

Supplementary material

A pilot interlaboratory comparison of protocols that simulate aging of nanocomposites and detect released fragments

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Materials as produced, before aging

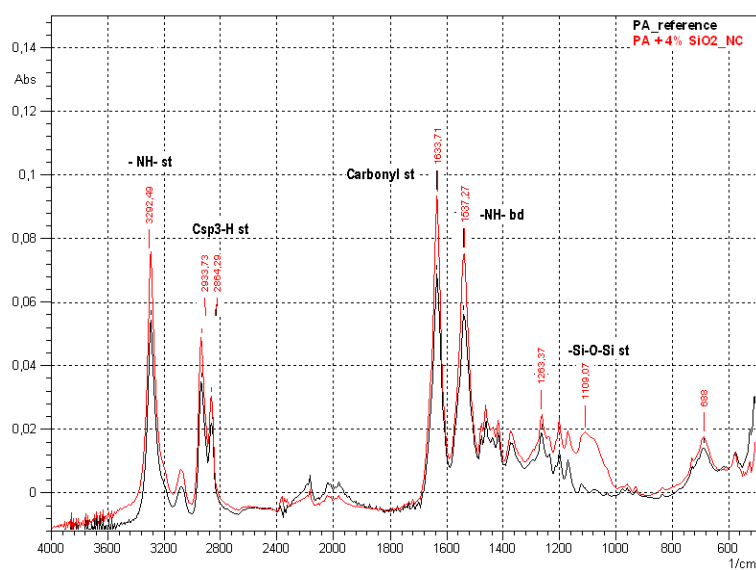


Fig. S1. Attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectra of neat polyamide (PA) (black) and PA nanosilica composite (red) before aging.

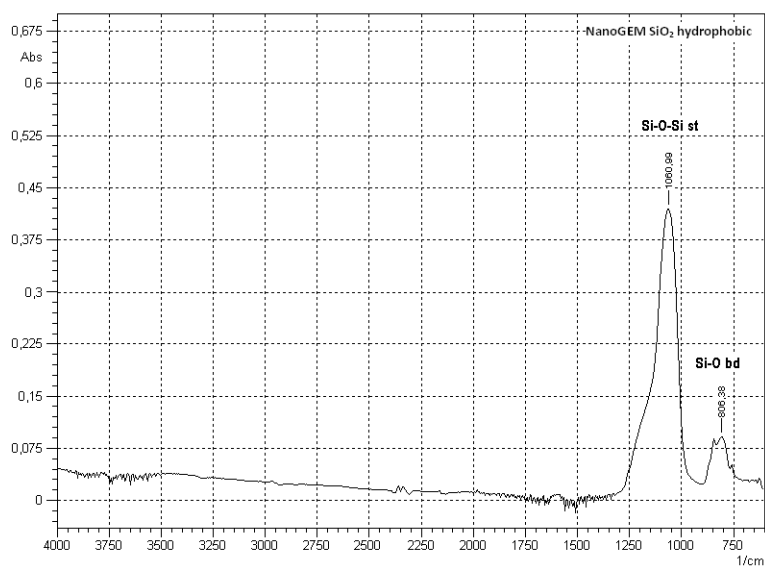


Fig. S2. Transmission Fourier-transform infrared (FTIR) spectrum of nanosilica.

Thermogravimetric analyses (TGA) of nanosilica, polyamide (PA)–nanosilica composite and neat PA before the aging was performed. The results showed that the peaks at 387 and at 494 °C correspond to compounds coming from the thermal degradation of the polymer. Moreover, the peak corresponding to the presence of siloxane surface modifier of nanosilica (at 429 °C) could not be observed because of overlapping with the peaks coming from thermal degradation compounds.

