

New versus Naturally Aged Greenhouse Cover Films: Degradation and Micro-Nanoplastics Characterization under Sunlight Exposure

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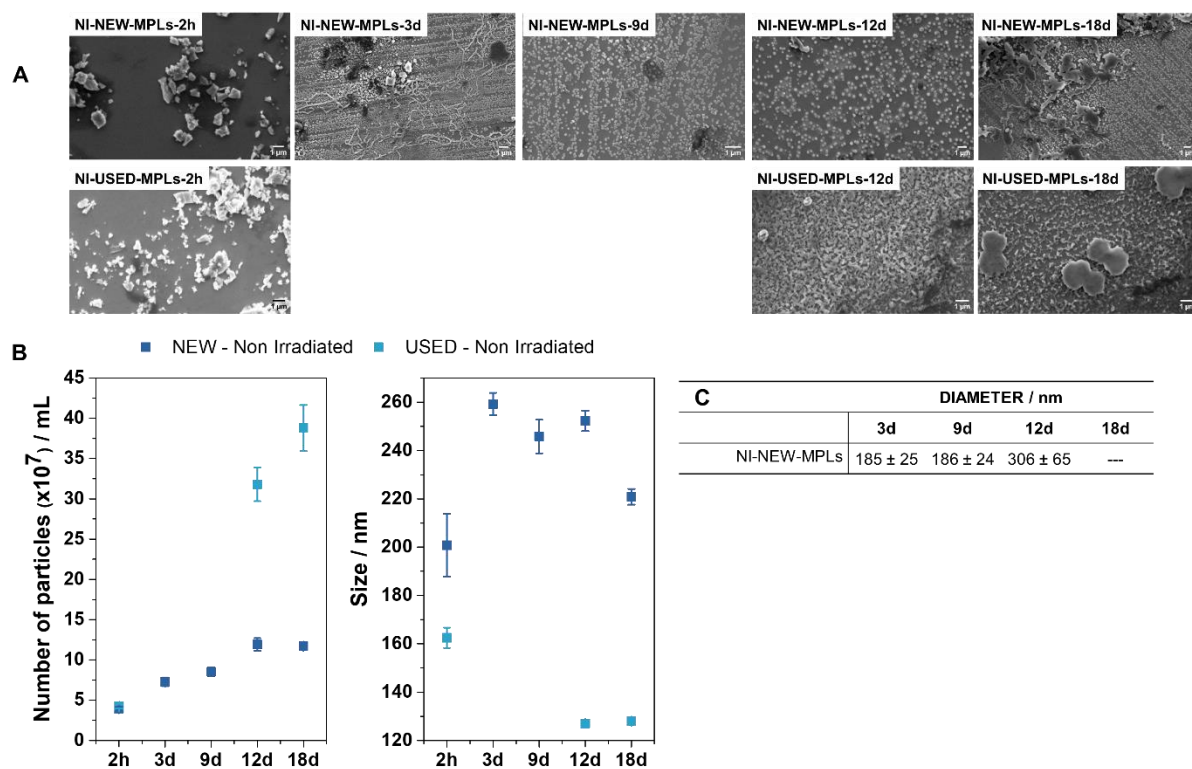


Figure S1. A. SEM micrographs showing particles with diameters < 1 μm released from the NI-new-MPLs and NI-used-MPLs. Scale bar: 1 μm . **B.** Concentration and size of the particles released from the NI-new-MPLs and NI-used-MPLs obtained by NTA at different aging times. Error bars represent the standard deviation from recording five videos of 60 seconds each. **C.** Inset table summarising the diameter of the particles calculated from SEM images using Fiji software for the NI-New-MPLs.

