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

Supplemental Information

Fragmentation and release of pristine and functionalized carbon nanotubes from epoxy-nanocomposite during accelerated weathering

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Making of Epoxy-MWCNT composite

Epoxies are made of a polymer formed by reaction of a hardening agent (EpiCure) and a prepolymer (EPON 862). The composite was made of Epon 862 (bisphenol F epoxy) and the curing agent EpiCure W that were provided by Miller-Stephenson Chemical Company, Figure S1 shows the molecular structures of these chemicals. Pyrrole (C_4H_5N, ≥98%), ammonium persulfate (APS, $(NH_4)_2S_2O_8$, 98%) and *p*-toluene sulfonic acid (PTSA, $C_7H_8O_3S$, ≥98.5%) were purchased from Sigma-Aldrich.

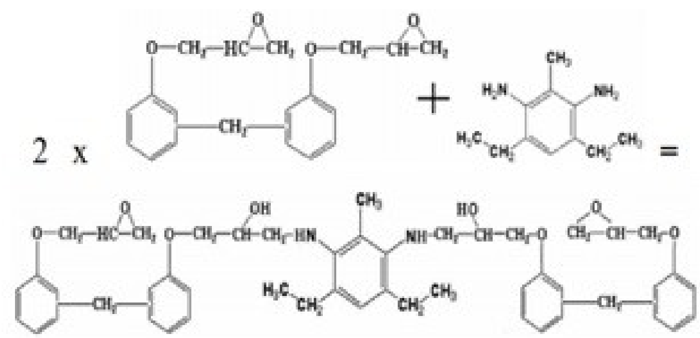


Figure S1. Epoxy is the reaction product of two molecules of EPON 862 and one molecule of the curing agent, and the MWCNT were added in the mix before the thermoset reaction.

Table S1 Polymers and nanocomposites used for the study

Polymer	Additive
Epoxy	None
Epoxy	Pure CNT, 1 wt%
Epoxy	COOH-CNT, 1 wt%
Epoxy	NH_2-CNT, 1 wt%

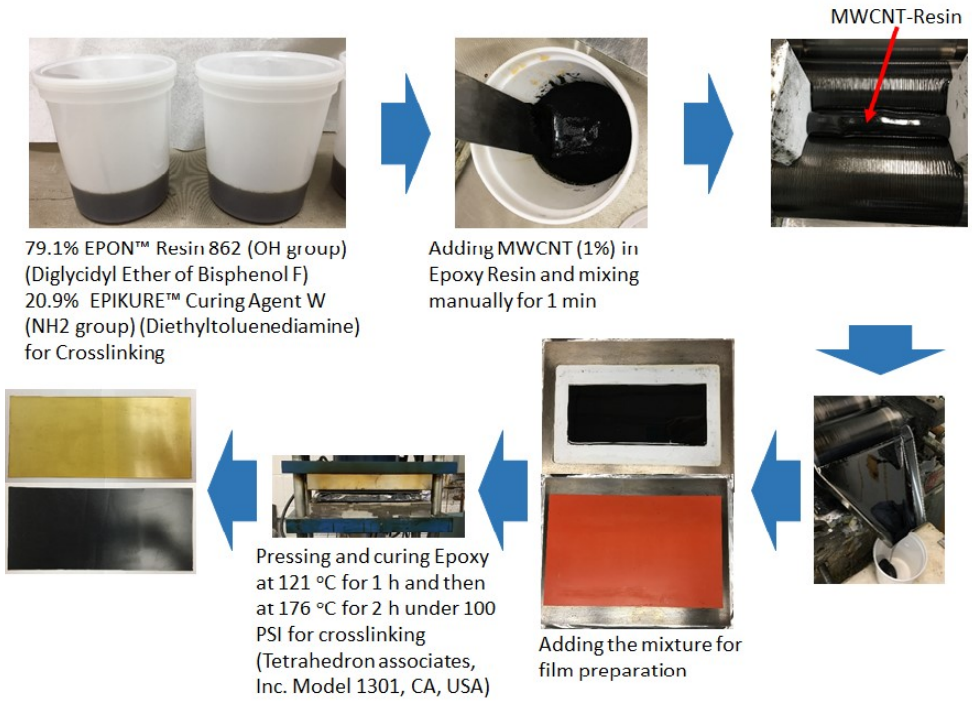
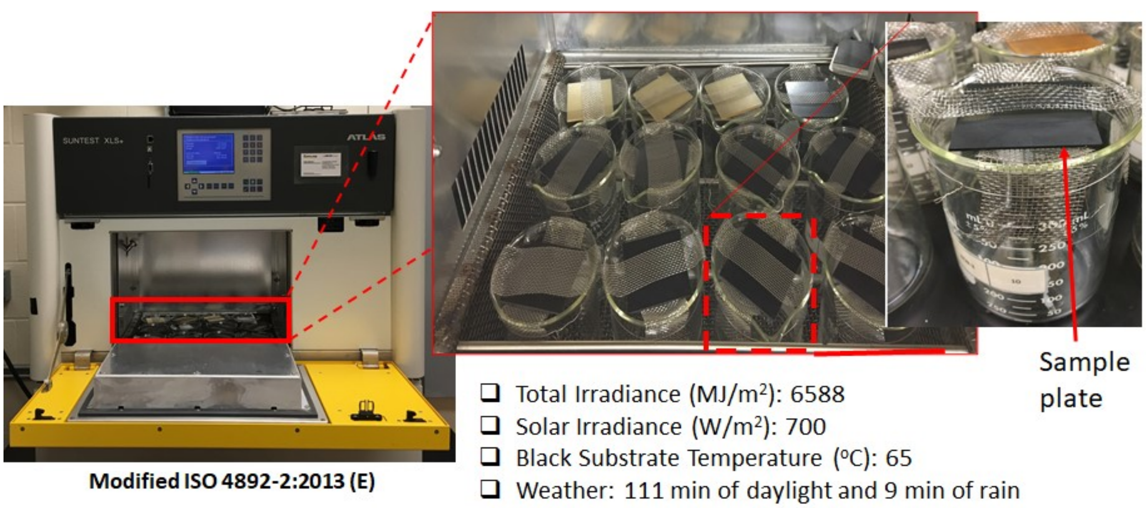


