Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Release from nanomaterials during their use phase: Combined mechanical and chemical stresses applied to simple and to multi-filler nanocomposites mimicking wear of nano-reinforced tires

Wendel Wohlleben[1], Jessica Meyer[2,4], Julie Muller[3], Philipp Müller[1], Klaus Vilsmeier[1], Burkard Stahlmecke[2], Thomas A.J. Kuhlbusch[2]

[1]BASF SE, Dept. Material Physics, 67056 Ludwigshafen, Germany
[2]Institute for Energy and Environmental Technology, Air Quality & Sustainable Nanotechnology Unit, Bliersheimer Strasse 58-60, 47229 Duisburg, Germany
[3]Nanocyl, Rue de l'Essor 4, 5060 Sambreville, Belgium
[4]present address: Bundesanstalt für Arbeitsschutz und Arbeitsmedizin (BAuA), 44149 Dortmund, Germany

Corresponding authors:
Wendel Wohlleben, Email: wendel.wohlleben@basf.com
Thomas Kuhlbusch, Email: tky@iuta.de

Supporting online information

Polyurethane elastomer family

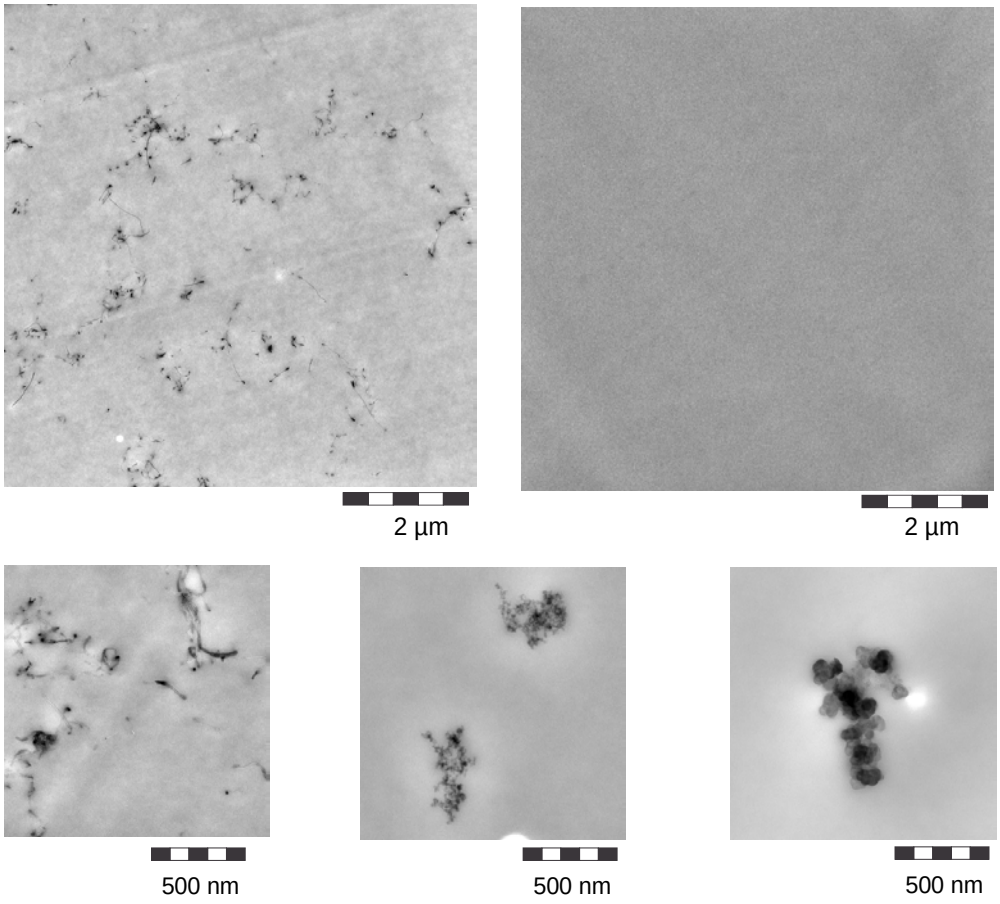


Figure SI_1 TEM cross-sections of PU materials. A) PU_CNT with larger field-of-view to reflect the degree of dispersion; b) PU reference; c) PU_CNT at higher magnification; d) PU_SiO2; e) PU_CB.

Table SI_1 assessment of the release of fragments from aged PU surfaces after UV+rain (2480h ISO 4892, resulting in 535 MJ/m^2), with increasing mechanical shear for sampling. Identical data as plotted in Figure 2, Figure 3, and Figure SI_3

	Sampling shear	AUC measurement	UV-Vis measurement	
		Size-selective evaluation	Absorption evaluation	Turbidity evaluation
		Fragment mass, in mg/m^2	absorption at 400 nm	wavelength at which absorption=1, in nm
		Systematic error ± 10	Systematic error ± 0.01	Systematic error ± 2 nm
Neat PU	24h immersion	7	0.07	318
	24h shaker	51	0.10	338
	1h sonication	71	0.45	373
PU_CB	24h immersion	5	0.08	327
	24h shaker	30	0.18	348
	1h sonication	18	0.24	352
PU_CNT	24h immersion	13	0.05	293
	24h shaker	18	0.07	322
	1h sonication	9	0.09	324
PU_SiO2	24h immersion	33	0.07	326
	24h shaker	149	0.12	345
	1h sonication	106	0.48	378