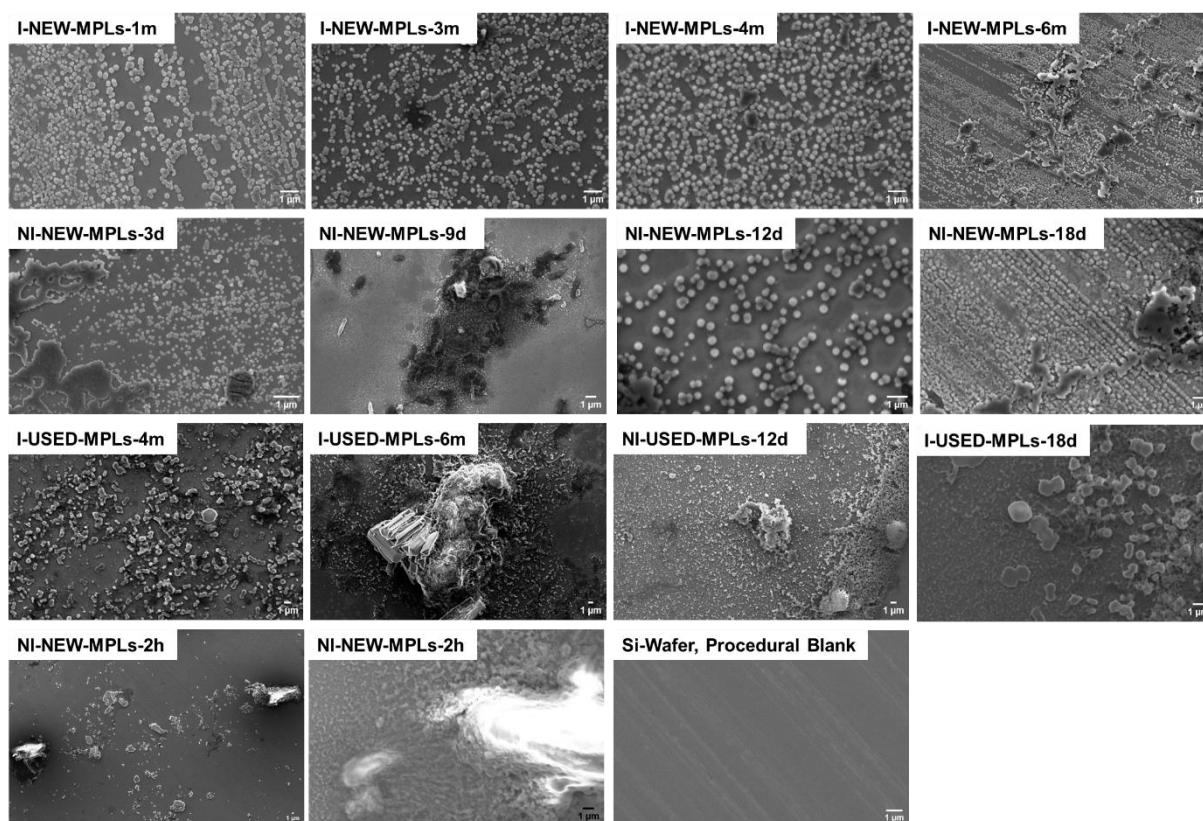


Figure S2. Additional SEM images for the leachates under simulated sunlight irradiation and dark conditions. Under irradiation conditions selected in this work, 3 days of irradiation corresponds to ~ 1 month of average sunlight in the Iberian Peninsula (see Material and methods). Non-irradiated samples were kept in the dark for the same time as the irradiated samples, i.e., 3, 9, 12 and 18 days. SEM images of a plain silicon wafer were used as a procedural blank. No particles were found in the silicon wafer. Scale bar: 1 μm .

Table S1. Values of concentration, mean size, percentile, and particles per frame of particles released from the new, used, irradiated, and non-irradiated MPLs obtained by NTA at different aging times. Under irradiation conditions selected in this work, 3 days of irradiation corresponds to ~ 1 month of average sunlight in the Iberian Peninsula (see Material and methods). Non-irradiated samples were kept in the dark for the same time as the irradiated samples, i.e., 3, 9, 12 and 18 days. Control samples and Milli-Q water as procedural blank were also analyzed. D90: 90% of the total particles are smaller than this size; D50: 50% are smaller than this size; D10: 10% are smaller than this size. *samples were filtered due to the presence of large material.

