7	7	31
74-177	15	15	72
Total	**22**	**22**	**110**

Table S15. Total number of microplastics formed from irradiation of **PP with different times** of irradiation and placed into ***stagnant*** *water*.

Size Range [µm]	0 h	24 h	48 h
841+	0	0	9
240-841	0	4	8
177-240	3	32	9
74-177	13	35	32
Total	**16**	**71**	**58**

Table S16. Total number of microplastics formed from irradiation of **PP with 300 nm UV light** for 72 h per side as designated by morphology (fragment, fiber, or cluster) in ***turbulant*** *water*.

Size Range [µm]	Fragments	Fibers	Clusters	Size Range Total
841+	37	0	0	37
240-841	6	7	0	13
177-240	17	25	3	45
74-177	9	47	15	71
Total	**69**	**79**	**18**	**166**

Table S17. Total number of microplastics formed from irradiation of **PP with 300 nm UV light** for 72 h per side as designated by morphology (fragment, fiber, or cluster) in ***stagnant*** *water*.

Size Range [µm]	Fragments	Fibers	Clusters	Size Range Total
841+	1	0	0	1
240-841	0	6	0	6
177-240	3	10	3	16
74-177	2	26	12	40
Total	**6**	**42**	**15**	**63**

5. FTIR Characterization of Polymers

4.1 Characterization of Varying Thickness PP Samples with differential scanning calorimetry (DSC)

DSC was performed on polymer samples to assess the change in thermal properties of the samples, which gives insight into the mechanical properties. Samples were evaluated with a heat, cool, heat cycling that the exotherms from the 2_{nd} heat cycle are shown in Fig. S1.

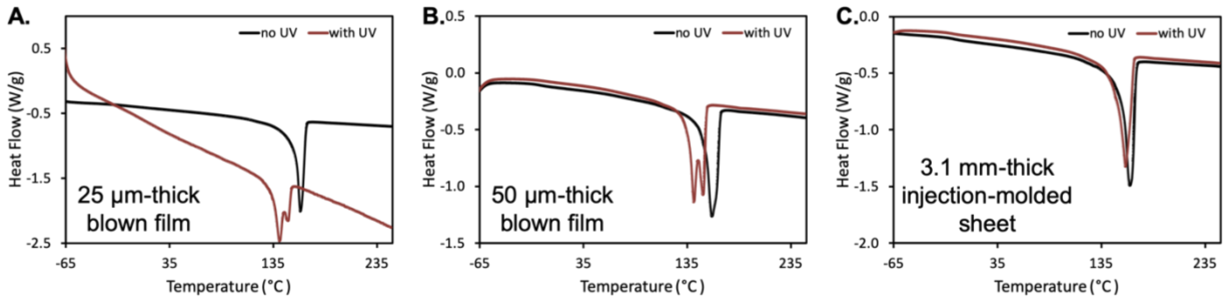


Fig. S1 DSC exotherms of A. 25 μm-thick PP blown film, B. 50 μm-thick PP blown film, and C. 3.1 mm-thick injection-molded sheet without (black) and with (marron) 72 h per side UV light irradiation. Exotherms represent the second heating cycle (-70 to 250 ºC, 10 ºC/min).

Noticeably, irradiating the thin films with UV light (Fig. S1A and S1B) causes a change in the melting peak, with a doublet forming. This indicates that there are 2 distinct phases of the polymers, likely the result of the photodegraded samples having a portion of the sample with decreased molecular weights and increased crystallinity.

Exotherms were fit to determine enthalpic values and are presented in Table S18. Taken together, we can for all thickness that UV light irradiation causes an increase in crystallinity and the onset of melting occurs at a lower temperature, which indicates the sample contains smaller molecular weight units as the result of photodegradation.

Table S18. DSC calculated values of polymer samples with varying thickness.

Sample	**Glass Transition (T_g) temperature (ºC)**	**Onset of Melting Temperature (ºC)**	**Enthalpy of Fusion (ΔH_f) (J/g)**	**% Crystallinity***
25 μm PP no UV	-8.62	155.33	94.432	45.62
25 μm PP 72h per side UV light	-0.34	133.46	98.285	47.48
50 μm PP no UV	-7.08	150	85.319	41.22
50 μm PP72h per side UV light	-4.13	135.15	86.991	42.02
3.1 mm PP no UV	-7.33	154.5	87.634	42.34
3.1 mmPP 72h per side UV light	-9.58	147.88	92.160	44.52

*Crystallinity calculated by normalizing enthalpy values to polymer heats of fusion modeled for 100% crystalline polymer.[3]

4.2 Characterization of PP, PE, and PET

Absorbance of UV Photons

Fig. S2 show UV-visible spectra were collected for PP, PE, and PET thin films. These results reveal that microplastic counts are inversely proportional to the absorbance UV photons. This suggest that polymers that are able to absorb photons, likely keeping photodegradation at the surface of the films.