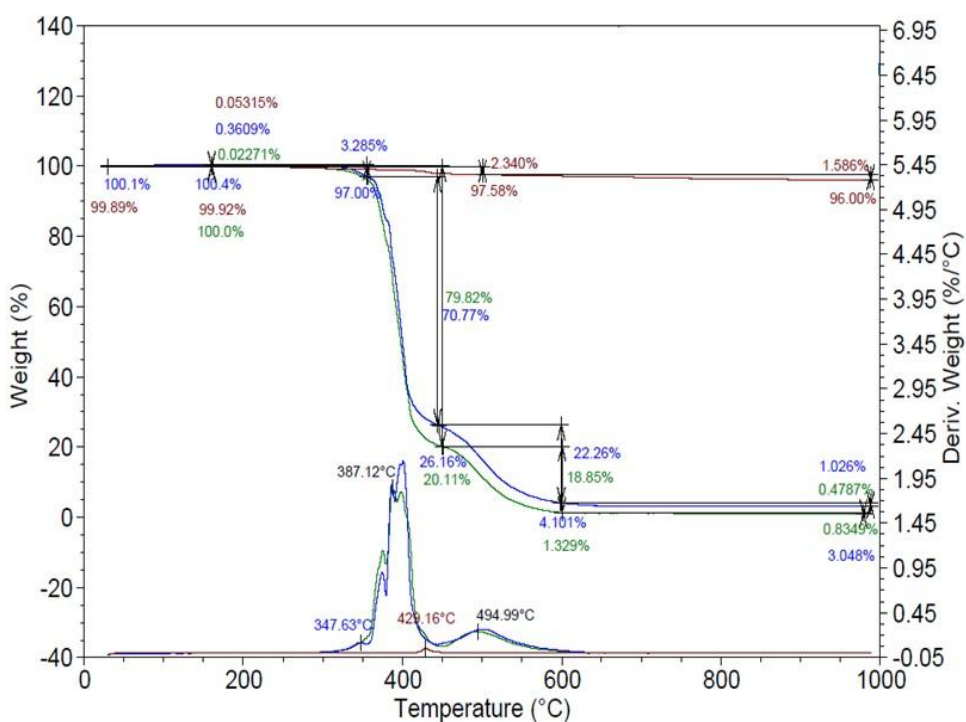


Fig. S3. Thermogravimetric analysis (TGA) and derivative themograms of neat PA (green), PA nanosilica composite (blue) and nanosilica (brown) before they were aged. The thermal degradation of the samples was carried out in presence of air.

The following table summarises the percentage of organic and inorganic materials obtained by TGA. The inorganic material and the residue observed in the neat PA sample indicate the presence of some silicon derivatives from impurities. The results obtained for nanocomposite sample confirmed the presence of SiO₂ at approximately 3 mass %.

Table S1. Summary of thermogravimetric analysis results on as-produced materials

	Mass loss 160–450 °C	Mass loss 450–600 °C	Mass loss 600– 1000 °C	Ash (residue)
Neat polyamide (PA)	79.82 %	18.85 %	0.48 %	0.83 %
PA nanosilica composite	70.49 %	22.17 %	1.02 %	3.04 %
nanosilica	Mass loss 160–500 °C		Mass loss 500–1000 °C	Ash (residue)
	2.34 %		1.59 %	96.08 %

To further assess the distribution of nanosilica in PA, the surface of the as-produced composite was measured by X-ray photoelectron spectroscopy (XPS), thus averaging only the top 10 nm of the plates. Silicon is clearly identified in the top 10 nm, corresponding to 5.6 mass % SiO_2 . The nanofiller is hence homogeneously distributed up to the irradiated surface, and should emerge on the surface as soon as the polymer degrades. The detailed line shape analysis of the Si photoelectrons reveals that part of the silicon is present as siloxanes, attributed to the hydrophobic surface treatment of the specific nanosilica before compounding, and explaining the surplus signal above the nominal nanosilica content of 4 mass %.

Finally, thin-cut slices of the composite were imaged by transmission electron microscopy (TEM), revealing that the nanofiller is overall homogeneously distributed, but not fully individualised. It is compounded in agglomerates that are tenfold larger than the average primary particle diameter.

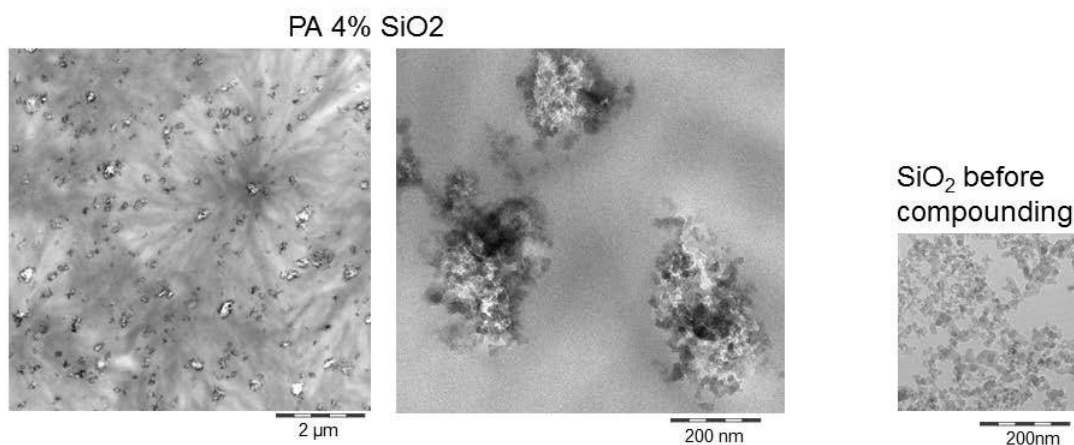


Fig. S4. Transmission electron microscopy (TEM) images of thin cuts of the polyamide (PA)–nanosilica composite and of the nanosilica before compounding.