| NEW | | | | | | | |
|----------------|---------------|-------------------------------|----------------|----------------|--------------|--------------|--------------|
| | | particle/mL ($\times 10^7$) | particle/frame | Mean size (nm) | size D10 | size D50 | size D90 |
| Irradiated | 1 m | 7.7 ± 0.5 | 7.8 ± 0.6 | 238 ± 13 | 120 ± 9 | 200 ± 10 | 398 ± 23 |
| | 3 m | 9.1 ± 0.9 | 10.3 ± 0.9 | 215 ± 7 | 125 ± 11 | 196 ± 5 | 315 ± 15 |
| | 4 m | 9.5 ± 0.5 | 9.6 ± 0.4 | 206 ± 5 | 109 ± 6 | 197 ± 3 | 306 ± 6 |
| | 6 m | 11.7 ± 1.3 | 11.7 ± 1.2 | 221 ± 4 | 122 ± 7 | 206 ± 7 | 343 ± 11 |
| Non-Irradiated | 2 h | 4.0 ± 0.2 | 3.5 ± 0.2 | 201 ± 13 | 111 ± 7 | 181 ± 16 | 315 ± 19 |
| | 3 d | 7.3 ± 0.5 | 7.1 ± 0.6 | 259 ± 5 | 137 ± 5 | 240 ± 9 | 408 ± 15 |
| | 9 d | 8.5 ± 0.6 | 10.2 ± 0.7 | 246 ± 7 | 128 ± 6 | 217 ± 7 | 400 ± 8 |
| | 12 d | 11.9 ± 0.8 | 12.0 ± 1.0 | 252 ± 4 | 140 ± 9 | 228 ± 2 | 392 ± 14 |
| | 18 d* | 11.7 ± 0.4 | 10.6 ± 0.4 | 221 ± 3 | 128 ± 4 | 204 ± 2 | 333 ± 10 |
| USED | | | | | | | |
| | | particle/mL ($\times 10^7$) | particle/frame | Mean size (nm) | size D10 | size D50 | size D90 |
| Irradiated | 4 m* | 40.2 ± 3.3 | 15.7 ± 1.5 | 132 ± 1 | 88 ± 3 | 121 ± 2 | 182 ± 2 |
| | 6 m* | 31.6 ± 0.8 | 11.7 ± 0.3 | 143 ± 2 | 95 ± 2 | 134 ± 2 | 198 ± 4 |
| Non-Irradiated | 2 h | 4.2 ± 0.2 | 3.9 ± 0.3 | 163 ± 4 | 99 ± 4 | 143 ± 5 | 250 ± 6 |
| | 12 d* | 31.8 ± 2.1 | 13.0 ± 1.2 | 127 ± 1 | 85 ± 3 | 117 ± 2 | 177 ± 5 |
| | 18 d* | 38.8 ± 2.9 | 16.5 ± 1.4 | 128 ± 2 | 90 ± 1 | 119 ± 1 | 178 ± 6 |
| | Milli-Q Water | 1.0 ± 0.1 | 0.9 ± 0.1 | 193 ± 21 | 113 ± 8 | 176 ± 17 | 284 ± 33 |