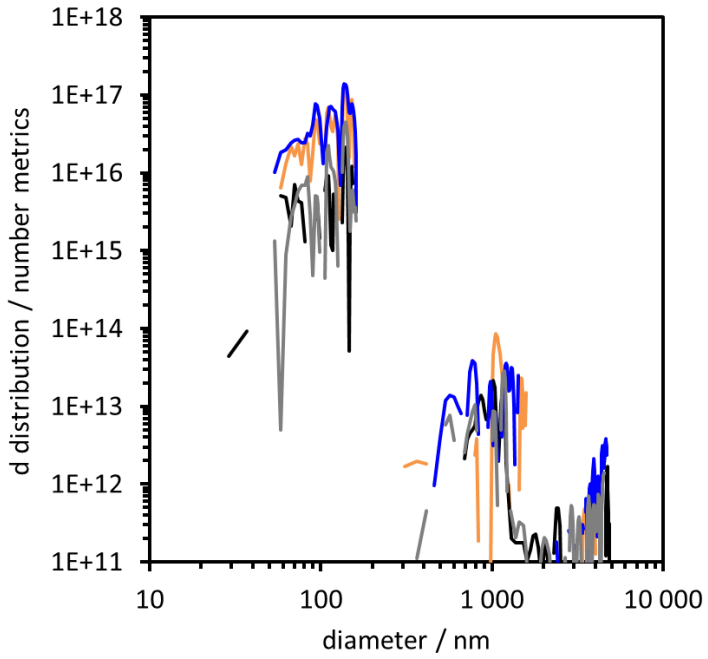


Figure SI_2 Number metrics representation of the full size distributions of fragments sampled by immersion and sonication from the four PU materials after UV aging (with rain) for 535 MJ/m^2. Measured by AUC, converted from mass metrics (Fig 8a) to number metrics. Neat TPU (orange); TPU_CNT (black); TPU_CB (grey); TPU_SiO2 (blue);

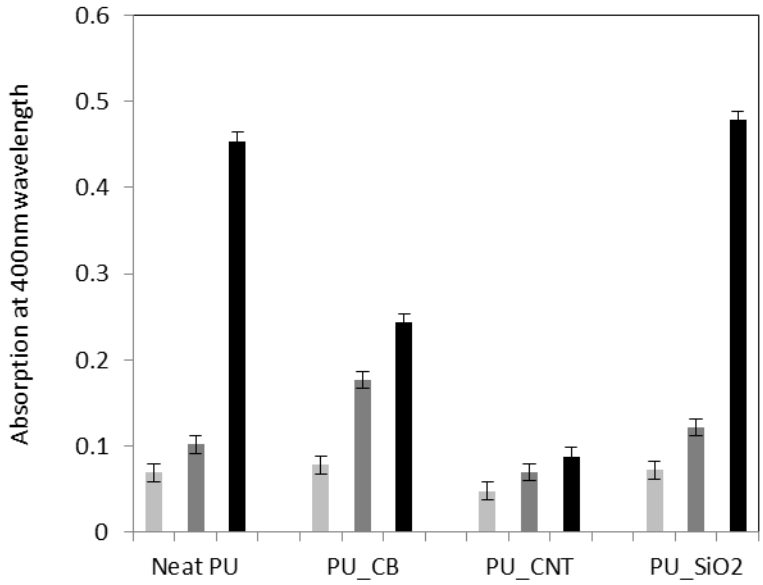


Figure SI_3 Spectroscopic analysis of increasing shear during sampling. 24h immersion (light grey), 24h shaker (dark grey), 1h sonication bath (black).