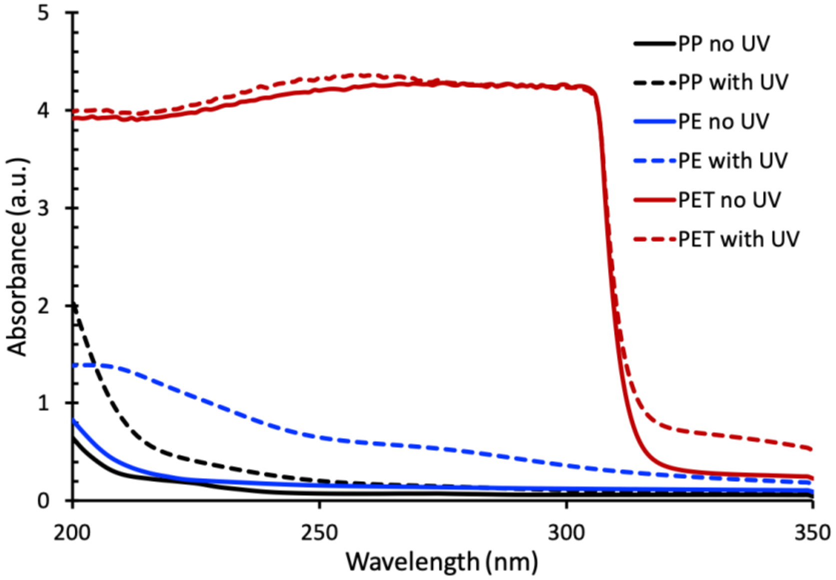


Fig. S2 UV-visible spectra of PP, PE, and PET that were pristine, or no UV (solid), and irradiated (with UV, dashed) with 254 nm UV light for 72 h per side.

ATR-FTIR Calculation of Surface Crystallinity

Crystallinity was quantified through analysis of ATR-FTIR spectra. Fig. S3 shows representative spectra for non-irradiated and irradiated PP (Fig. S3A), PE (Fig. S3B), and PET (Fig. S3C).

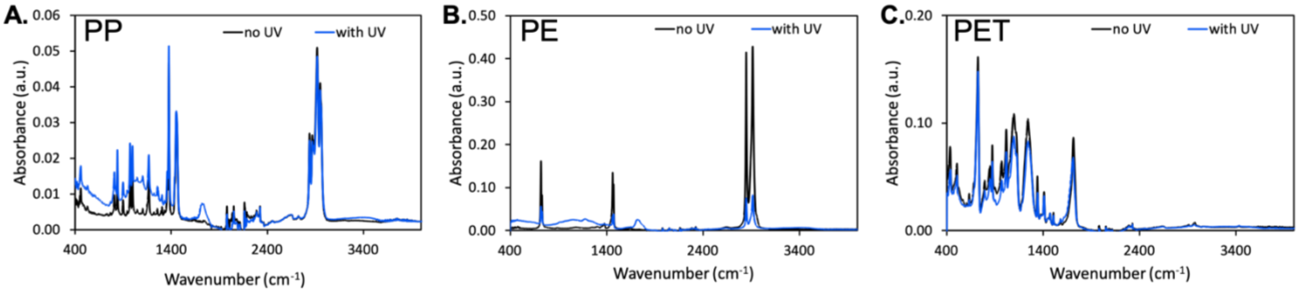


Fig. S3 ATR-FTIR spectra of PP (A), PE (B), and PET (C) that were pristine, or no UV (black), and irradiated (with UV, blue) with 254 nm UV light for 72 h per side. The FTIR spectra were used to calculate crystallinity of the polymers.