Bulk material after aging

The probing depth of the attenuated total reflection (ATR) technique for an ideal sample-prism contact is a function of incident angle, wavelength, and refractive indices of both the prism and the polymer. For the ZnSe prism (refractive index 2.4) and 45° incident angle used in this study, the probing depth in the PA polymer (refractive index 1.53) in the region between 800 and 3600 cm^{-1} is approximately between 0.5 and 2.5 μm from the surface. The probing depth in a silica material (refractive index 1.46) is slightly greater than that in the PA material. Therefore, chemical changes in the neat PA and PA nanosilica composite resulting from UV irradiation detected by ATR-FTIR were mostly within the 2.5- μm material layer from the exposed surface.

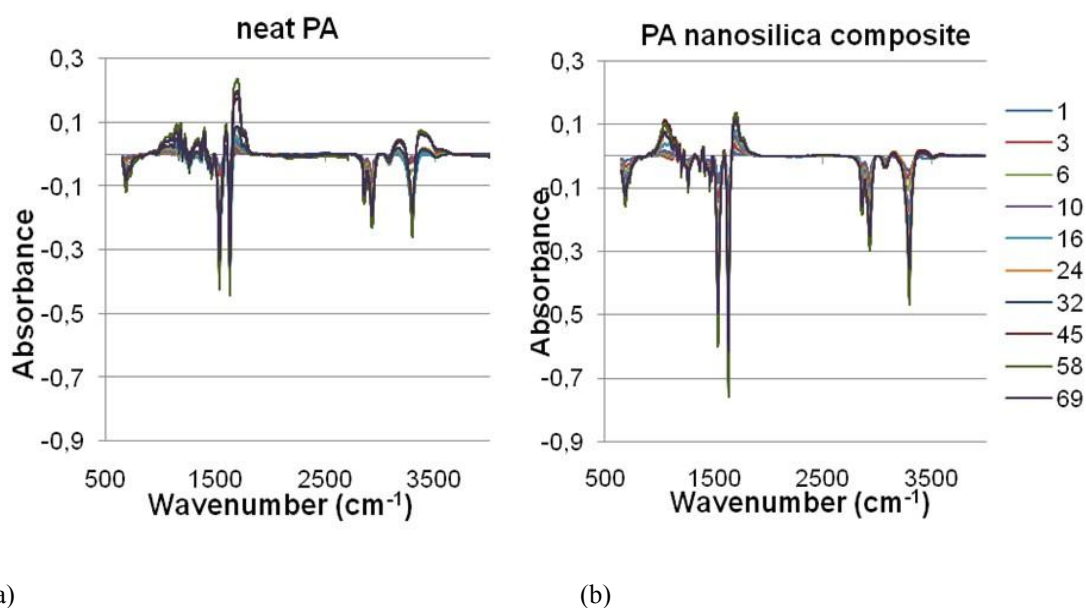


Fig. S5. Difference attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectra of neat polyamide (PA) (a) and PA–nanosilica composite (b) recorded at different UV irradiation periods from 1 day to 69 days (12 to 833 MJ m^{-2}) without rain.