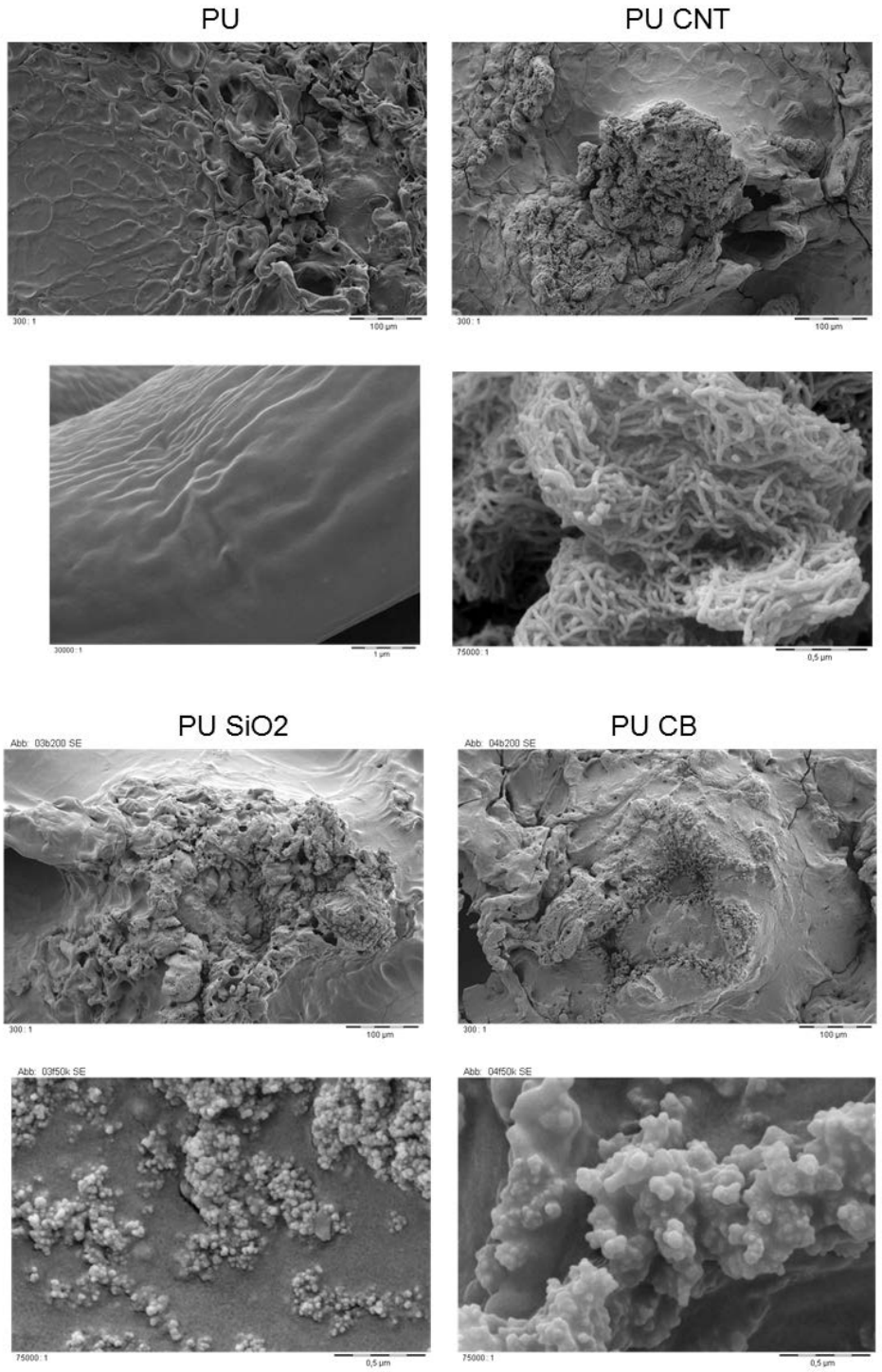


Figure SI_4 Surface structure of PU and PU nanocomposites after UV and rain aging for 672h, by SEM.

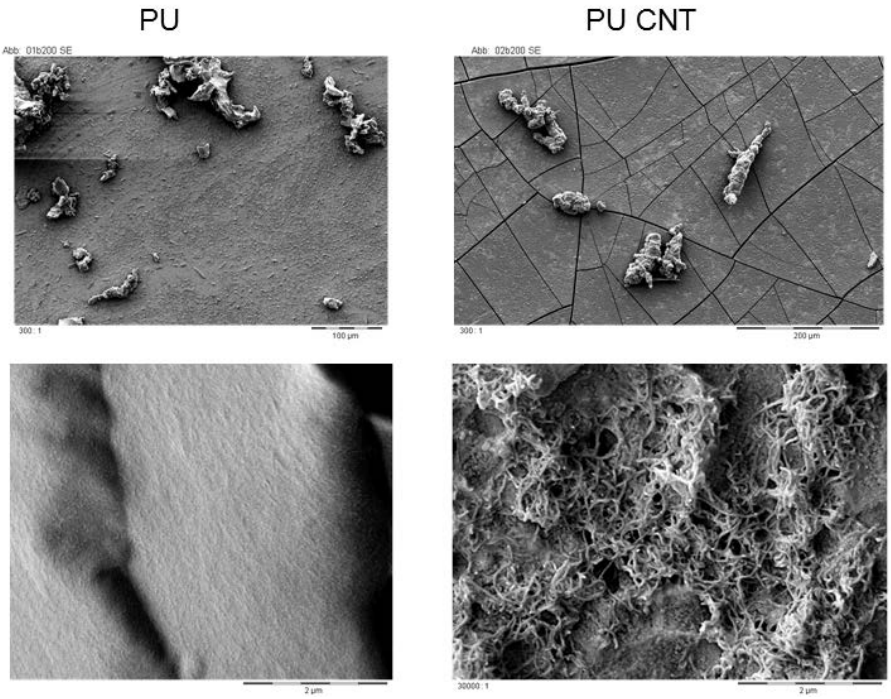


Figure SI_5 Surface structure of PU and PU nanocomposites after UV (no rain) aging for 672h, by SEM.

