

Environmental degradation of microplastics: How to measure fragmentation rates to secondary micro- and nanoplastic fragments and dissociation into dissolved organics

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Supporting Information

Scanning electron microscopy (SEM)

Scanning Electron Microscopy was used to compare the surface textures of the polymer powder grains before and after UV aging and also to analyze particle shapes and sizes of the released micro- and nanoplastic fragments. The microplastic powder particles were fixed onto Leit-C-plast tape on a standard SEM stub and coated with 8 nm platinum. The NanoRelease dispersion containing the micro- and nanoplastic fragments was centrifuged 3 times for 3 hours at 12 000 rpm ($\approx 10\,500$ rcf) to enforce the sedimentation of the smallest particles onto a carbon film supported copper grid (400 mesh). After each 3 hour centrifugation step the supernatant was removed and the centrifuge tubes were refilled with ultrapure water to remove the released water-soluble organics (monitored via UV Vis: SI Figure 4). Subsequently, the copper grid was dried and coated with 6 nm platinum. The measurements were performed with a Zeiss Gemini 500 SEM that was operated at 3kV, using secondary electrons for improved topography contrast.

Attenuated total reflectance Fourier-transform infrared spectroscopy (ATR FT-IR)

The chemical composition of the microplastic surfaces before and after UV aging were analyzed by FT-IR spectroscopy and any spectral changes investigated, as described earlier.¹ The chemical compositions were determined using a ThermoFisher IS50 FT-IR spectrometer with a diamond ATR accessory (IS50-ATR). The FT-IR spectra were recorded in the region of 4000-400 cm^{-1} with 32 scans at a resolution of 4 cm^{-1} .

Gel permeation chromatography (GPC)

The molar mass distributions of the studied polymer powders before and after UV aging were determined by Gel Permeation Chromatography (GPC) as described earlier.¹ In short, a modular GPC system with a combination of columns (HFIP-LG Guard column, 2 x PL HFIPgel columns, 300 x 7.5 mm, 3-100 μm , Agilent) was combined with a refractive index detector (8 μl , Agilent). The temperature was set to 35°C and the flow rate to 1.0 mL/min. Calibration was conducted using a polymethylmethacrylate calibration kit (with a known molar mass distribution) and 12 calibration points. Approximately 6 mg of each sample was dissolved in approximately 4 mL eluent (1,1,1,3,3,3 – Hexafluoro-2-propanol, Alfa Aesar) over 5 hours on a shaking table at room temperature. The resulting solutions were filtered through Millipore-Millex-FG 0.2 μm filters prior to injection. The crosslinking degree can be determined via GPC, if it can be compared to a non-crosslinked sample (before aging). The resulting Area x in the GPC chromatogram corresponds to a concentration y of the non-crosslinked sample. In the next step, the area of the soluble fraction of an unknown crosslinked sample can be set in proportion to the area of the 100 % dissolved sample. Formally this is not a measurement of the crosslinking degree, because the polymer content of a sample is determined, but the crosslinking degree can be calculated via

$$y_{\text{unknown}} / y_{100\% \text{dissolved}} = \% \text{ polymer in solution} \quad (1)$$

$$\text{crosslinking degree} = 100 \% - \% \text{ polymer in solution} \quad (2)$$

The results are recorded in 5 % steps only, but due to the small sample amount available the observed trends can be more accurately assessed via the GPC approach than by solving, filtering and weighing the crosslinked fraction.

Single particle counter

The secondary microplastic particles $>1 \mu\text{m}$ were counted with an Abakus[®] Mobil Fluid laser particle counter (Klotz GmbH) equipped with a laser sensor LDS 2148(0) (1-139 μm). For this purpose 0.7 mL of the NanoRelease dispersion was filled up to 500 mL with ultrapure water. For sensor protection the sample was filtered with a 190 μm pre-filter (nylon, Rotert). The measurement was performed with 200 mL of the sample. Data evaluation was performed with C.A.R. Lab. Duplicate samples were measured and values for blank measurements were subtracted.

Analytical ultracentrifugation with refractive index detector (AUC-RI)

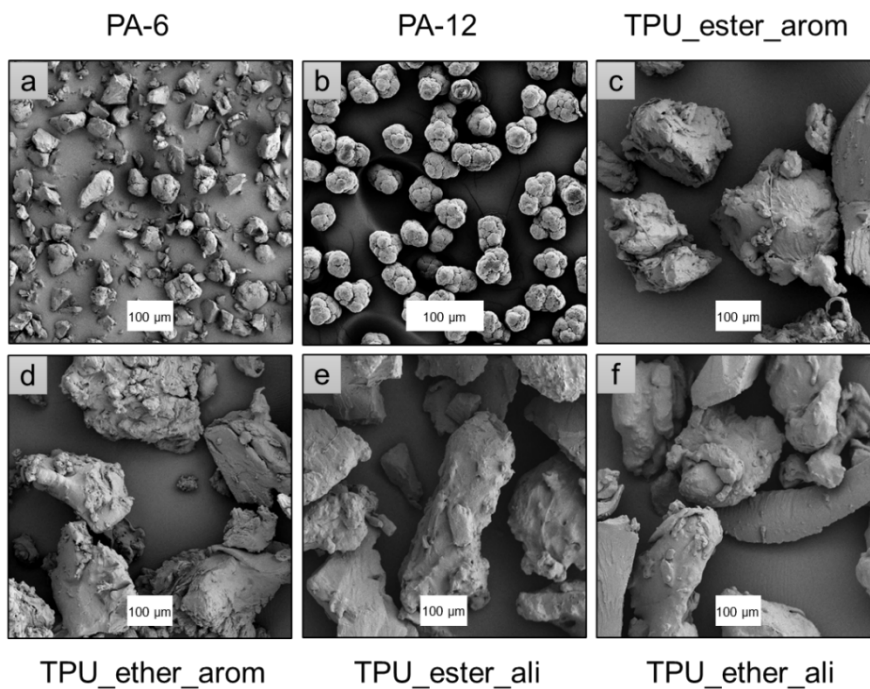
Analytical Ultracentrifugation served to determine the concentration of secondary nanoplastics after application of the adapted NanoRelease protocol, as well as to assess their particle size distribution. The chosen measurement parameters were based on previous investigations in literature, enabling quantitative detection of fragment traces down to 10 ppm and with size and concentration accuracy better than 10 %.²⁻⁴ The AUC-Beckman XL centrifuge is equipped with an interference optical system synchronized to the centrifugal rotation, so that the colloidal sedimentation profile during centrifugation is monitored over time. By adjusting the centrifugation speed, the mass concentration and particle size distribution were determined in three overlapping size intervals of 10-150 nm (12 000 rpm \triangleq 10 500 rcf), 40-800 nm (3 000 rpm \triangleq 650 rcf) and 300-5000 nm (1 000 rpm \triangleq 70 rcf); with 3 hours centrifugation time each. For data evaluation of the absorption profiles (resolved in time and radius) SedFit v14.0 was used with the corresponding polymer density (SI Table 1).⁵ Duplicate samples were measured and values for blank measurements were subtracted.