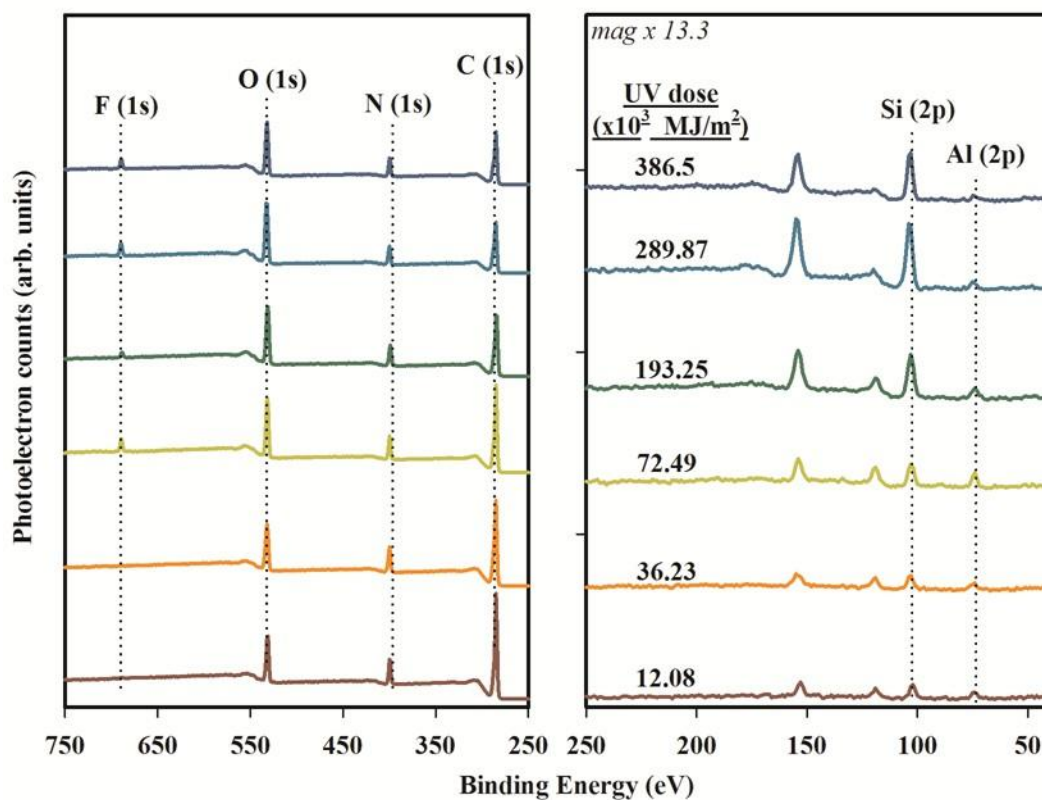


Fig. S6. Representative X-ray photoelectron (XPS) spectra of polyamide (PA)-4 % nanosilica composite collected at different UV doses.