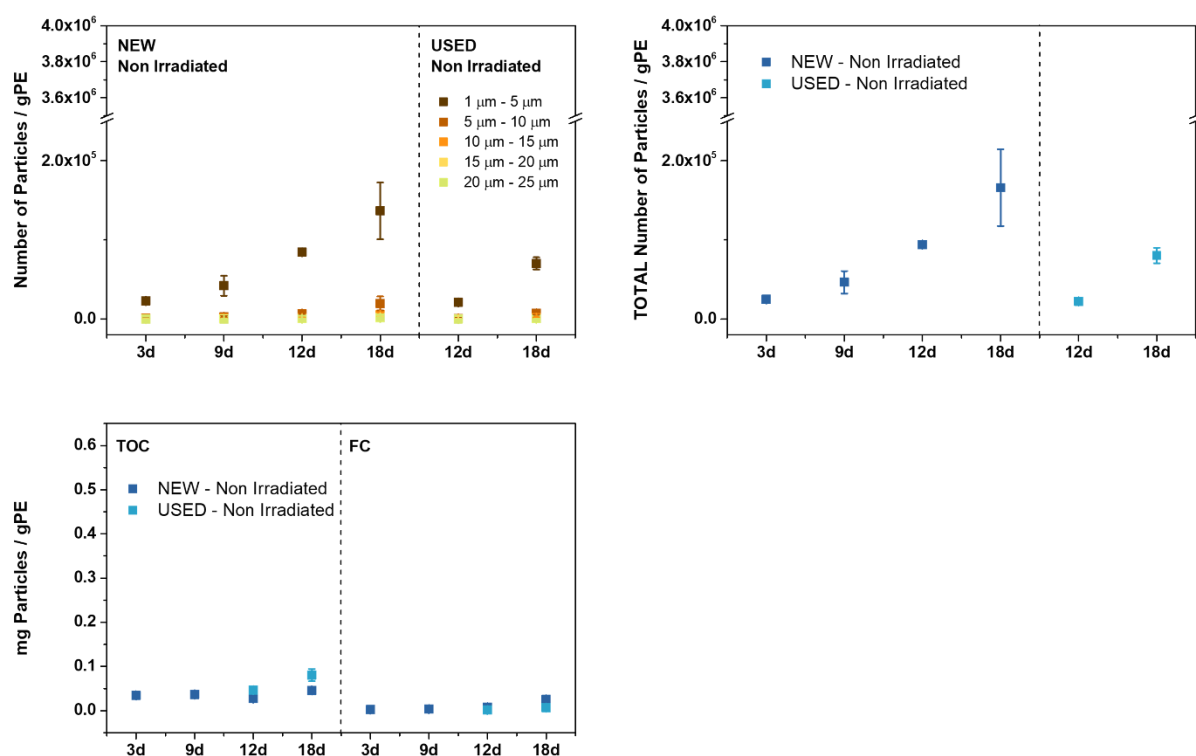


Figure S3. A. Concentration of particles in the leachates obtained by FC expressed as the number of particles per gPE for NI-new-MPLs and NI-used-MPLs. **B.** Total concentration of particles in the leachates obtained by FC expressed as the number of particles per gPE. **C.** Total carbon in the leachates for the NI-new-MPLs and NI-used-MPLs measured by TOC analyzer and FC. The mg Particles / g PE was calculated following the procedure described elsewhere.¹

Table S2. Values of the number of particles per gPE and mgParticles/gPE represented in Figure 3 and Figure S3.