For PP, IR bands in the 900-1050 cm^{-1} region correspond to various CH$_3$ and C-C vibrations from amorphous and crystalline bands.[4] The ratio of the absorbance of the band at 998 cm^{-1} and 974 cm^{-1} can be calibrated to a percent crystallinity using the following equation:[5]

$$X = \frac{A_{998}}{A_{974}} * 61.5$$

where X is the percent crystallinity, A_{998} is the intensity of the band corresponding the crystalline fraction and A_{974} corresponds to the intensity of the band corresponding to the amorphous region. A calibration of 61.5 was reported in the literature.[5]

For PE, an IR bending doublet band appears between 1456-1472 cm^{-1} that has been characterized previously and methods have been evaluated for determining PE crystallinity.[6-8] The area of the crystalline band of the CH$_2$ wagging deformation was located around 1472 cm^{-1} and was compared to the integrated intensities of the amorphous wagging deformation bands between 1456 - 1466 cm^{-1}. After fitting the peaks using Omnic software (ThermoFisher), percent crystallinity was then calculated using the following equation:

$$X = 1 - \left[\frac{\left(1 - \frac{I_{cr}}{I_{am}}\right)}{\left(\frac{1.233}{1 + \frac{I_{cr}}{I_{am}}}\right)} \right] \times 100$$

where X is the percent crystallinity, I_{cr} is the integrated intensity of the crystalline region, I_{am} is the sum of the integrated intensity of the amorphous region and 1.233 is the calculated intensity ratio of I_{cr}/I_{am}.

For PET, ATR-FTIR was also used to determine crystallinity at the surface that has previously been reported in the literature.[9] Upon normalizing the spectra to the phenyl ring stretch (~1408 cm^{-1}), the areas of the C-O-C bond stretch band was evaluated for amorphous phase (~1090 cm^{-1}) and crystalline phase (~1120 cm^{-1}) were calculated. The degree of crystallinity was calculated with the following equation:

$$X = \left(1 - \frac{A_{1120}}{A_{1090}}\right) * 100$$

where is the X is the percent crystallinity, A_{1120} is the normalized absorbance of the crystal band and A_{1090} is the normalized absorbance of the amorphous band.

Fig. S4 demonstrates the change in the surface crystallinity between pristine (non-irradiated) films and films irradiated with 254 nm UV light for 72 h on each side. It can be observed that both PE and PET have and increase in surface crystallinity, however, PE has a larger change, which results in the polymer having greater brittleness than irradiated PET.

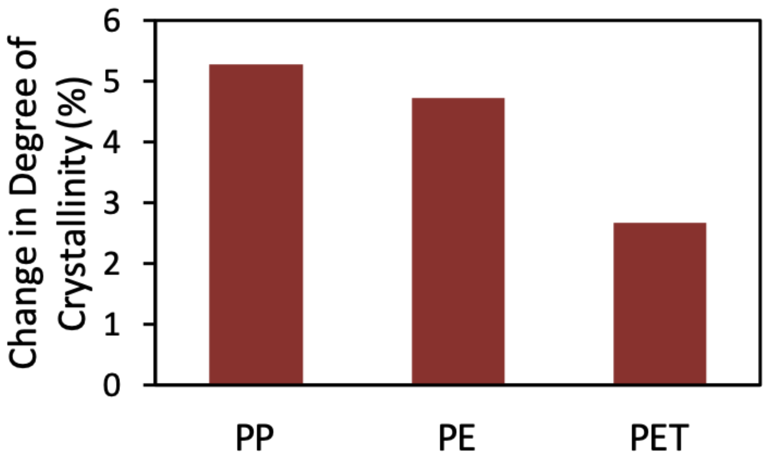


Fig. S4 The change in crystallinity, as measured with ATR-FTIR, of PP, PE, and PET irradiated with 254 nm UV light for 72 h per side as compared to the non-irradiated, pristine films.

DSC Analysis

Table S19. DSC measured characteristics of irradiated polymer samples. Cells without values represent exotherms with no noticeable glass transition.

Sample	**Glass Transition (T_g) temperature (ºC)**	**Onset of Melting Temperature (ºC)**	**Enthalpy of Fusion (ΔH_f) (J/g)**	**% Crystallinity***
25 µm PP no UV	-8.62	155.33	94.432	45.62
25 µm PP 72h per side UV light	-0.34	133.46	98.285	47.48
25 µm PE no UV	-	105.66	92.316	31.51
25 µm PE 72h per side UV light	-	96.5	103.91	35.46
23 µm PET no UV	82.37	252.4	33.314	23.80
23 µm PET 72h per side UV light	84.74	252.52	46.176	32.98

*Crystallinity calculated by normalizing enthalpy values to polymer heats of fusion modeled for 100% crystalline polymer.[3]

4.3 Characterization of PP Irradiated for Varying Times

DSC Analysis

Table S20. DSC measured characteristics of 25 µm PP thin films samples that had been irradiated for varying amounts of time per side. Cells without values represent exotherms with no noticeable glass transition.