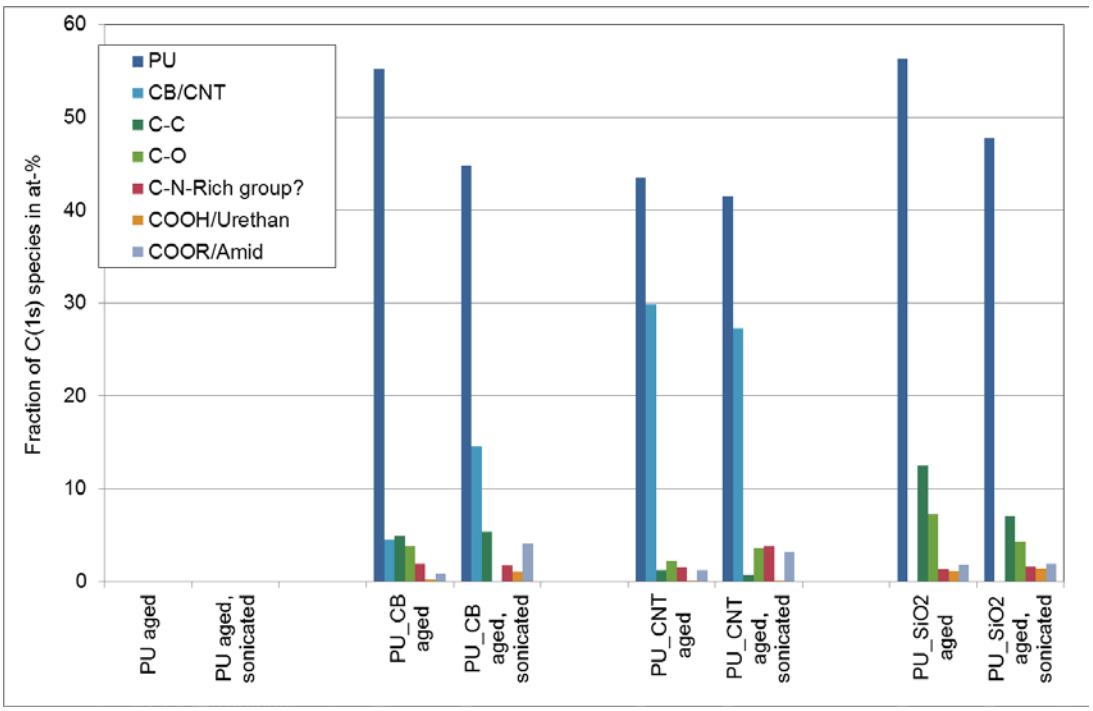


Figure SI_6 Analysis of the specimen surface after aging, and after sonication sampling: C(1s) line fit results, using a non-aged neat PU as reference (dark blue), and separate positive control measurements of CB and CNT (light blue).

Highly filled natural rubber

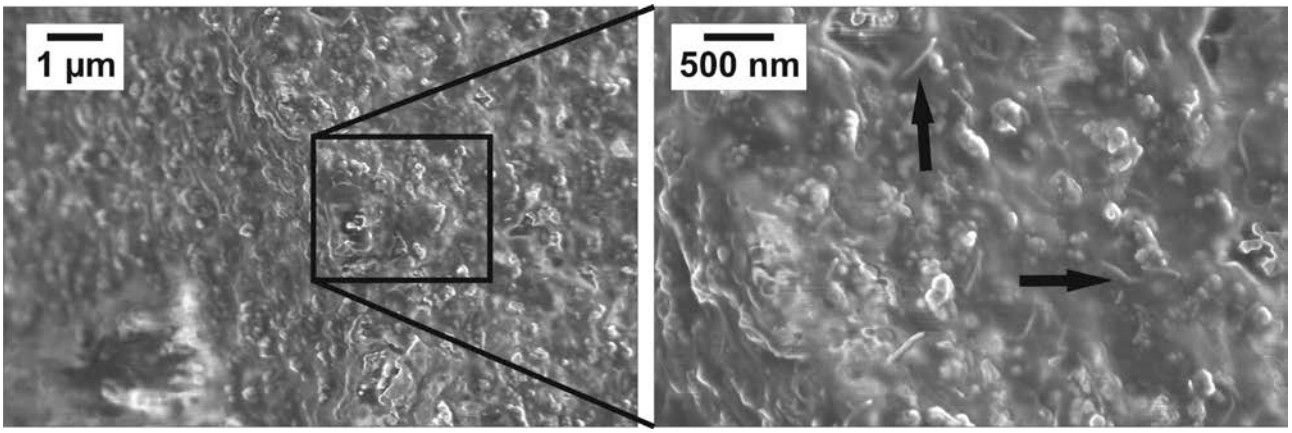


Figure SI_7: SEM images in two different magnifications of as-prepared natural rubber + CB + CNT. The specimen was sliced out of the bulk sample and prepared on a SEM stub. Both the CB (cauliflower like structures) as well as the CNT (long tube-like structures) can be identified. The arrows point to CNT embedded in the sample.