| NEW – Number of Particles / gPE - FC | | | | | | | |
|---------------------------------------|------|---|---|---|---|---|---|
| | | 1-5 μm | 5-10 μm | 10-15 μm | 15-20 μm | 20-25 μm | TOTAL |
| Irradiated | 1 m | 2.5 x 10 ⁴ ± 5.2 x 10 ³ | 2.1 x 10 ³ ± 6.7 x 10 ² | 1.3 x 10 ³ ± 6.4 x 10 ² | 6.1 x 10 ² ± 1.6 x 10 ² | 4.4 x 10 ² ± 1.2 x 10 ² | 3.0 x 10 ⁴ ± 6.8 x 10 ³ |
| | 3 m | 4.5 x 10 ⁵ ± 4.9x 10 ⁵ | 2.1 x 10 ⁴ ± 1.2x 10 ⁴ | 8.2 x 10 ³ ± 2.9 x 10 ² | 3.9 x 10 ³ ± 2.5 x 10 ³ | 2.6 x 10 ³ ± 1.3 x 10 ³ | 4.9 x 10 ⁵ ± 5.1 x 10 ⁵ |
| | 4 m | 6.7x 10 ⁵ ± 2.5x 10 ⁵ | 5.3 x 10 ⁴ ± 8.9 x 10 ³ | 1.5 x 10 ⁴ ± 3.2 x 10 ³ | 7.0 x 10 ³ ± 1.6 x 10 ³ | 5.1 x 10 ³ ± 1.1 x 10 ³ | 7.5 x 10 ⁵ ± 2.6 x 10 ⁵ |
| | 6 m | 1.9x 10 ⁶ ± 1.9x 10 ⁶ | 8.9 x 10 ⁴ ± 1.2 x 10 ⁴ | 2.8 x 10 ⁴ ± 4.3 x 10 ³ | 1.2 x 10 ⁴ ± 1.2 x 10 ³ | 6.4 x 10 ³ ± 1.4 x 10 ³ | 2.0 x 10 ⁶ ± 1.9 x 10 ⁶ |
| Non-Irradiated | 3 d | 2.3x 10 ⁴ ± 3.4x 10 ³ | 9.9 x 10 ² ± 6.4x 10 ¹ | 4.7 x 10 ² ± 1.2 x 10 ² | 2.2 x 10 ² ± 3.7 x 10 ¹ | 1.0 x 10 ² ± 2.0 x 10 ¹ | 2.5 x 10 ⁴ ± 3.6 x 10 ³ |
| | 9 d | 4.2 x 10 ⁴ ± 1.3x 10 ⁴ | 2.8 x 10 ³ ± 1.2 x 10 ³ | 1.1 x 10 ³ ± 2.2 x 10 ² | 2.5 x 10 ² ± 1.8 x 10 ² | 1.5 x 10 ² ± 1.3 x 10 ² | 4.6 x 10 ⁴ ± 1.4 x 10 ⁴ |
| | 12 d | 8.5x 10 ⁴ ± 2.5x 10 ³ | 6.9 x 10 ³ ± 4.5 x 10 ² | 1.8 x 10 ³ ± 4.5 x 10 ² | 5.2 x 10 ² ± 2.7 x 10 ² | 3.9 x 10 ² ± 1.3 x 10 ² | 9.4 x 10 ⁴ ± 3.8 x 10 ³ |
| | 18 d | 1.4x 10 ⁵ ± 3.6x 10 ⁴ | 2.0 x 10 ⁴ ± 8.7 x 10 ³ | 5.5 x 10 ³ ± 2.6 x 10 ³ | 2.4 x 10 ³ ± 7.8 x 10 ² | 1.5 x 10 ³ ± 6.3 x 10 ² | 1.7 x 10 ⁵ ± 4.9 x 10 ⁵ |
| USED – Number of Particles / gPE - FC | | | | | | | |
| | | 1-5 μm | 5-10 μm | 10-15 μm | 15-20 μm | 20-25 μm | TOTAL |
| Irradiated | 4 m | 1.3x 10 ⁵ ± 2.9x 10 ⁴ | 6.2 x 10 ³ ± 3.7 x 10 ³ | 1.1 x 10 ³ ± 1.0 x 10 ³ | 6.0 x 10 ² ± 3.3 x 10 ² | 3.0 x 10 ² ± 1.8 x 10 ² | 1.4 x 10 ⁵ ± 3.4 x 10 ⁴ |
| | 6 m | 5.6x 10 ⁴ ± 9.5x 10 ³ | 3.9 x 10 ³ ± 1.2 x 10 ³ | 2.3 x 10 ³ ± 2.3 x 10 ² | 1.0 x 10 ³ ± 5.3 x 10 ² | 4.1 x 10 ² ± 3.7 x 10 ² | 6.4 x 10 ⁴ ± 1.2 x 10 ³ |
| Non-Irradiated | 12 d | 2.1x 10 ⁴ ± 3.2x 10 ³ | 8.4 x 10 ² ± 6.3 x 10 ² | 3.6 x 10 ² ± 1.7 x 10 ² | 1.7 x 10 ² ± 5.6 x 10 ² | 3.7 x 10 ² ± 3.2 x 10 ² | 2.3 x 10 ⁴ ± 4.1 x 10 ³ |
| | 18 d | 7.0x 10 ⁴ ± 7.8x 10 ³ | 7.3 x 10 ³ ± 1.5 x 10 ³ | 2.0 x 10 ³ ± 2.7 x 10 ² | 4.2 x 10 ² ± 1.1 x 10 ² | 2.8 x 10 ² ± 5.7x 10 ¹ | 8.0 x 10 ⁴ ± 9.7x 10 ³ |
| | | | | | | | |
| NEW – mg Particles / gPE – FC vs TOC | | | | | | | |
| | | FC | TOC | | | | |
| Irradiated | 1 m | 6.0 x 10 ⁻² ± 9.3 x 10 ⁻³ | 4.6 x 10 ⁻² ± 4.3 x 10 ⁻³ | | | | |
| | 3 m | 4.3 x 10 ⁻² ± 6.6 x 10 ⁻³ | 3.8 x 10 ⁻² ± 3.6 x 10 ⁻³ | | | | |
| | 4 m | 7.9 x 10 ⁻² ± 1.2 x 10 ⁻³ | 9.4 x 10 ⁻² ± 9.0 x 10 ⁻³ | | | | |
| | 6 m | 1.3 x 10 ⁻¹ ± 1.7 x 10 ⁻² | 1.6 x 10 ⁻¹ ± 3.6 x 10 ⁻² | | | | |
| Non-Irradiated | 3 d | 2.1 x 10 ⁻³ ± 4.4 x 10 ⁻⁴ | 3.5 x 10 ⁻² ± 4.4 x 10 ⁻³ | | | | |
| | 9 d | 3.6 x 10 ⁻³ ± 7.7 x 10 ⁻⁴ | 3.6 x 10 ⁻² ± 4.6 x 10 ⁻³ | | | | |
| | 12 d | 7.6 x 10 ⁻³ ± 1.6 x 10 ⁻³ | 2.7 x 10 ⁻² ± 3.4 x 10 ⁻³ | | | | |
| | 18 d | 2.6 x 10 ⁻² ± 5.4 x 10 ⁻³ | 4.6 x 10 ⁻² ± 5.7 x 10 ⁻³ | | | | |
| USED – Number of Particles / gPE - FC | | | | | | | |
| | | FC | TOC | | | | |
| Irradiated | 4 m | 7.2 x 10 ⁻³ ± 2.3 x 10 ⁻³ | 2.2 x 10 ⁻¹ ± 2.5 x 10 ⁻² | | | | |
| | 6 m | 8.6 x 10 ⁻³ ± 2.7 x 10 ⁻³ | 5.4 x 10 ⁻¹ ± 6.0 x 10 ⁻² | | | | |
| Non-Irradiated | 12 d | 1.4 x 10 ⁻³ ± 5.0 x 10 ⁻⁴ | 4.6 x 10 ⁻² ± 7.8 x 10 ⁻³ | | | | |
| | 18 d | 6.9 x 10 ⁻³ ± 2.4 x 10 ⁻³ | 8.0 x 10 ⁻² ± 1.4 x 10 ⁻² | | | | |