Sample	**Glass Transition (T_g) temperature (ºC)**	**Onset of Melting Temperature (ºC)**	**Enthalpy of Fusion (ΔH_f) (J/g)**	**% Crystallinity***
25 µm PP no UV	-8.62	155.33	94.432	45.62
25 µm PP 24 h per side UV light	-4.81	145.11	96.49	46.61
25 µm PP 48 h per side UV light	-	138.72	97.534	47.48
25 µm PP 72 h per side UV light	-0.34	133.46	98.285	47.48

*Crystallinity calculated by normalizing enthalpy values to polymer heats of fusion modeled for 100% crystalline polymer.[3]

ATR-FTIR Analysis

PP films were irradiated with 254 nm UV light for increasing amounts of time. ATR-FTIR spectra were collected and shown in Figure S3. From these spectra, the carbonyl index was calculated using the following equation:

$$Carbonyl\ Index = \frac{\mathrm{Area}_{1715}}{\mathrm{Area}_{974}}$$

where the absorbance at 1715 cm^{-1} indicates the area under the carbonyl peak and the absorbance at 974 cm^{-1} indicates the area under the CH_3 rocking band, which is chosen as a reference peak because it is understood to remain unchanged throughout the photodegradation process.[10]

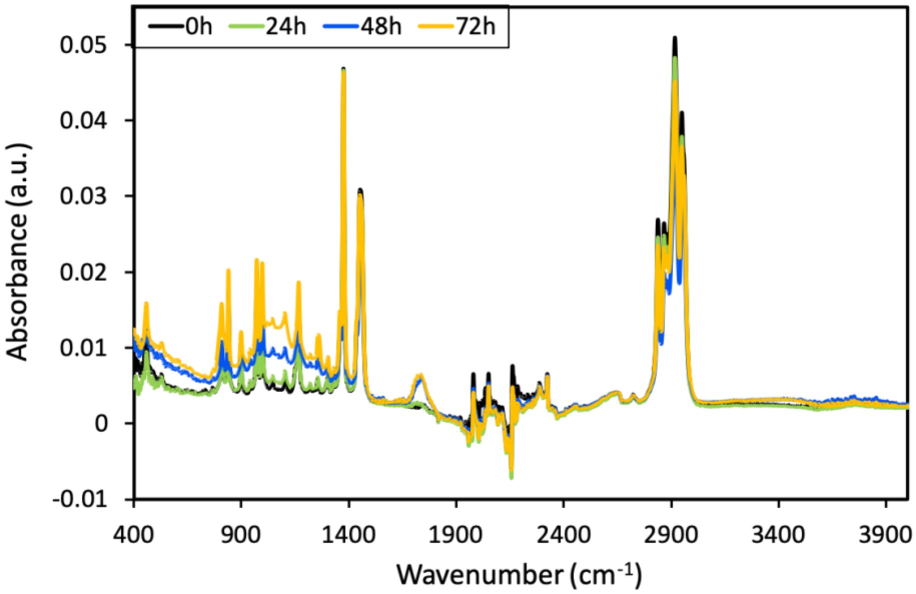


Fig. S5 ATR-FTIR spectra of PP irradiated with 254 nm UV light for 0 (black), 24 (green), 48 (blue) or 72 h (gold) per side.

4.4 Characterization of PP Irradiated with Varied Wavelengths of UV Light

DSC Analysis

Table S21. DSC measured characteristics of 25 µm PP thin films samples that had been irradiated with 254 or 300 nm light for 72 h per side. Cells without values represent exotherms with no noticeable glass transition.