Total organic carbon (TOC)

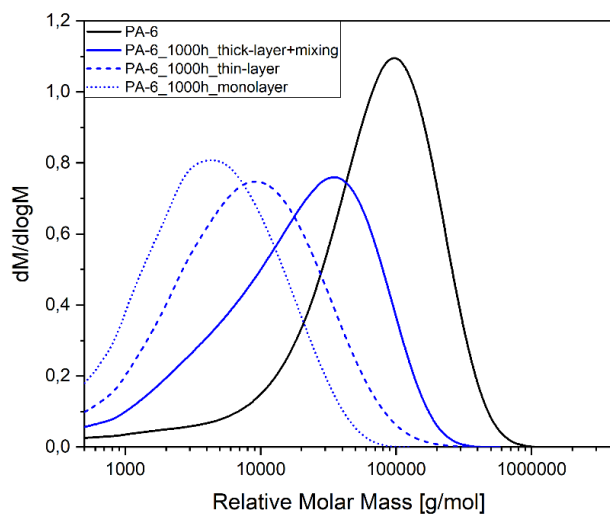
To determine the concentration of released water-soluble organics, the sample was diluted with ultrapure water with dilution factors of 1:10 and 1:20 and total carbon (sample combusted catalytically on a Pt/Al₂O₃ catalyst in an oxygen stream at ca. 680 °C) and total inorganic carbon (sample acidified with 25 wt.-% phosphoric acid) were quantified as CO₂ via NDIR detection (Shimadzu TOC-L). TOC was calculated as the difference between total carbon and total inorganic carbon.

Ultraviolet-visible spectroscopy (UV Vis)

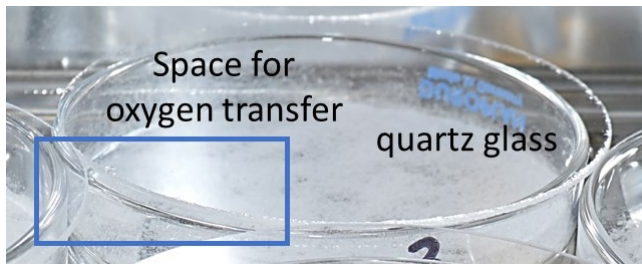
UV Vis was applied to determine which species (plastic fragments and/or water-soluble organics) was released during the ultrasonication mechanical treatment in the adapted NanoRelease protocol. The washing steps for preparation of copper grids for SEM analysis were also monitored via UV Vis. In both cases an Ocean-Optics USB2000 (Ocean Optics GmbH,) spectrometer was employed using a 1 mm path length cell to monitor effects on the absorbance. The samples were normalized based on the absorption of an ultrapure water with surfactant blank. In the range of 400-700 nm of the unfiltered samples the turbidity of light-scattering particles could be detected, which is why the absorption at 500 nm was used as proof for their existence.⁶ For increased selectivity, a 0.02 µm syringe filter was optionally used to remove all particulate fragments from the dispersion (signal at 500 nm went to zero). The remaining UV Vis signal at 265 nm wavelength served as proxy for water-soluble organics.⁷⁻¹⁰



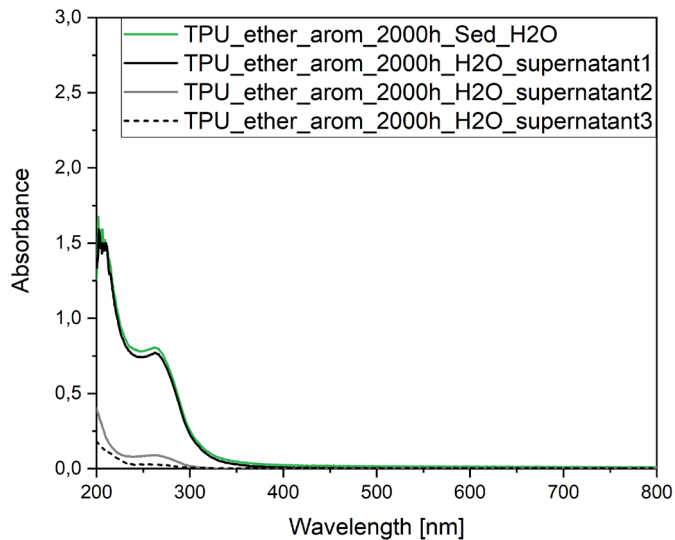
SI Figure 1: Shapes and sizes of the polymer powders used for UV aging experiments: (a) PA-6, (b) PA-12, (c) TPU_ester_ arom, (d) TPU_ether_ arom, (e) TPU_ester_ ali, (f) TPU_ether_ ali.