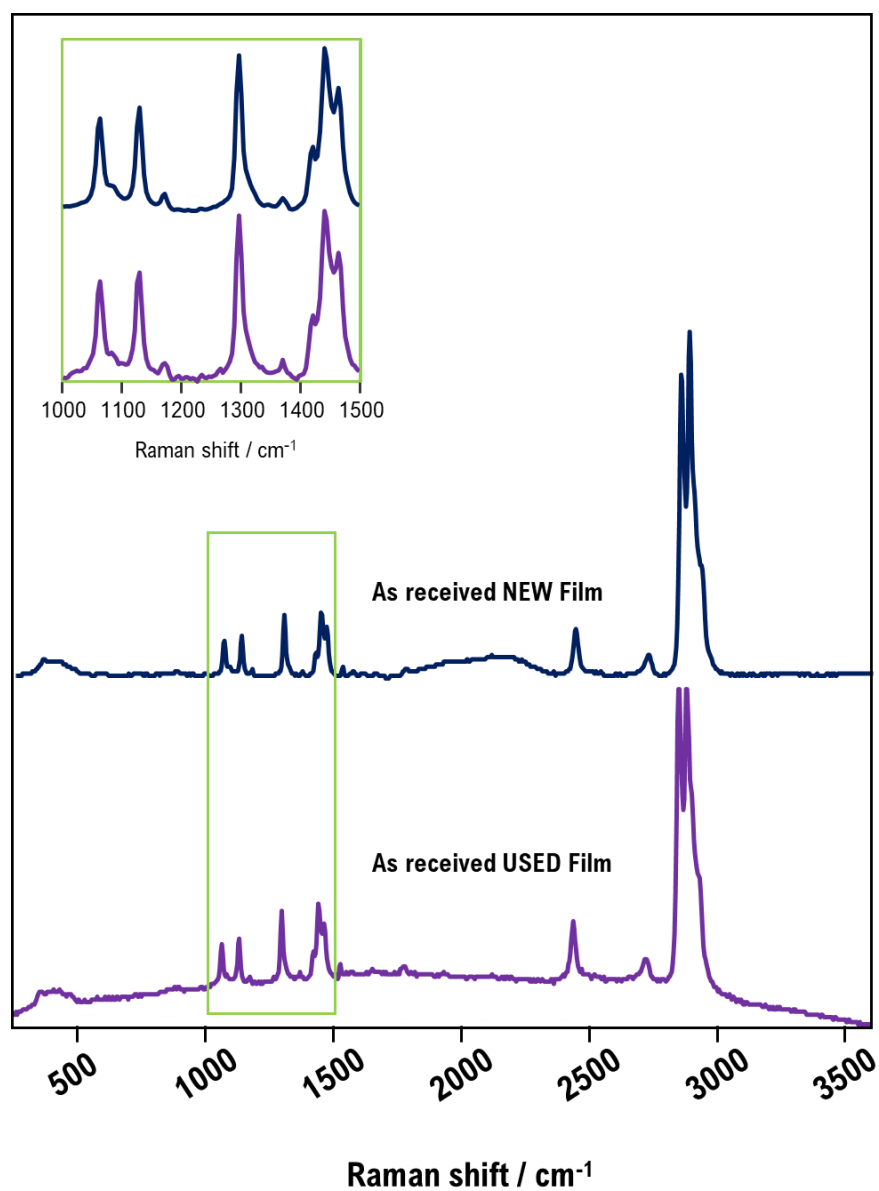


Figure S4. Raman spectra for the as-received films using a 532 nm laser line. A zoom-in view of the region from 1000 cm^{-1} to 1500 cm^{-1} to better visualize the band centered at 1083 cm^{-1} is represented in the inset.