Figure S2. Preparation of Epoxy-MWCNT composites



Sample location

PE-3 months (1)	PE-6 months (2)	PE-12 months (3)	EPC-3 months (4)
ECC-6 months (8)	ECC-3 months (7)	EPC-12 months (6)	EPC-6 months (5)
ECC-12 months (9)	ECN-3 months (10)	ECN-6 months (11)	ECN-12 months (12)

Figure S3. Modified Experimental Setup, Sample positions were rotated daily to ensure even spraying

Figure S4. Gradual discoloration of pure epoxy as the aging progresses. Sample panels degraded and started breaking and crumbled as the materials ages.

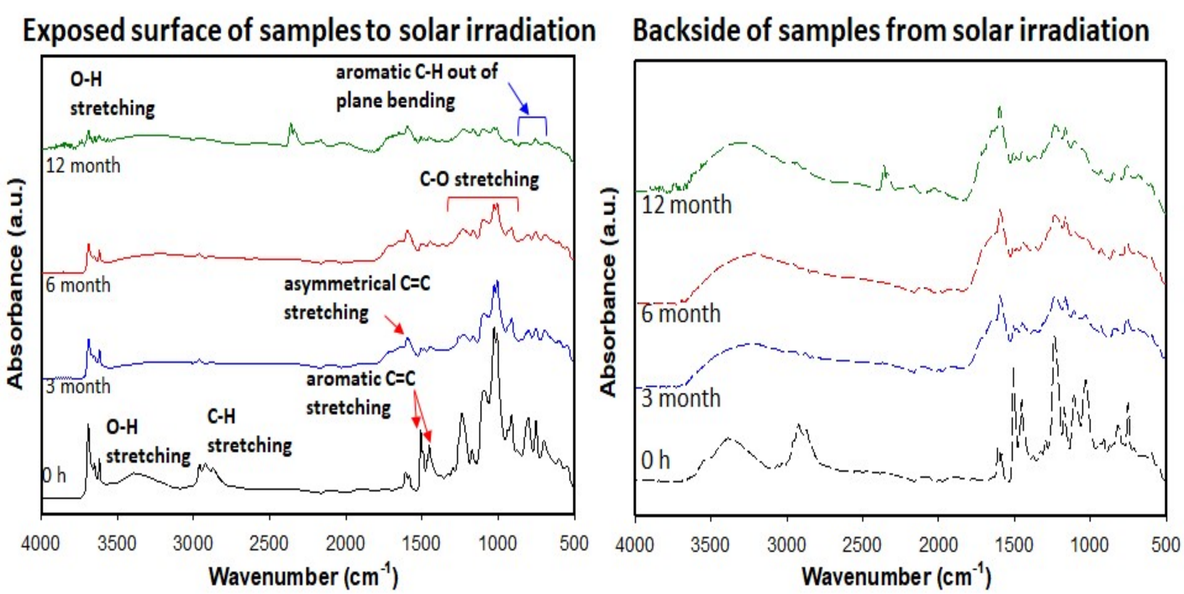


Figure S5. FTIR analysis of surface of aged epoxy-CNT composite plates

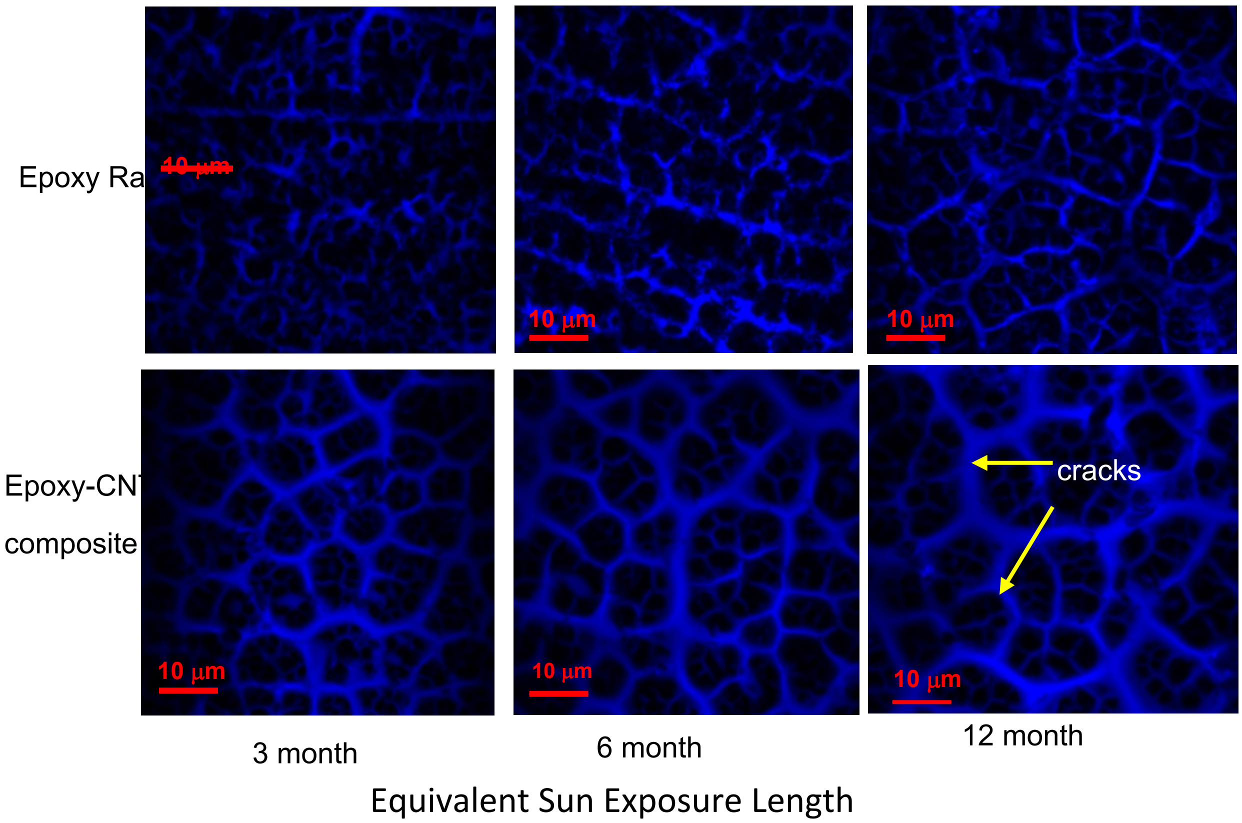


Figure S6. Imaging using Zyglo fluorescent penetrant dye, $\mathbf{l}_{peak}$ = 365 nm, Laser Confocal microscopy, 40X, Cracks widened with extended weathering