SI Figure 2: Evaluation of different set-ups in the UV aging device via exemplary shown for PA-6. Aged monolayers showed the highest shift to low molecular masses, but also the thin-layers showed no bimodal distribution, indicating that all polymer was affected by aging, independent from their position in the petri dish.

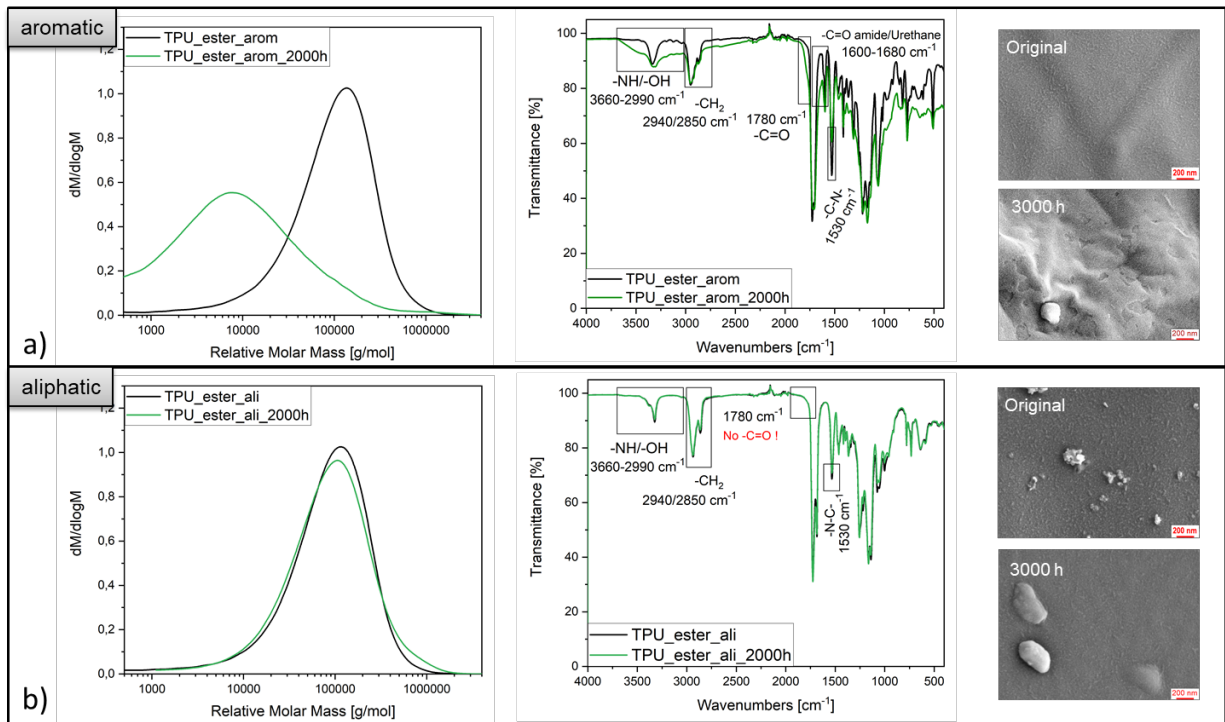


SI Figure 3: Set-up in the UV aging device. The petri dishes were covered with quartz glass to avoid windblown dispersal of the powders, but some space was left for oxygen transfer.

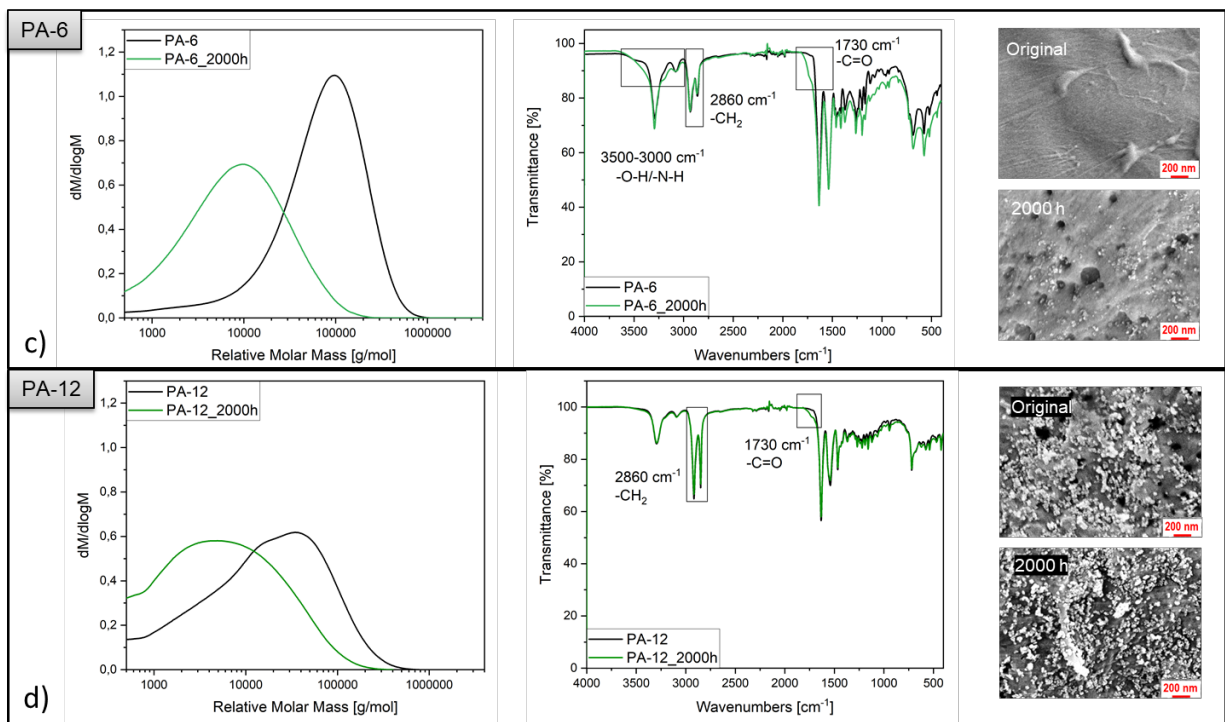


SI Figure 4: Monitoring of washing steps (exemplary for TPU_ether_ arom) to remove the released water-soluble organics in the dispersion by centrifugation. The supernatant after the first centrifugation step shows an intense absorption. After the third washing step the amount of water-soluble organics was significantly reduced resulting in a weak absorption.