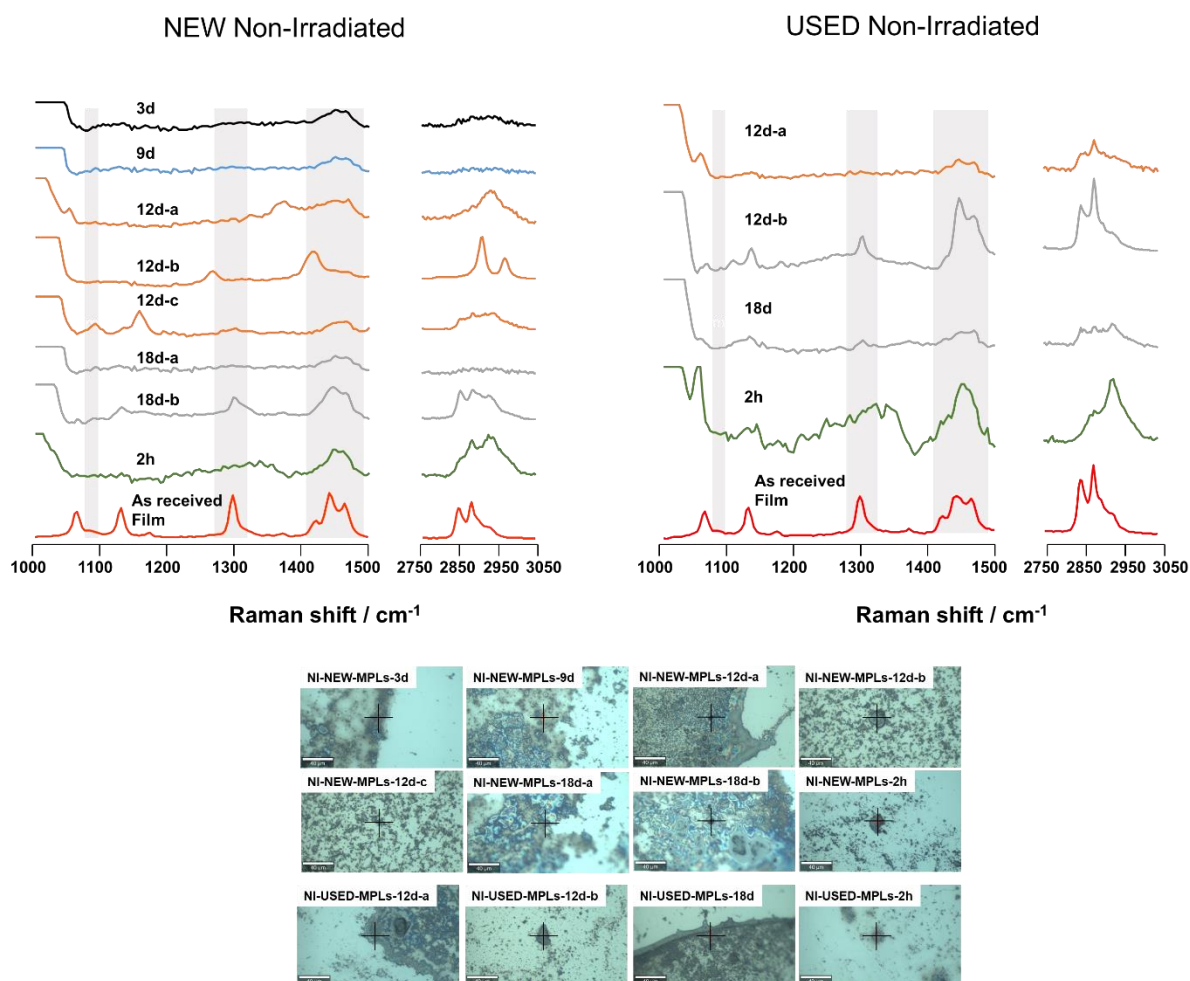


Figure S5. Raman spectra for the leachates from NI-new-MPLs and NI-used-MPLs were acquired using a 532 nm laser line at different aging times. Non-irradiated samples were kept in the dark for the same time as the irradiated samples, i.e., 3, 9, 12 and 18 days. Several spots were analyzed for all the samples showing low-crystalline PE NPLs. Bright-field Images showing the different spots where the Raman spectra were recorded in the leachates for the new-MPLs and used-MPLs at different aging times. Scale bar: 40 μm .

Table S3. Raman peak assignments for the LDPE greenhouse coversheets.^{2,3}

| As-received New Film | As-received Used Film | Raman Peak Assignment |
|----------------------|-----------------------|--|
| 1064 | 1064 | C-C stretching (Consecutive trans) |
| 1086 | 1086 | C-C stretching (Amorphous Phase) |
| 1129 | 1129 | C-C stretching (Consecutive trans) |
| 1296 | 1297 | CH ₂ twisting (Consecutive trans) |
| 1418 | 1418 | CH ₂ bending (Orthorhombic crystalline phase) |
| 1442 | 1442 | Bending CH ₂ (Amorphous trans Phase) |
| 1460 | 1460 | Bending CH ₂ (Amorphous phase) |
| 2848 | 2848 | Symmetric C-H stretching mode (Sensitive to crystallinity) |
| 2881 | 2881 | Antisymmetric C-H stretching (sensitive to crystallinity) |