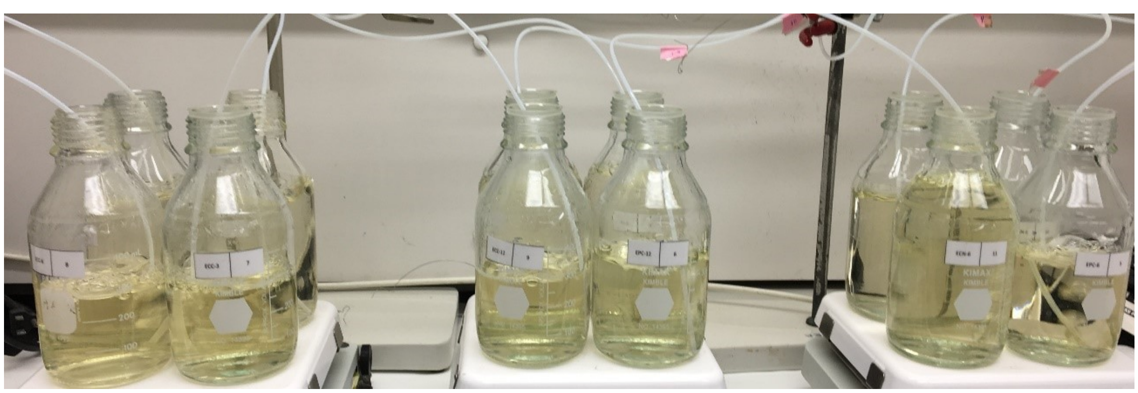


Figure S7. Washwater evaporation and leachate concentration Setup
Water from each flask sample in the SunTest chamber were *collected every day* (avg 200 ml), and *transferred* to bottles, and gradually evaporated by bubbling nitrogen. Water temperature in the bottles was 60-65 ^{o}C. Wash water collected for 12 test days (1500 ml) is reduced to 150 ml, were store in air-tight jars (4 ^{o}C)