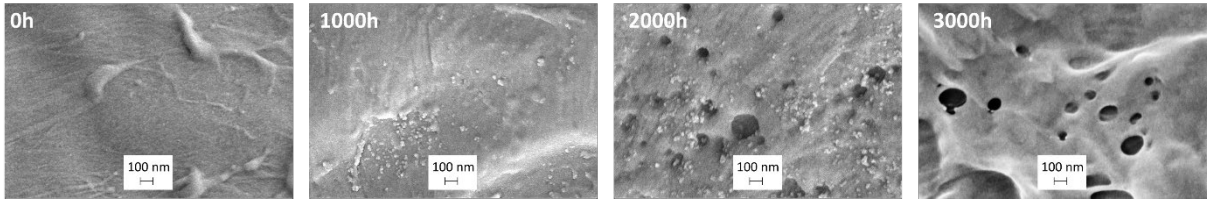
TPU_ester



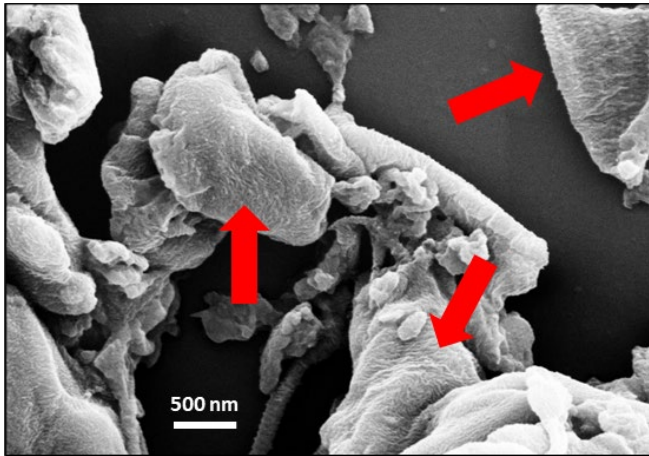
PA



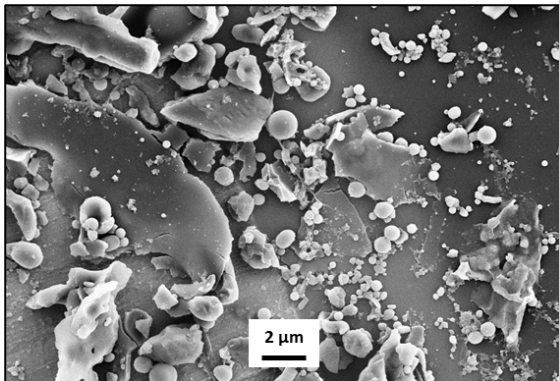
SI Figure 5: Characterization of primary microplastic powders before and after UV aging. Results for both of the PAs and TPU_ester_ arom show a reduction in the molar mass distribution (not for TPU aliphatic), an increase of carbonyl- and hydroxyl functional groups (not for TPU aliphatic) and an affected surface texture (nano-sized fragments on the surface of PA) with increasing duration of UV irradiation.



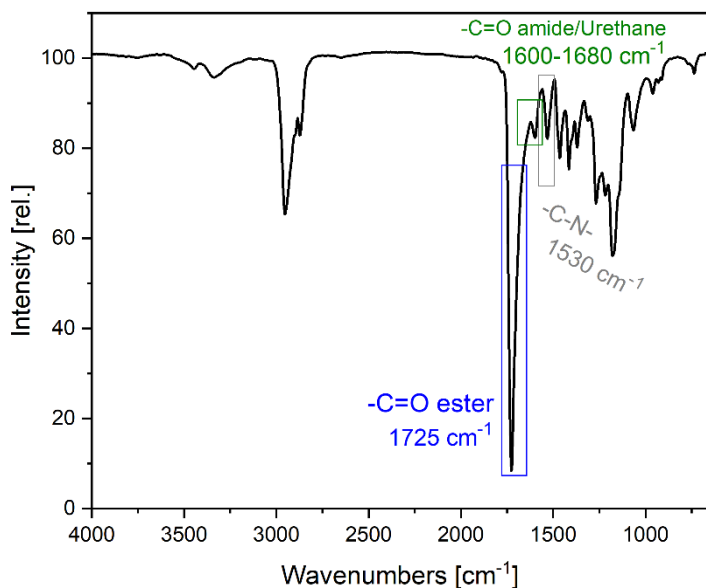
SI Figure 6: Evolution of the PA-6 surface with increasing UV irradiation: In the beginning, nanosized-surface structures are formed (1000 h), then holes in the surface occur (2000 h) and finally deeper holes are formed (3000 h).



SI Figure 7: Surface texture of released PA-6 plastic fragments. Lamella-like structures were observed, that indicate a high percentage of crystallinity.

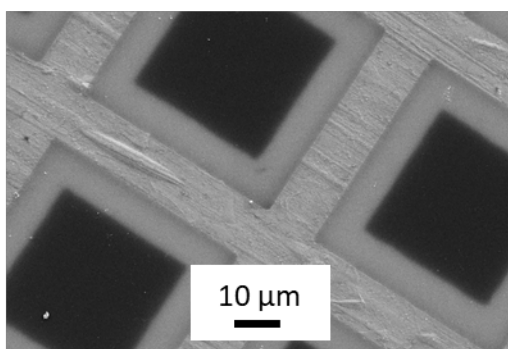


SI Figure 8: Released plastic fragments from TPU_ether_ arom. Next to TPU particles with irregular shape and relatively sharp edges one also observes spherical particles, attributed to SiO₂ anticaking agent used in the polymer production.