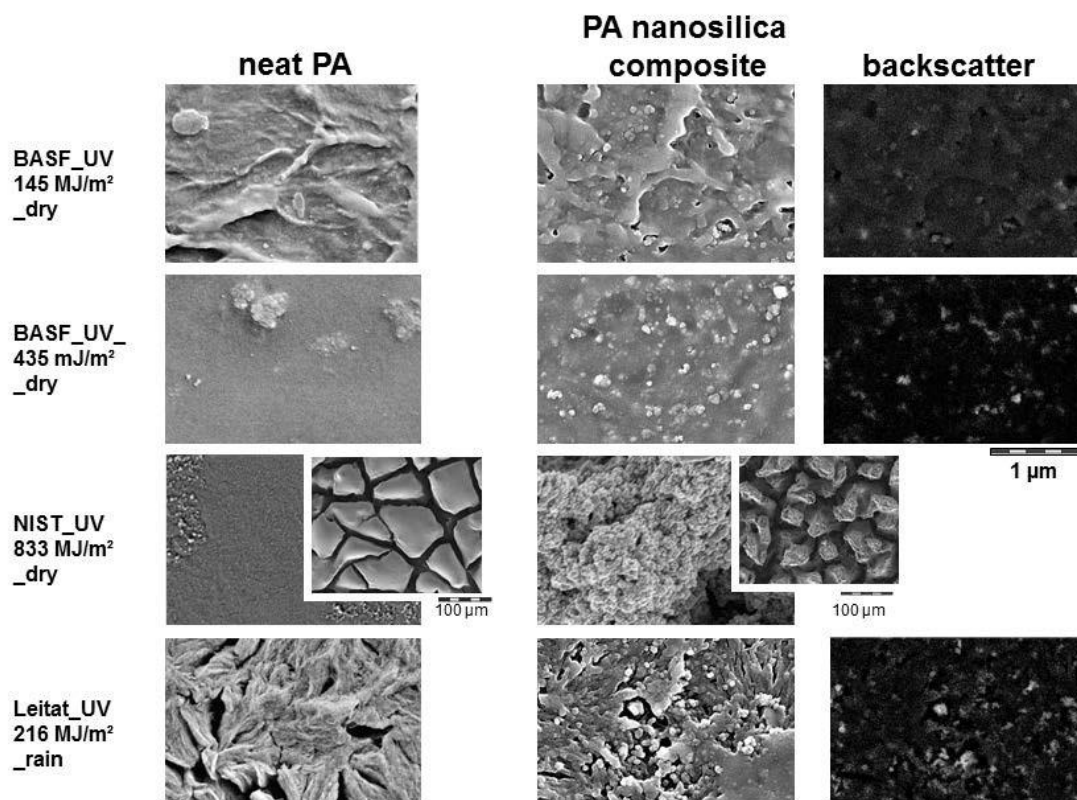


Fig. S7. Scanning electron microscopy (SEM) scans of the aged surfaces, all at the same 1 μm scale except for the two insets as indicated there. Left column, the neat polyamide (PA) without nanofillers degrades with little surface feature on a micrometre scale by dry UV irradiation, but is deeply cracked by rain and UV irradiation. Middle and right column, the nanofiller remains on the receding surface and covers it completely at the highest UV doses. Also after rain cycles, not all SiO_2 nanofillers are washed away, but many particles are uncovered within the cracks of the PA matrix, identified also by the bright backscatter electrons (right column).

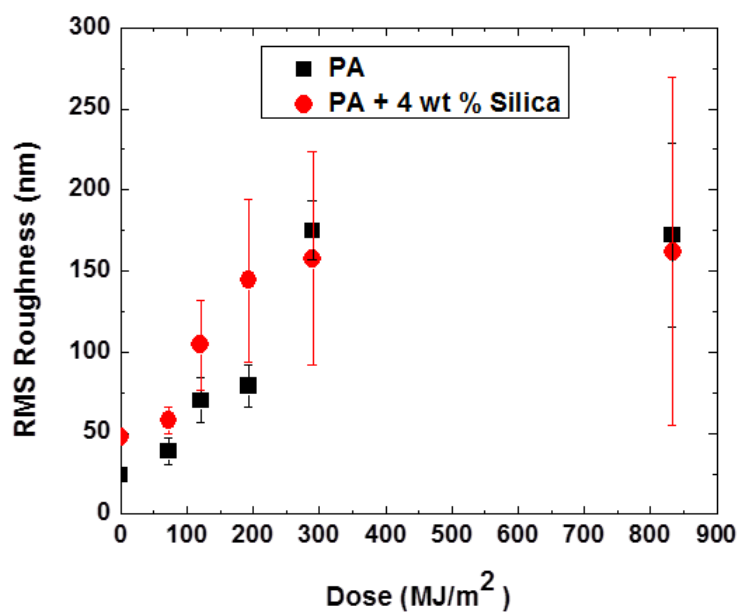


Fig. S8. Roughness analysis of the atomic force microscopy (AFM) height scans shown in Fig. 2.