(more on following pages →)

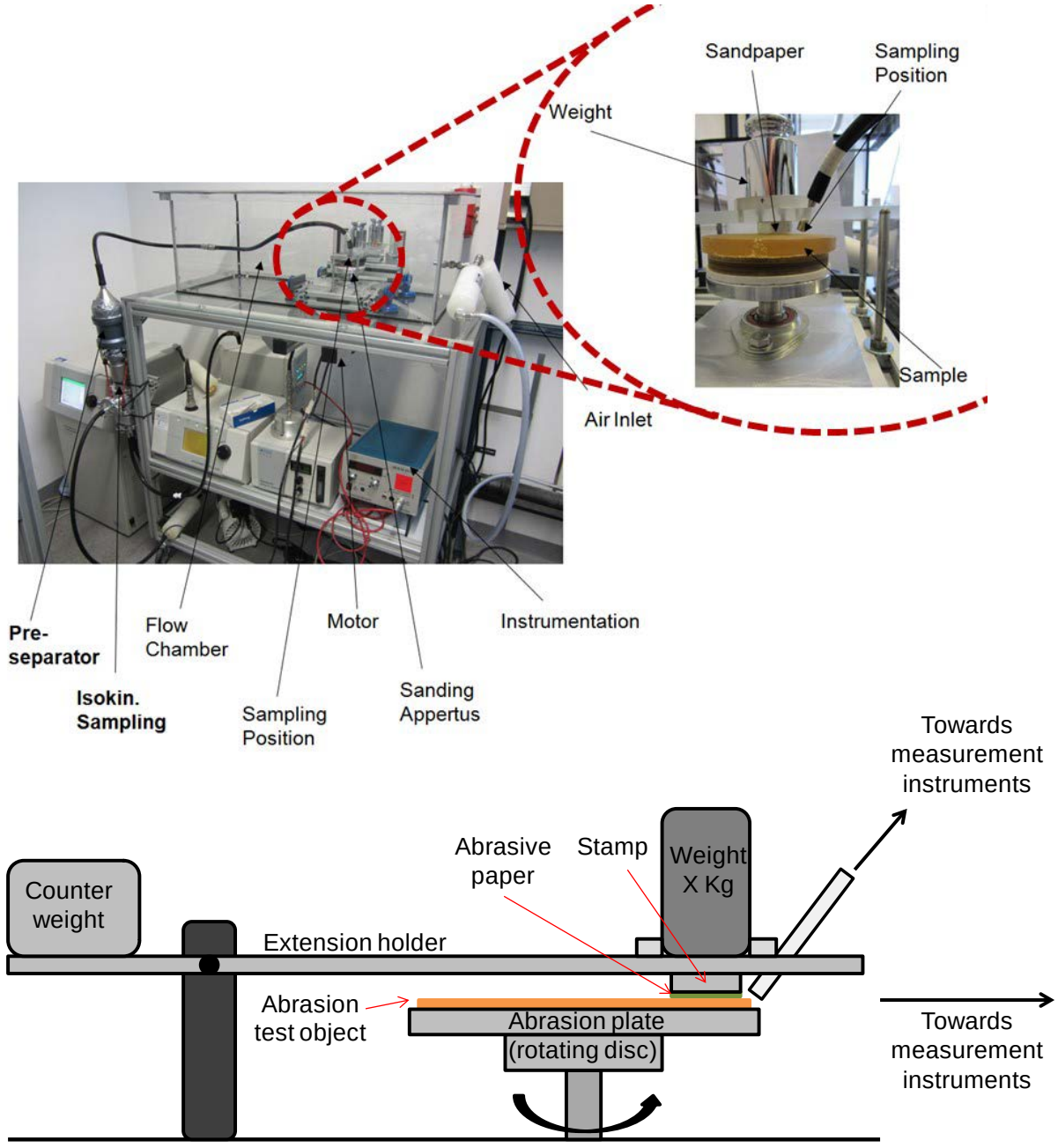


Figure SI_8: Sanding test rig in the IUTA laboratory for NR, NR+CB, NR+CB+CNT samples. Sanding was conducted while this set-up was in a particle-free enclosure.

a) b) c)

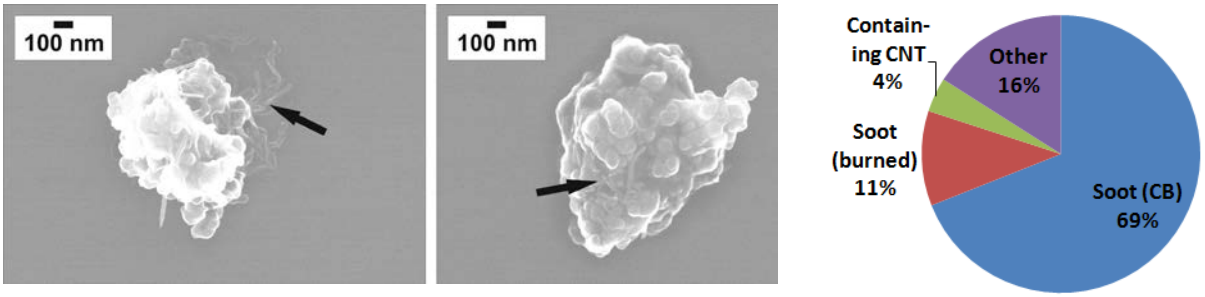
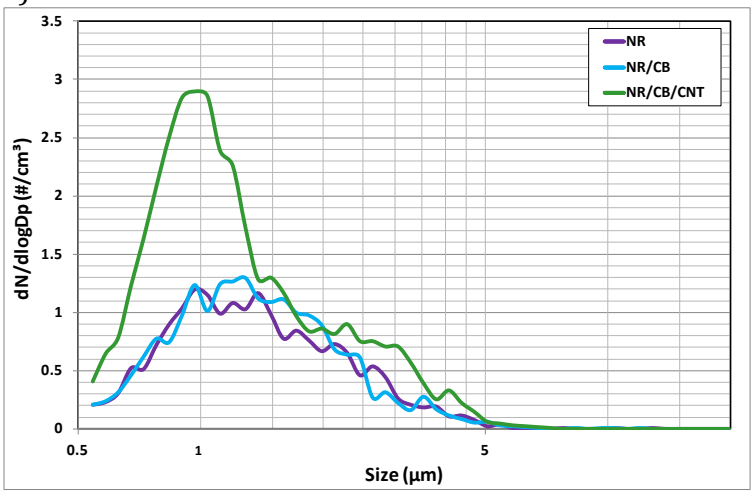