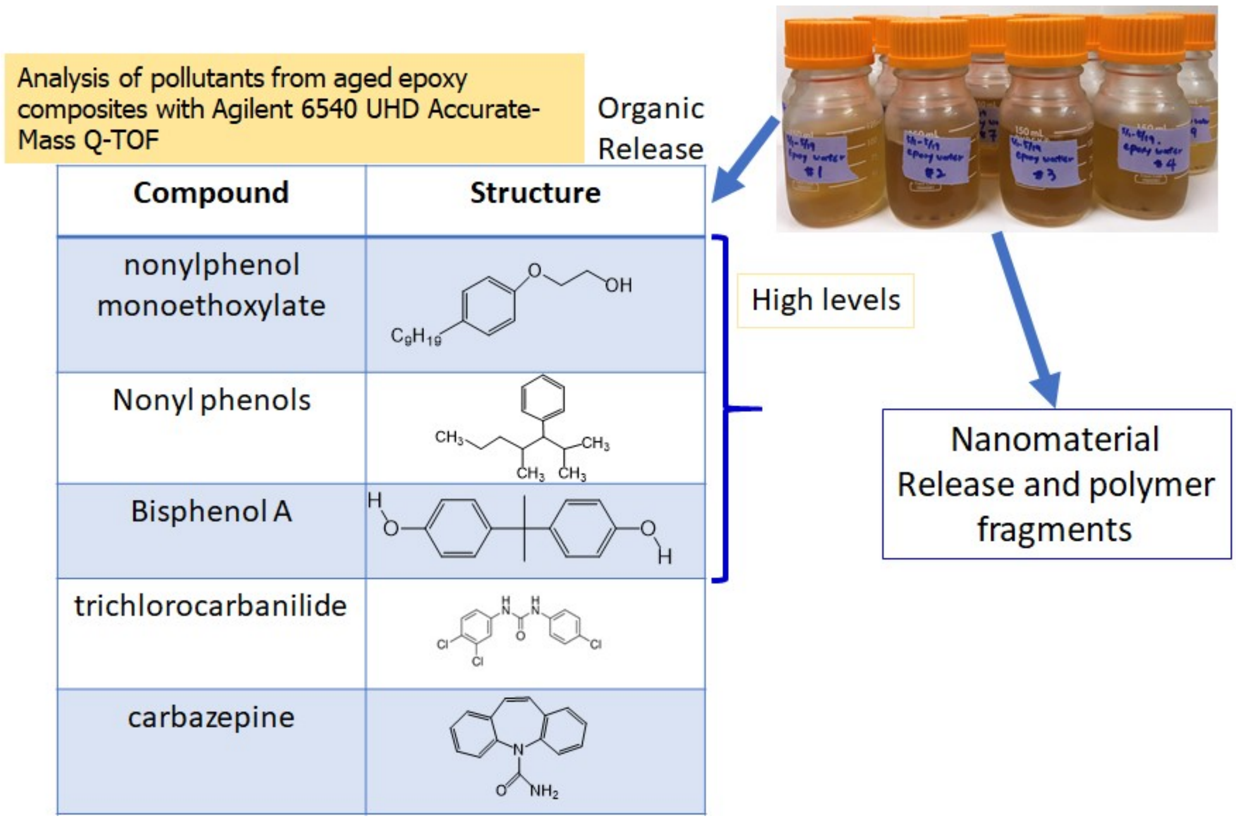


Figure S8. Release of pollutants from aged epoxy composites

Table S2. Raman band shift at the peak bands for the functionalized CNT

	CNT	CNT-COOH	CNT-NH2	CNT	CNT-COOH	CNT-NH2	CNT	CNT-COOH	CNT-NH2
	Fresh MWCNTs			Released NM after 3 months aging			Released NM after 12 months aging		
G peak wave Number (cm^{-1})	1580	1586	1590	1575		1580		1586	
D peak Wave number (cm^{-1})	1351	1359	1359	1348	1339	1362	1359	1356	1362