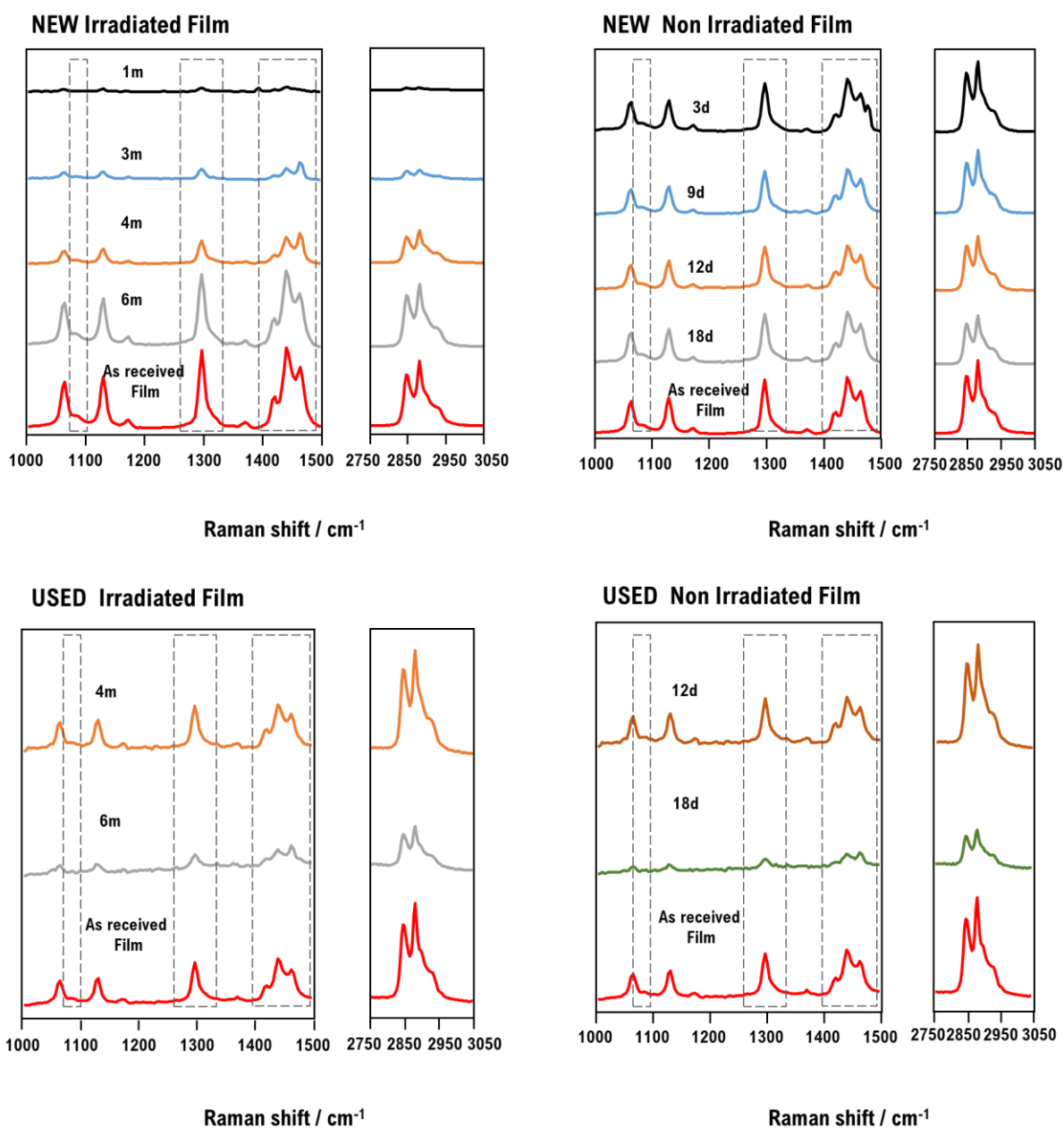


Figure S6. Raman spectra for the 5 mm x 5 mm MPLs after aging using a 532 nm laser line. Under irradiation conditions selected in this work, 3 days of irradiation corresponds to ~ 1 month of average sunlight in the Iberian Peninsula (see Material and methods). Non-irradiated samples were kept in the dark for the same time as the irradiated samples, i.e., 3, 9, 12 and 18 days.

References

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- 3 Y. Hiejima, T. Kida, K. Takeda, T. Igarashi and K. Nitta, Microscopic structural changes during photodegradation of low-density polyethylene detected by Raman spectroscopy, *Polym. Degrad. Stab.*, 2018, **150**, 67–72.