Figure SI_9: Analysis of airborne fragments from sanding of NR_CB_CNT, sampled by NAS. On the SEM scans, the arrows point a) to CNT protruding from a released fragment, b) to CNT still embedded within a released fragment. c) Attribution of nanostructures to specific nanomaterials as observed on 100 particles by manual evaluation of SEM and EDX scans. Soot (CB) refers to agglomerates consisting of the engineered carbon black primary particles already present within the rubber sample. They are usually composed of compact agglomerates with relatively big primary particle sizes. Soot (burned) denotes small soot particles presumably formed during the abrasion process by the locally produced heat. These particles show loose dendritic structures with relatively smaller primary particle sizes.

a)



b)

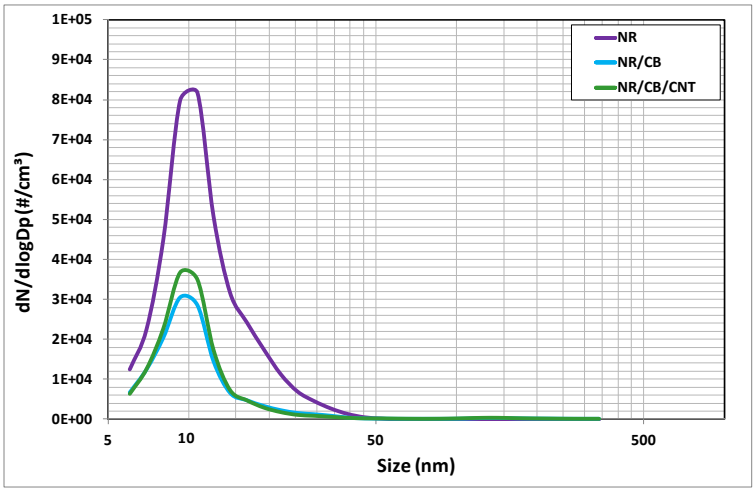


Figure SI_10 Aerosol characterization during sanding. A) APS size distribution as determined in the sanding set-up; b) FMPS size distribution as determined in the sanding set-up.