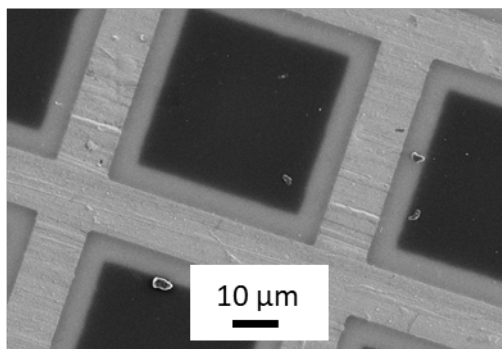


SI Figure 9: FT-IR spectrum of released organic residue after UV aging of TPU_ester_ arom. The residue had no particulate structure and was mainly composed of the polyester-polyol contained in the TPU soft segment.

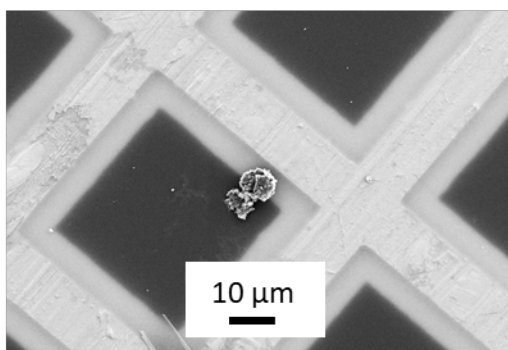
a) Blank_Filter



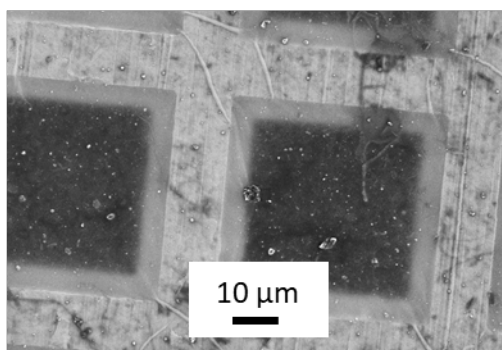
b) Blank_Sedimentation



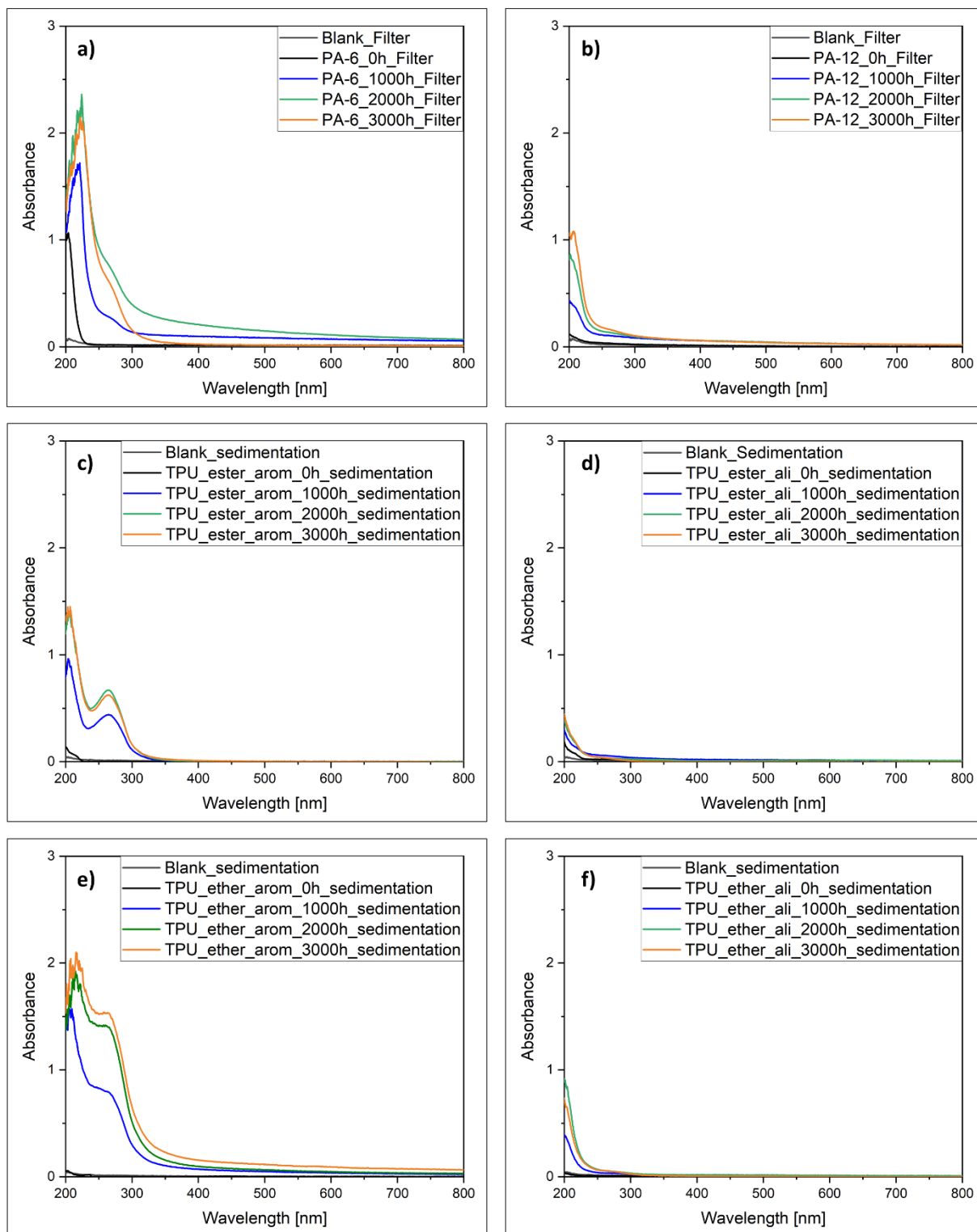
c) TPU_ester_ali_2000h



d) TPU_ether_ali_2000h



SI Figure 10: SEM images of NanoRelease dispersions: a) Blank_Filter, b) Blank_Sedimentation, c) TPU_ester_ali_2000h, d) TPU_ether_ali_2000h. No evaluable amount of released plastic fragments was present on the TEM grids.