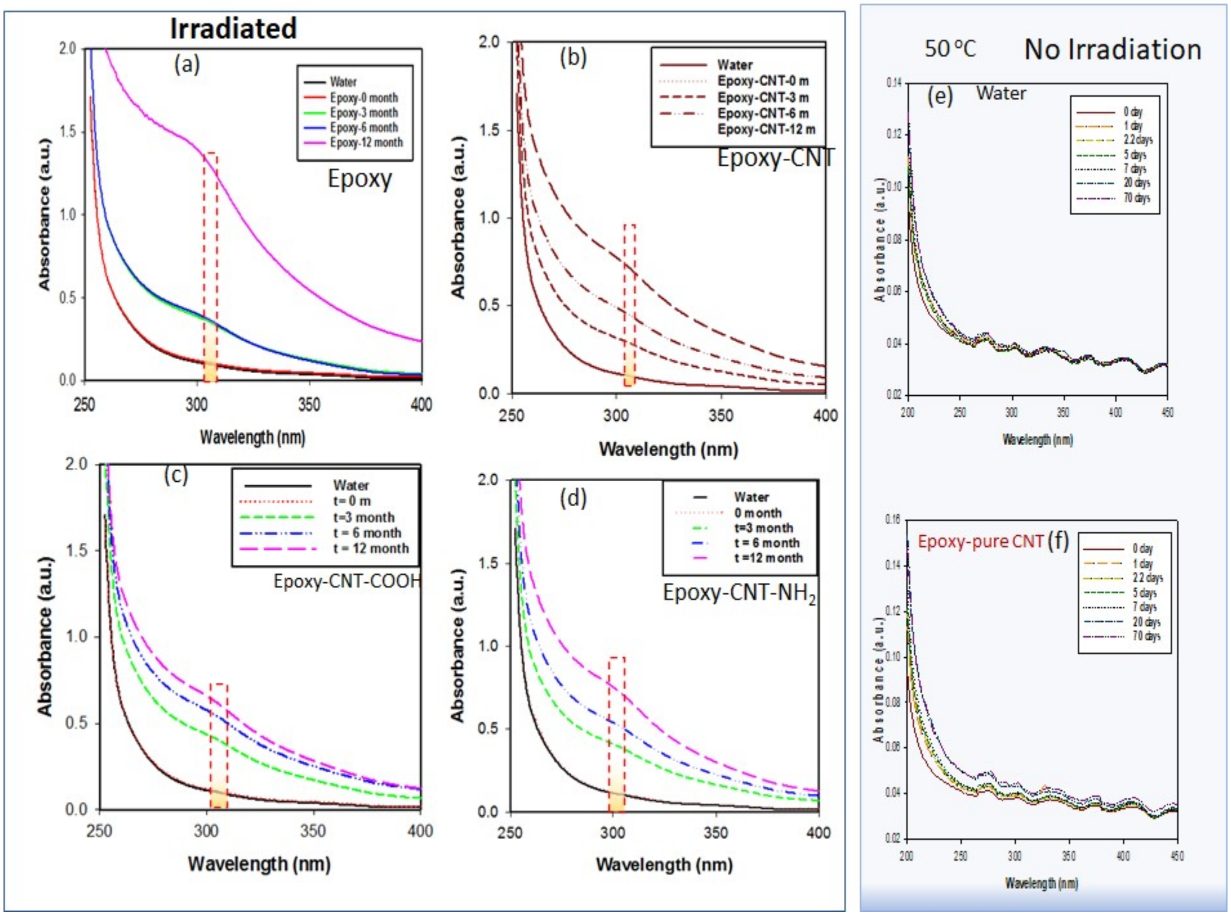


Figure S9. UV-vis spectroscopy leachate and released particles. Samples (a) to (d) are for irradiated sample wash water, and samples (e) and (f) are for non-irradiated sample water.

Dashed box represent UV-vis absorbance of MWCNT [1]