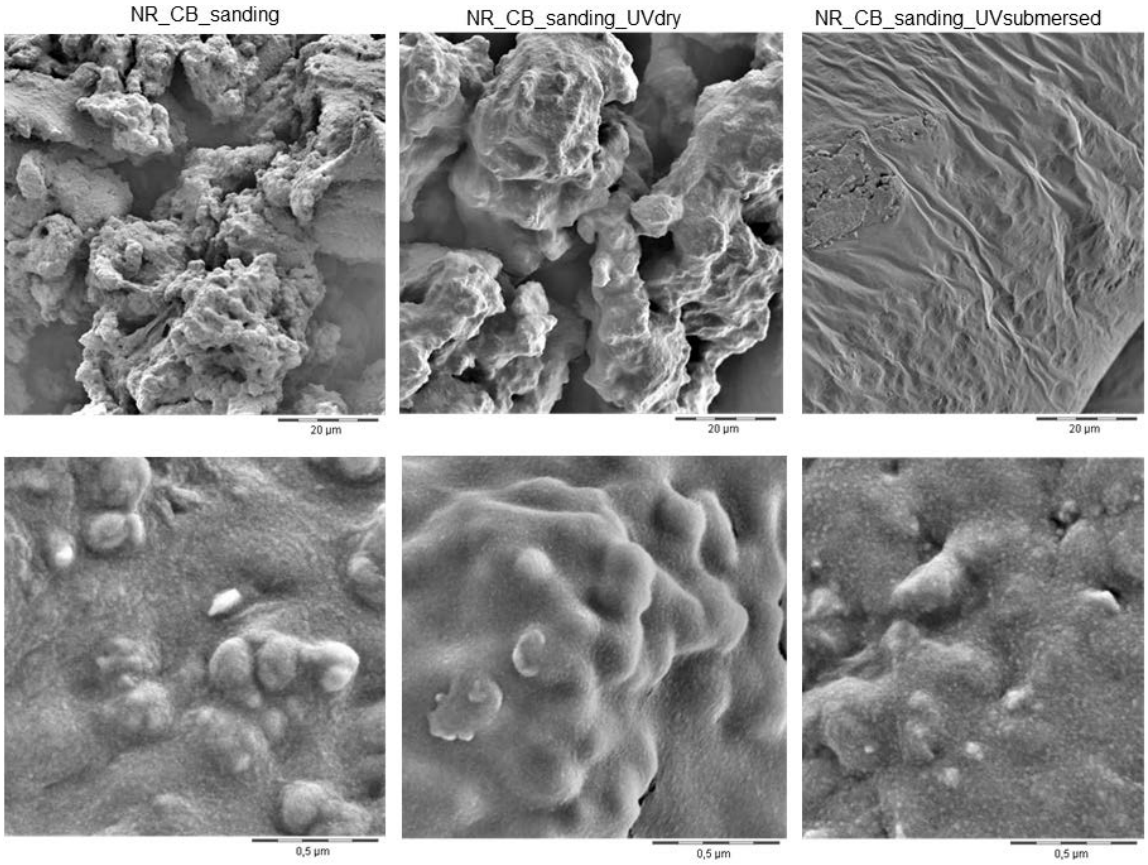


Figure SI_11 Morphology of NR_CB sanding fragments retrieved after immersion in M4 medium, in two magnifications, for the non-aged material, aged as dry powder, aged during submersion in M4 medium.

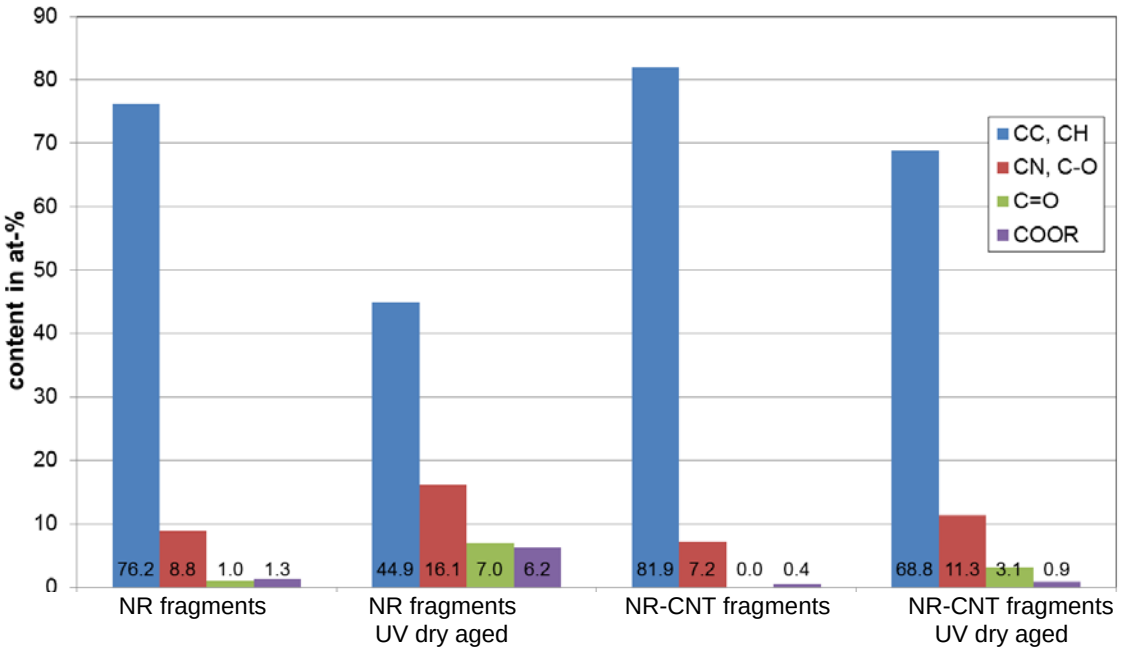


Figure SI_12 Surface chemistry as determined by XPS photoelectron spectra with C(1s) line fit, comparing the sanding fragments before and after aging (UV 720h dry).