SI Figure 11: UVVis spectra of NanoRelease dispersions with increasing duration of UV irradiation: a) PA-6, b) PA-12, c) TPU_ester_ arom, d) TPU_ester_ ali, e) TPU_ether_ arom, f) TPU_ether_ ali. Increasing absorbance intensity in the area between 400 and 700 nm indicates the presence of light-scattering particles, increasing absorbance intensity at 625 nm indicates the presence of water-soluble organics (e.g. TPU_ether_ arom).

SI Table 1: Technical information of the investigated polymer powders.

Polymer	Density [g/cm ³] ^[a]	T _g [°C] ^[b]	T _m [°C] ^[b]	Mean particle size d50 [μm] ^[c]	Specific surface area [m ² /g]
PA-6	1.00-1.20	53.0	211.8 / 219.9	42	0.376 ^[d]
PA-12	1.02-1.15	38.0	169.3 / 176.6	44	0.726 ^[d]
TPU_ester_ arom	1.19	-33.0	159.3	254	0.023 ^[c]
TPU_ether_ arom	1.12	-37.0	169.2	246	0.025 ^[c]
TPU_ester_ ali	1.14	-50.0	19.5 / 103.0	262	0.035 ^[c]
TPU_ether_ ali	1.05	-10.0	94.3 / 105.6 / 114.3	267	0.033 ^[c]

[a] Values adopted from material safety datasheets of polymer materials.

[b] Values determined by differential scanning calorimetry (-70 to 280°C, 2nd heating curve, 20 K/min).

[c] Values determined by Fraunhofer light scattering, ISO13320.

[d] Values determined by Brunauer Emmett & Teller, DIN ISO 9277-2014-01.

SI Table 2: Polydispersity (PDI), crosslinking degree, mass (M_w) and number (M_n) average molecular weight of UV aged primary microplastics showing a general reduction of molar mass and increasing polydispersity over aging time. Crosslinking after UV aging occurred for the aromatic TPUs.

Polymer	UV irradiation [h]	M_w [g/mol]	M_n [g/mol]	PDI	Crosslinking [wt.-%]
PA-6	0	57 900	16 400	3.5	0
	1000	34 100	7 300	4.7	0
	2000	15 000	2 000	7.5	0
	3000	8 300	1 400	6.0	0
PA-12	0	37 400	5 390	6.9	0
	2000	13 900	2 730	5.1	0
TPU_ester_ arom	0	148 000	33 200	4.4	0
	1000	93 200	9 500	9.8	35
	2000	35 700	1 400	26.0	35
	3000	18 600	900	21.0	50
TPU_ester_ ali	0	126 000	28 800	4.4	0
	1000	140 000	27 900	5.0	0
	2000	139 000	38 200	3.6	0
	3000	117 000	30 500	3.8	0
TPU_ether_ arom	0	137 000	32 600	4.2	0
	1000	90 300	9 000	10.0	20
	2000	27 900	1 100	26.4	20
	3000	12 000	700	17.7	50
TPU_ether_ ali	0	69 400	20 000	3.5	0
	1000	46 300	12 400	3.7	0
	2000	32 700	10 000	3.3	0
	3000	28 400	8 600	3.3	0

1 *SI Table 3: Concentration and diameter of nanoplastic fragments released with increasing duration of UV irradiation, determined via AUC-RI in three separate experiments covering*
2 *respectively the size intervals 10k rcf (10-150 nm), 650 rcf (40-880 nm), 70 rcf (300-5300 nm). Duplicate measurements were performed, blank values were subtracted. Determination*
3 *of diameter is only possible with a concentration > 0.02 mg/mL.*

Polymer	UV irradiation [h]	10k rcf [mg/mL]	D50 10k rcf [nm]	650 rcf [mg/mL]	D50 650 rcf [nm]	70 rcf [mg/mL]	D50 70 rcf [nm]
PA-6	0	0.000 ± 0.000	ND	0.007 ± 0.009	ND	0.007 ± 0.015	ND
	1000	0.021 ± 0.023	19 ± 1	0.009 ± 0.004	ND	0.014 ± 0.016	ND
	2000	0.101 ± 0.027	20 ± 3	0.039 ± 0.034	485 ± 25	0.075 ± 0.016	650 ± 60
	3000	0.118 ± 0.012	12 ± 1	0.000 ± 0.002	ND	0.000 ± 0.000	ND
PA-12	0	0.000 ± 0.001	ND	0.000 ± 0.002	ND	0.000 ± 0.001	ND
	1000	0.000 ± 0.001	ND	0.000 ± 0.002	ND	0.000 ± 0.001	ND
	2000	0.000 ± 0.001	ND	0.018 ± 0.002	ND	0.000 ± 0.000	ND
	3000	0.000 ± 0.002	ND	0.042 ± 0.010	265 ± 25	0.000 ± 0.008	ND
TPU_ester_ arom	0	0.013 ± 0.014	ND	0.006 ± 0.009	ND	0.030 ± 0.029	2700 ± 800
	1000	0.014 ± 0.021	ND	0.001 ± 0.005	ND	0.047 ± 0.008	2150 ± 1350
	2000	0.046 ± 0.000	19 ± 2	0.000 ± 0.003	ND	0.043 ± 0.004	2800 ± 100
	3000	0.002 ± 0.002	ND	0.000 ± 0.002	ND	0.000 ± 0.003	ND
TPU_ester_ ali	0	0.003 ± 0.016	ND	0.010 ± 0.005	ND	0.016 ± 0.003	ND
	1000	0.000 ± 0.002	ND	0.015 ± 0.019	ND	0.018 ± 0.002	ND
	2000	0.006 ± 0.004	ND	0.007 ± 0.002	ND	0.005 ± 0.015	ND
	3000	0.000 ± 0.000	ND	0.000 ± 0.001	ND	0.000 ± 0.001	ND
TPU_ether_ arom	0	0.007 ± 0.002	ND	0.002 ± 0.000	ND	0.019 ± 0.003	ND
	1000	0.041 ± 0.008	14 ± 7	0.000 ± 0.002	ND	0.011 ± 0.006	ND
	2000	0.063 ± 0.000	25 ± 8	0.016 ± 0.002	ND	0.073 ± 0.006	2450 ± 350
	3000	0.035 ± 0.005	16 ± 2	0.000 ± 0.009	ND	0.004 ± 0.007	ND
TPU_ether_ ali	0	0.004 ± 0.013	ND	0.000 ± 0.001	ND	0.056 ± 0.018	4500 ± 400
	1000	0.015 ± 0.006	ND	0.027 ± 0.010	410 ± 140	0.031 ± 0.011	3200 ± 100
	2000	0.008 ± 0.000	ND	0.012 ± 0.002	ND	0.063 ± 0.027	3800 ± 800
	3000	0.000 ± 0.000	ND	0.000 ± 0.001	ND	0.000 ± 0.001	ND