Released fragments

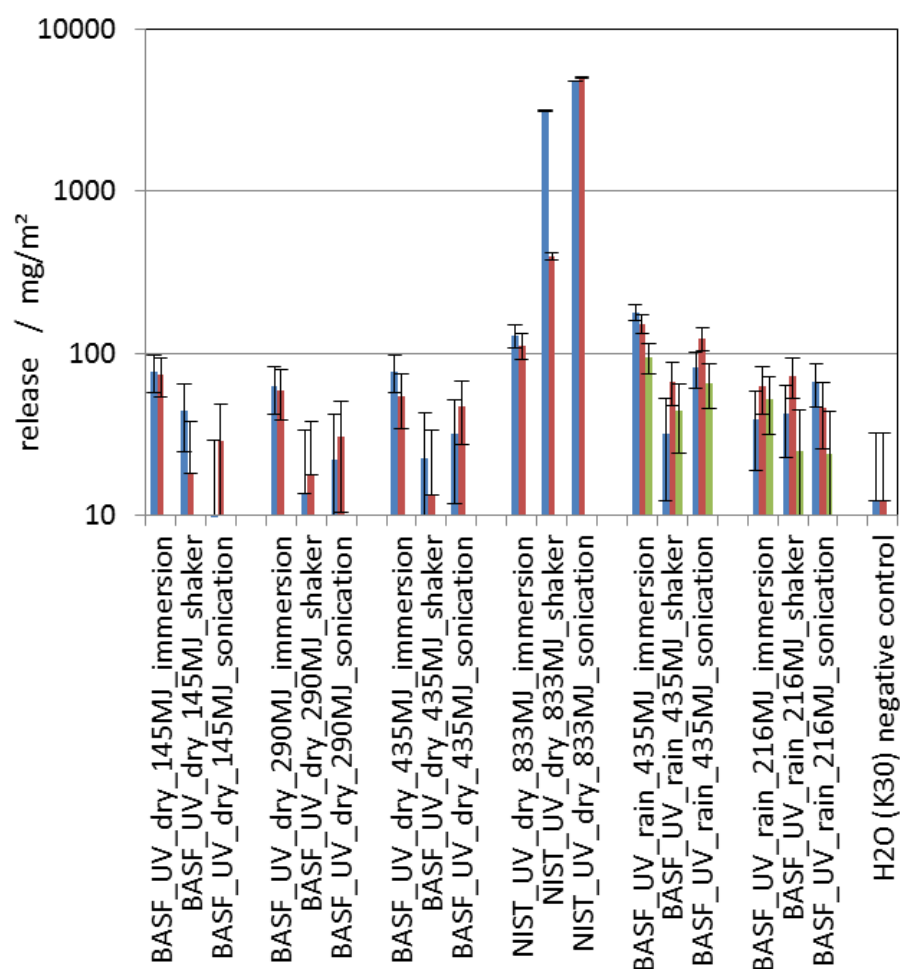


Fig. S9. Quantification of released fragments by immersion and analytical ultracentrifugation (AUC) measurement (size range above 1 μm). blue: neat polyamide (PA); red: PA nanosilica composite; green: PA nanosilica composite, reproduction of weathering, immersion, measurement.

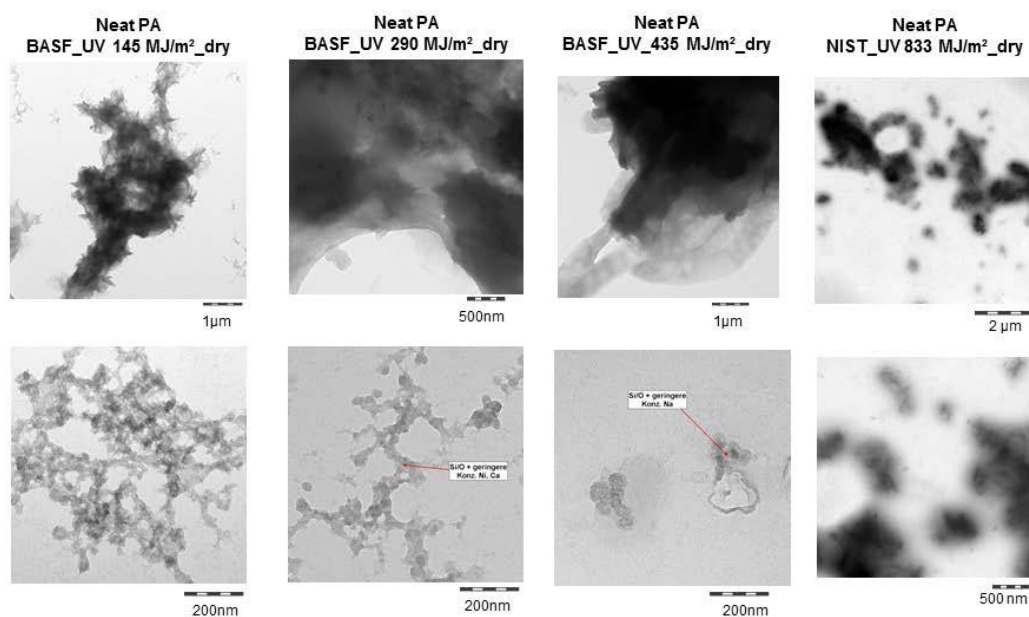


Fig. S10. Nanostructure of release from neat polyamide (PA): Transmission electron microscopy (TEM) of fragments from neat PA (UV irradiated at NIST or BASF, immersion and release at BASF). Fragments at the nanoscale are released, and also silicon-containing contaminations are not excluded. Hence the quantification of release from nanocomposite materials must be benchmarked against the identical material without nanofillers and must be complemented by chemical or morphological identification of release, e.g. by inductively coupled plasma–mass spectrometry (ICP-MS), scanning electron microscopy (SEM)–energy-dispersive X-ray spectroscopy (EDX), Fourier-transform infrared (FTIR), thermogravimetric analysis (TGA).