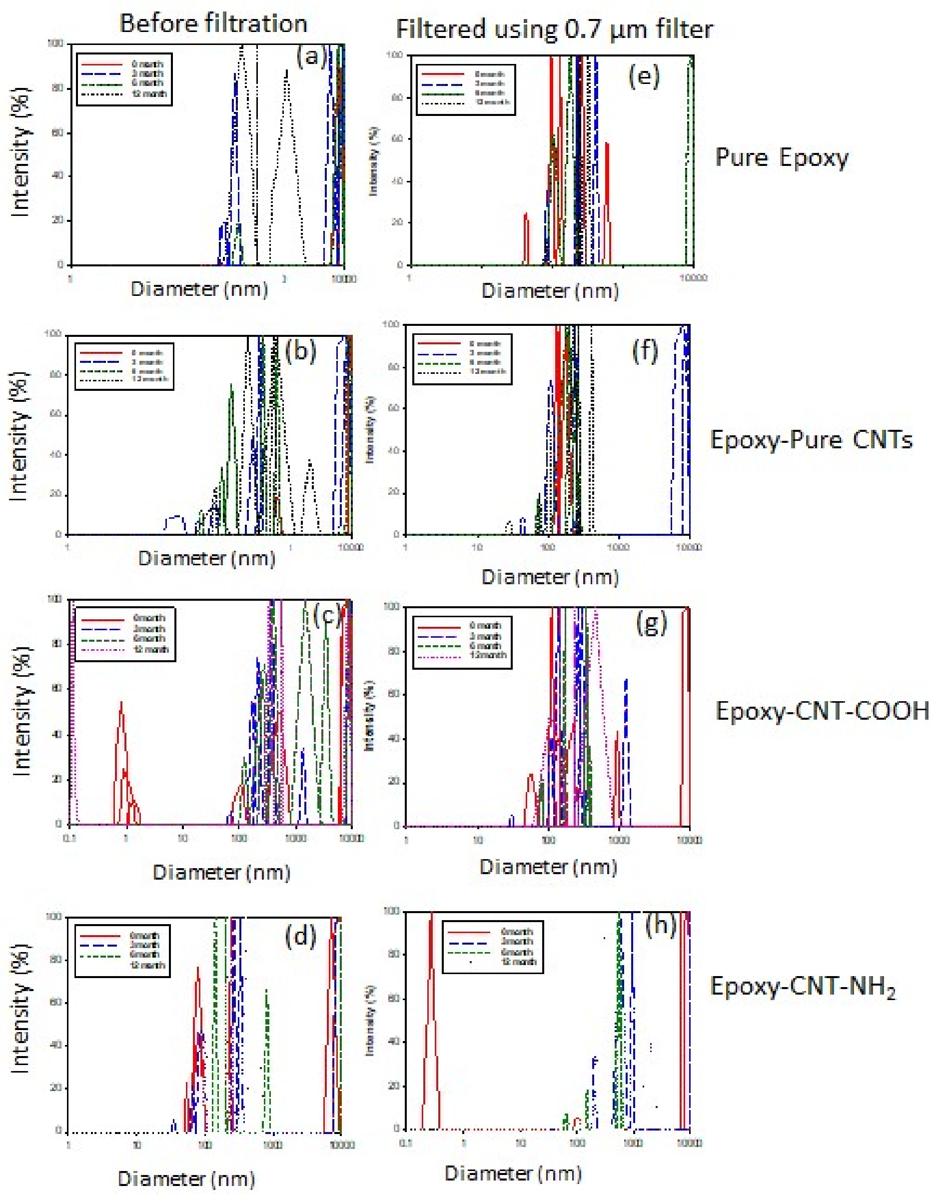


Figure S10. Polydispersed size distribution determined using dynamic light scattering (DLS) of wash water samples containing released fragments from (a) neat epoxy and epoxy composite of (b) CNT, (c) CNT-COOH, (d) CNT-NH_2 collected after 6 months of aging. The right column shows DLS analysis after filtering with 0.7 μm filter.

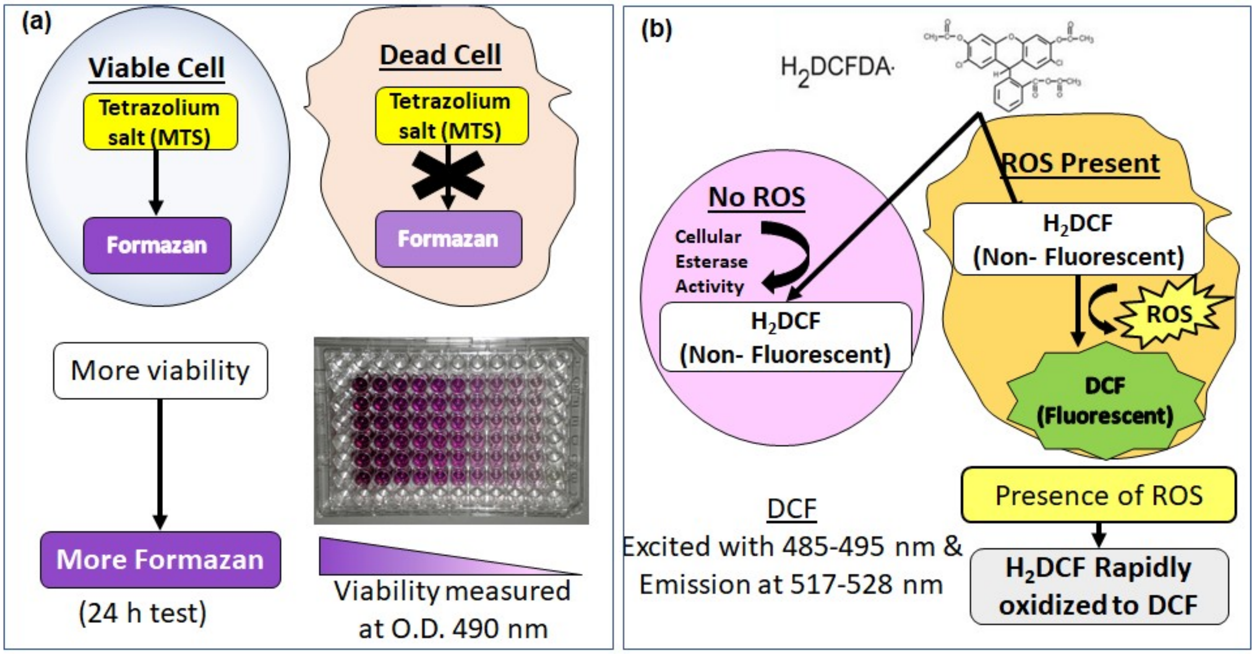


Figure S11. In vitro assessment of Toxicity of wash water from aged epoxy-MWCNT composite Measuring the ability of nanoparticles to cause cell death or damage to basic cellular functions, where (a) Cell Viability & Activity (MTS Assay) and Cell based assays measurements of cell proliferation in response to toxicity of released materials direct cytotoxicity, (b) Oxidative stress measurement via detection of reactive oxygen species Oxidative Stress Measurement via detection of reactive Oxygen Species (DCF Assay) which has in vivo and in vitro toxic effects

References

1. Abdulhameed, A., et al., *Optimization of surfactant concentration in carbon nanotube solutions for dielectrophoretic ceiling assembly and alignment: Implications for transparent electronics.* ACS omega, 2022. **7**(4): p. 3680-3688.