5 *SI Table 4: Particle counts (1 μm, 2 μm > 2 μm) per mL of microplastic fragments released with increasing duration of UV irradiation, determined via laser particle counter.*

6 *Duplicate measurements were performed, blank values were subtracted.*

Polymer	UV irradiation [h]	1 μm [10 ⁴ counts/mL]	2 μm [10 ⁴ counts/mL]	> 2 μm [10 ⁴ counts/mL]
PA-6	0	178.7 ± 41.6	22.8 ± 0.8	10.5 ± 3.3
	1000	264.3 ± 5.8	37.6 ± 3.2	20.4 ± 7.1
	2000	425.7 ± 41.0	36.8 ± 0.9	11.9 ± 1.3
	3000	111.2 ± 21.2	9.0 ± 1.6	1.9 ± 0.4
PA-12	0	22.2 ± 2.6	2.9 ± 0.6	2.4 ± 0.6
	1000	80.5 ± 8.4	14.3 ± 4.4	14.6 ± 8.9
	2000	62.2 ± 1.4	9.5 ± 0.4	8.1 ± 1.6
	3000	95.7 ± 19.0	14.0 ± 2.4	11.6 ± 0.5
TPU_ester_ arom	0	2.1 ± 0.2	0.2 ± 0.0	0.3 ± 0.1
	1000	19.6 ± 5.9	1.7 ± 0.3	1.5 ± 0.0
	2000	25.4 ± 7.5	2.6 ± 0.6	2.1 ± 0.5
	3000	26.0 ± 8.8	2.7 ± 0.8	2.4 ± 0.1
TPU_ester_ ali	0	8.3 ± 2.7	1.1 ± 0.3	1.2 ± 0.3
	2000	21.5 ± 12.9	2.8 ± 1.8	3.2 ± 1.3
TPU_ether_ arom	0	4.7 ± 0.7	0.6 ± 0.3	0.8 ± 0.6
	1000	53.6 ± 4.9	12.1 ± 0.8	17.4 ± 2.1
	2000	168.5 ± 43.8	23.9 ± 2.3	20.5 ± 0.8
	3000	289.6 ± 2.5	45.3 ± 1.4	43.2 ± 2.7
TPU_ether_ ali	0	12.2 ± 1.1	2.0 ± 0.2	2.4 ± 0.3
	2000	18.4 ± 5.2	4.3 ± 1.2	7.8 ± 0.2

7

8 *SI Table 5: Estimated lifetimes of PA-6 and TPU_ether_ arom particles until completely fragmented/dissolved.*
 9 *Calculation is based on highest fragmentation rate after 2000 h UV: 1.902 mg/g for PA-6, 1.178 mg/g for*
 10 *TPU_ether_ arom plus TOC of dissolved organics.*

PA-6						
UV irradiation	Particle diameter Dx50	Density	Volume	Mass	Released total mass	Thickness degraded surface layer
[h]	[m]	[g/m ³]	[m ³]	[g]	[g]	[nm]
0	42.000·10 ⁻⁶	1.20·10 ⁶	3.879·10 ⁻¹⁴	4.655·10 ⁻⁸	-	-
2000	41.317·10 ⁻⁶	1.20·10 ⁶	3.693·10 ⁻¹⁴	4.432·10 ⁻⁸	2.235·10 ⁻⁹	341.5

Lifetime of PA-6 particles			
Particle diameter	Number of layers	Artificial UV aging	Years in Europe
[μm]		[h]	
100	146.40	292 791	292.8
10	14.6	29 279	29.3
1	1.5	2 928	2.9

TPU_ether_ arom						
UV irradiation	Particle diameter Dx50	Density	Volume	Mass	Released total mass	Thickness degraded surface layer
[h]	[m]	[g/m ³]	[m ³]	[g]	[g]	[nm]
0	246.000·10 ⁻⁶	1.12·10 ⁶	7.795·10 ⁻¹²	8.730·10 ⁻⁶	-	-
2000	244.616·10 ⁻⁶	1.12·10 ⁶	7.664·10 ⁻¹²	8.584·10 ⁻⁶	1.465·10 ⁻⁷	691.8

Lifetime of TPU_ether_ arom particles			
Particle diameter	Number of layers	Artificial UV aging	Years in Europe
[μm]		[h]	
100	72.28	144 554	144.5
10	7.23	14 455	14.5
1	0.72	1 455	1.4

12 *SI Table 6: Absorbance of NanoRelease samples at 265 nm (dissolved organics) and 500 nm (micro- and*
 13 *nanoplastic fragments). The dispersions were filtered (0.02 μm) for a comparison of the intensities with and without*
 14 *particles and to determine the TOC after 0 and 2000 h of the dissolved organics.*