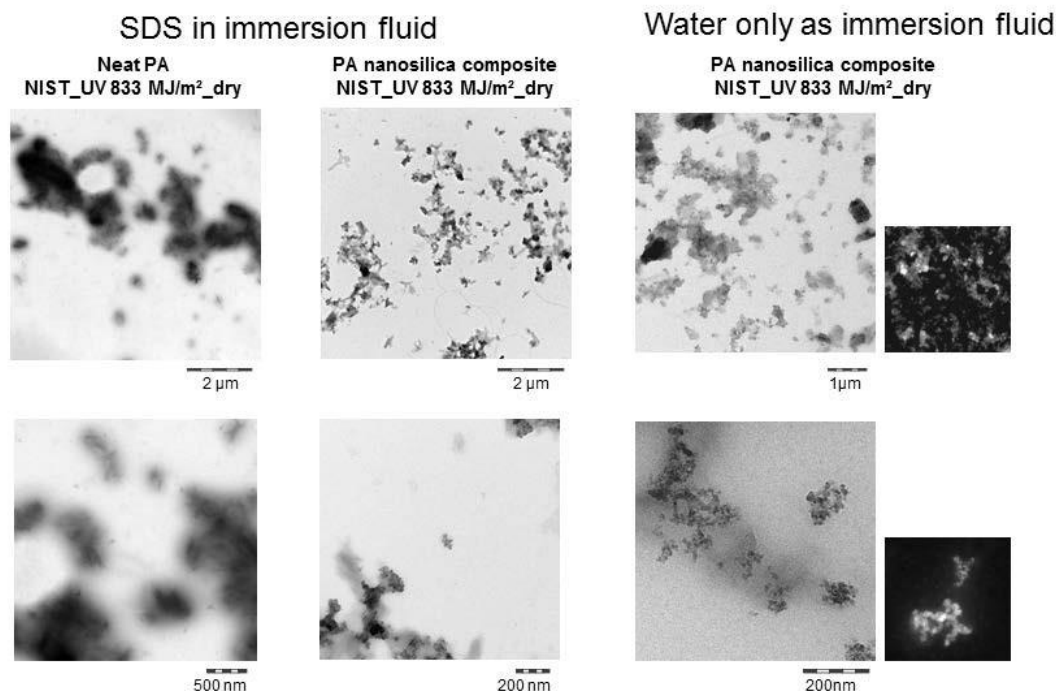


Fig. S11. Influence of the presence of sodium dodecyl sulfate (SDS) in the immersion fluid, investigated by transmission electron microscopy (TEM) of released fragments of neat PA (left column) and of PA nanosilica composite (middle and right columns). All samples were UV irradiated at NIST, followed by immersion and release at BASF. Additionally dark field TEM was performed on selected samples (insets, same scale). Qualitatively the same structures are released regardless of SDS in the immersion fluid. However, if SDS is used during immersion, an additional preparation step was performed to remove it before TEM imaging. Without this step, the TEM or scanning electron microscopy (SEM) images are dominated by dried SDS structures.

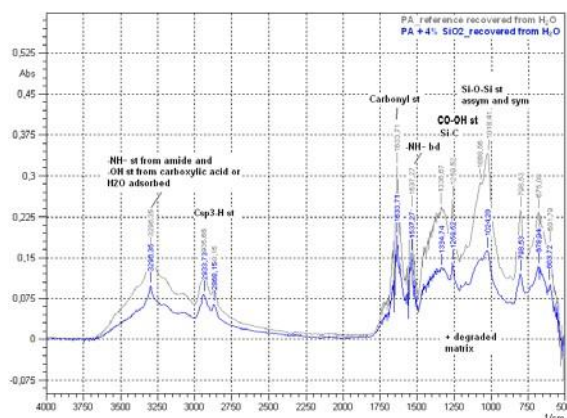


Fig. S12. (a) Fourier-transform infrared (FTIR) spectra of recovered fragments after aging of neat polyamide (PA) (grey) and PA nanosilica composite (blue)

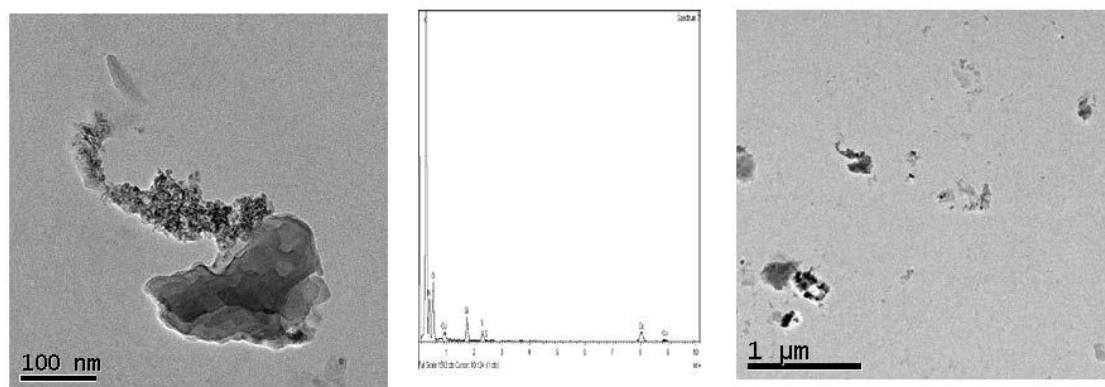


Fig. S13. Transmission electron microscopy (TEM) analysis was performed from calcinated fragments recovered from run-off water of UV + rain weathering of polyamide (PA) nanosilica composite. The presence of nanosilica and silicon contamination was confirmed by EDX.