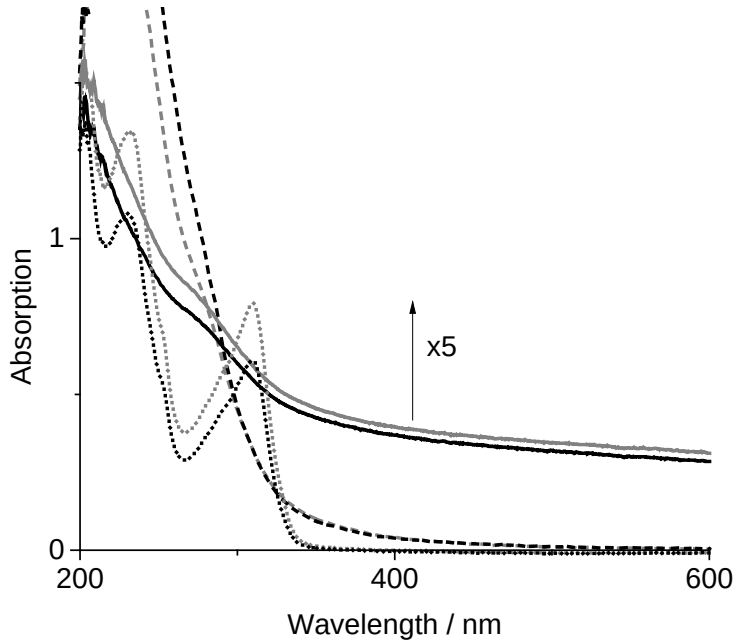


Figure SI_13 Absorption of suspensions in M4 medium: NR_CB (grey) and NR_CB_CNT (black). Sanding fragments (solid lines); Sanding fragments aged by UV light in M4 medium (dashed lines); Sanding Fragments aged dry by UV light, then suspended (dotted lines). All suspensions prepared at 10 g/L solid content, except the dry-aged materials (dotted lines) whose absorption saturated the detector at 10 g/L so that the data shown was obtained at concentrations reduced to 2 g/L.

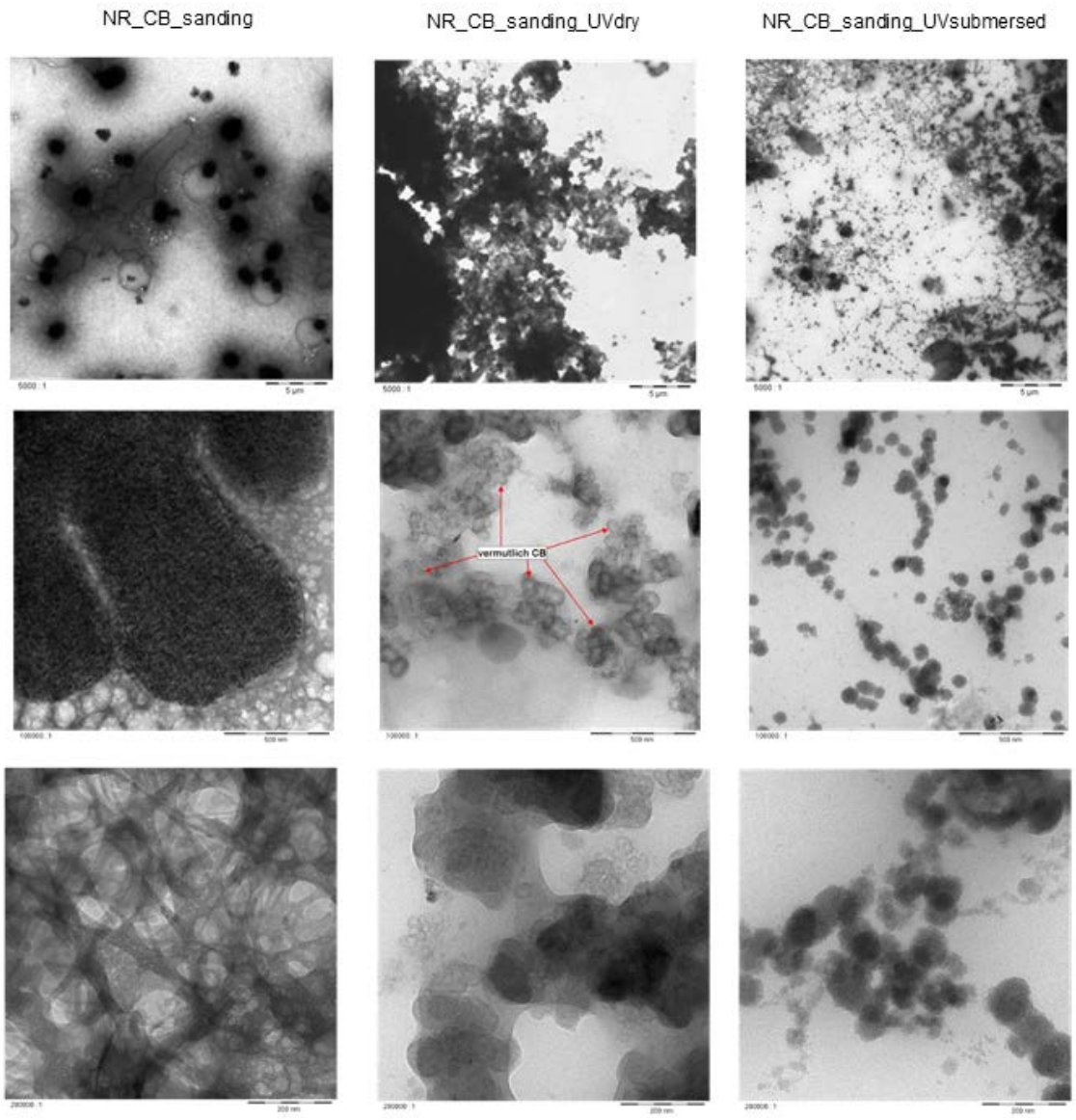


Figure SI_14 Morphology of fragments released from NR_CB sanding fragments after immersion in M4 medium and filtration with 5µm to remove the original sanding fragments. TEM scans in three magnifications (scale bars from top to bottom: 5µm, 500nm, 200nm), for the non-aged material, aged as dry powder, aged during submersion in M4 medium.