Polymer	UV irradiation [h]	Absorbance 265 nm (filtered)	TOC (filtered w/o SDS) [mg/g]	Absorbance 500 nm (unfiltered)
PA-6	0	-	2.8	0.023 \pm 0.006
	1000	0.225 \pm 0.005	-	0.063 \pm 0.022
	2000	0.403 \pm 0.034	46.1	0.132 \pm 0.016
	3000	0.614 \pm 0.027	-	0.030 \pm 0.013
PA-12	0	-	-	-
	2000	0.133 \pm 0.020	-	0.042 \pm 0.003
TPU_ester_ arom	0	-	0.3	-
	1000	0.457 \pm 0.017	-	-
	2000	0.712 \pm 0.045	10.1	-
	3000	0.688 \pm 0.063	-	-
TPU_ester_ ali	0	0.017 \pm 0.007	-	-
	2000	0.044 \pm 0.010	-	-
TPU_ether_ arom	0	0.004 \pm 0.004	0.1	0.007 \pm 0.006
	1000	0.691 \pm 0.002	-	0.026 \pm 0.024
	2000	1.192 \pm 0.010	15.6	0.058 \pm 0.007
	3000	1.220 \pm 0.103	-	0.086 \pm 0.029
TPU_ether_ ali	0	0.009 \pm 0.001	-	-
	2000	0.069 \pm 0.015	-	-

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16

17 *SI Table 7: Source data and results of fitting fragmentation rates on the example of TPU_ether_ arom with the direct*
 18 *fragmentation equation, in line with the ongoing update of the fragmentation description in Full Mult model*
 19 *(<https://github.com/apraetorius/fragmentation>).*

		10nm-to- 150nm	40nm-to- 800nm	300nm-to- 5000nm	Dissolved organics
Source data from present paper	0 h UV	0.05 mg/g	0.02 mg/g	0.14 mg/g	0.08 mg/g
	1000 h UV	0.32 mg/g	0.01 mg/g	0.08 mg/g	N/A mg/g
	2000 h UV	0.49 mg/g	0.25 mg/g	0.56 mg/g	15.6 mg/g
<i>Fitting results</i>	k_{frag} [1/h]	5.25×10^{-7}	2.1×10^{-7}	4.7×10^{-7}	-
	$k_{\text{frag-all}}$ [1/h]	2.6×10^{-7}	9.4×10^{-8}	2.4×10^{-7}	6.3×10^{-6}

20 k_{frag} : rate constant for fragmentation from parent particle to given size class (disregarding dissolved
 21 organics)

22 $k_{\text{frag-all}}$: rate constant for fragmentation from parent particle to given size class accounting for loss
 23 to dissolved organics (also expressed as rate constant, but only accounting for direct loss from
 24 parent particle)

25 **References SI:**

- 26 1. Pfohl, P.; Roth, C.; Meyer, L.; Heinemeyer, U.; Gruending, T.; Lang, C.; Nestle, N.; Hofmann, T.;
27 Wohlleben, W.; Jessl, S., Microplastic extraction protocols can impact the polymer structure. *Microplastics*
28 *and Nanoplastics* **2021**, *1*, (1).
- 29 2. Walter, J.; Löhr, K.; Karabudak, E.; Reis, W.; Mikhael, J.; Peukert, W.; Wohlleben, W.; Cölfen, H.,
30 Multidimensional Analysis of Nanoparticles with Highly Disperse Properties Using Multiwavelength
31 Analytical Ultracentrifugation. *ACS Nano* **2014**, *8*, (9), 8871-8886.
- 32 3. Mehn, D.; Rio-Echevarria, I. M.; Gilliland, D.; Kaiser, M.; Vilsmeier, K.; Schuck, P.; Wohlleben, W.,
33 Identification of nanomaterials: A validation report of two laboratories using analytical ultracentrifugation
34 with fixed and ramped speed options. *NanoImpact* **2018**, *10*, 87-96.
- 35 4. Wohlleben, W.; Meier, M. W.; Vogel, S.; Landsiedel, R.; Cox, G.; Hirth, S.; Tomovic, Z., Elastic CNT-
36 polyurethane nanocomposite: synthesis, performance and assessment of fragments released during use.
37 *Nanoscale* **2013**, *5*, (1), 369-80.
- 38 5. Schuck, P.; Balbo, A., Analytical Ultracentrifugation in the Study of Protein Selfassociation and
39 Heterogeneous Protein-Protein Interactions. In *Protein-Protein Interactions: A Molecular Cloning Manual*,
40 Cold Spring Harbor Laboratory Press, 2005.
- 41 6. Wohlleben, W.; Kingston, C.; Carter, J.; Sahle-Demessie, E.; Vázquez-Campos, S.; Acrey, B.; Chen, C.-
42 Y.; Walton, E.; Egenolf, H.; Müller, P.; Zepp, R., NanoRelease: Pilot interlaboratory comparison of a
43 weathering protocol applied to resilient and labile polymers with and without embedded carbon nanotubes.
44 *Carbon* **2017**, *113*, 346-360.
- 45 7. Li, X.; Zhao, X.; Ye, L., Stress photo-oxidative aging behaviour of polyamide 6. *Polymer International* **2012**,
46 *61*, (1), 118-123.
- 47 8. Ties, K.; Rossbach, V., Thermo-oxidative degradation of polyamide 6 and polyamide 6,6 - Structure of
48 UVVIS-active chromophores. *Die Makromolekulare Chemie* **1990**, *191*, (4), 757-771.
- 49 9. Taniguchi, M.; Lindsey, J. S., Database of Absorption and Fluorescence Spectra of >300 Common
50 Compounds for use in PhotochemCAD. *Photochem Photobiol* **2018**, *94*, (2), 290-327.
- 51 10. Shimadzu, UV Talk Letter. **2009**, Vol. 2.

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