TGA analysis can determine the percentages of organic and inorganic contents in a sample, and should help to quantify the composition of the fragments. Such analysis for the recovered fragments after UV + rain aging of PA nanosilica composite is illustrated in Fig. S14 and summarised in Table S2. The change in mass due to loss of water (<160 °C) is not included for the discussion. The loss of mass between 160 and 500 °C, which is due to loss of organic material, of the nanocomposite appeared to be higher than that of the neat PA (Table S2, Fig. S14). The higher organic content of the nanocomposite may be attributed to the siloxane surface coating on the silica nanoparticles. This may be substantiated by the peak at 426 °C in the derivative TGA curve in Fig. S14. The other peaks observed in the derivative TGA curves in this temperature range correspond to the thermal degradation temperatures of the PA matrix in the recovered fragments. The residual mass in the 500 to 1000 °C range, where the presence of nanosilica shows a pronounced difference before aging, was similar for recovered fragments from both neat PA and PA nanosilica composite (Table S2). The absolute value of TGA residue from the released fragments (of both neat PA and its nanocomposite) was more than a factor of 10 higher than that of the non-aged neat PA (Table S1). Therefore, the fragments were clearly dominated by the polymer matrix and partially influenced by inorganic impurities, but they also did contain nanosilica.

From the TGA results presented here, it is clear that TGA was not capable of providing the quantity of nanosilica in the release fragments.

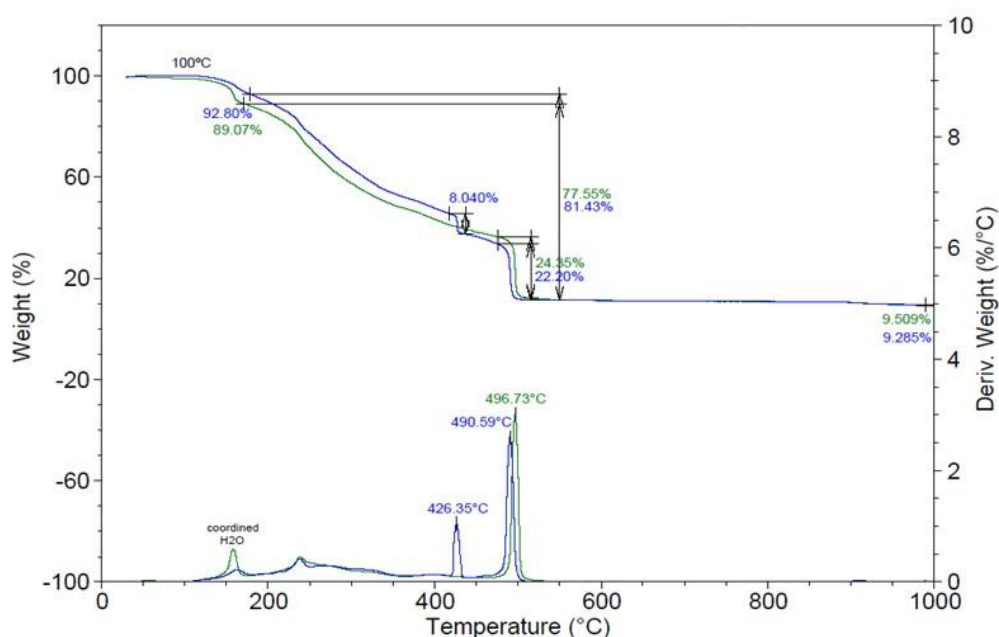


Fig. S14. Thermogravimetric analysis (TGA) thermograms of recovered fragments from run-off waters during UV + rain aging of neat polyamide (PA) (green) and PA–nanosilica composite (blue). The lower thermograms are the derivative TGA curves, showing peak temperatures of several thermal degradation processes. The analysis was carried out in air.

Table S2. Summary of thermogravimetric analysis results for fragments recovered from run-off waters during UV + rain aging

Organic material (mass loss 160–500 °C)	Inorganic material (mass loss 500–1000 °C)	Inorganic and oxidised organic material ash	
Neat polyamide (PA)	87.1 ± 0.7 %	2.2 ± 0.2 %	10.7 ± 0.8%
PA nanosilica	87.8 ± 0.7 %	2.2 ± 0.3 %	10.0 ± 0.4 %