Sample	**Glass Transition (T_g) temperature (°C)**	**Onset of Melting Temperature (°C)**	**Enthalpy of Fusion (ΔH_f) (J/g)**	**% Crystallinity***
25 µm PP no UV	-8.62	155.33	94.432	45.62
25 µm PP 254 nm UV light	-0.34	133.46	98.285	47.48
25 µm PP 300 nm UV light	-	138.06	95.064	45.92

*Crystallinity calculated by normalizing enthalpy values to polymer heats of fusion modeled for 100% crystalline polymer.[3]

ATR-FTIR Analysis

PP films were irradiated with either 254 or 300 nm UV light for 72 h per side. The FTIR spectra of the films were collected and the carbonyl index was calculated as described above. Figure S4 shows the carbonyl index for the irradiated plastic increases for both wavelengths of irradiation and while not significant, the 300 nm UV light irradiation displayed a smaller increase in carbonyl index. The larger the increase, the greater elongation to break; therefore, these results support that samples irradiated with longer wavelengths have a slower rate of degradation of mechanical properties and therefore have fewer microplastics formed.

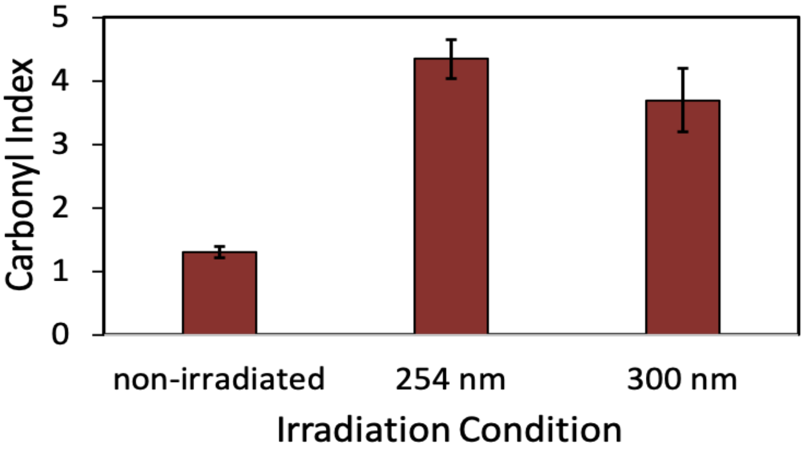


Fig. S6 PP films irradiated with 254 or 300 nm UV light shows an increase in carbonyl index for both wavelengths as compared to the non-irradiated film, though 300 increases to a lesser extent. Bars represent averages with error calculated as standard deviations of duplicate FTIR spectra of two different films.

6. References

1. Goodfellow, Material Properties, http://www.goodfellowusa.com/, (accessed December 2019).
2. I. Salinas, A. Finke, B. R. Hinderliter, K. B. Lodge and M. A. Maurer-Jones, Effects of Dry, Wet-Dry Cycling, and Aqueous Immersion on Polypropylene and Polyethylene cable Insulation Mechanical Properties, *Proceedings - American Nuclear Society*, 2019, **EnvDeg 2019**, 906-913.
3. R. Blaine, Polymer Heats of Fusion, TN048, TA Instruments, New Castle, DE.
4. T. A. Huy, R. Adhikari, T. Lüpke, S. Henning and G. H. Michler, Molecular deformation mechanisms of isotactic polypropylene in α- and β-crystal forms by FTIR spectroscopy, *Journal of Polymer Science Part B: Polymer Physics*, 2004, **42**, 4478-4488.
5. F. J. Lanyi, N. Wenzke, J. Kaschta and D. W. Schubert, A method to reveal bulk and surface crystallinity of Polypropylene by FTIR spectroscopy - Suitable for fibers and nonwovens, *Polym. Test.*, 2018, **71**, 49-55.
6. G. Zerbi, G. Gallino, N. Del Fanti and L. Baini, Structural depth profiling in polyethylene films by multiple internal reflection infra-red spectroscopy, *Polymer*, 1989, **30**, 2324-2327.
7. G. R. Strobl and W. Hagedorn, Raman spectroscopic method for determining the crystallinity of polyethylene, *Journal of Polymer Science: Polymer Physics Edition*, 1978, **16**, 1181-1193.
8. S. Abbate, M. Gussoni and G. Zerbi, Infrared and Raman intensities of polyethylene and perdeuteropolyethylene: Factor group splittings, *The Journal of Chemical Physics*, 1979, **70**, 3577-3585.

9. K. Aljoumaa and M. Abboudi, Physical ageing of polyethylene terephthalate under natural sunlight: correlation study between crystallinity and mechanical properties, *Applied Physics A*, 2015, **122**, 6.
10. K. Rajakumar, V. Sarasvathy, A. Thamarai Chelvan, R. Chitra and C. T. Vijayakumar, Natural Weathering Studies of Polypropylene, *J. Polym. Environ.*, 2009, **17**, 191.