Environmental Aging of Polymer-Nano Composites and Release of Carbon Nanotube

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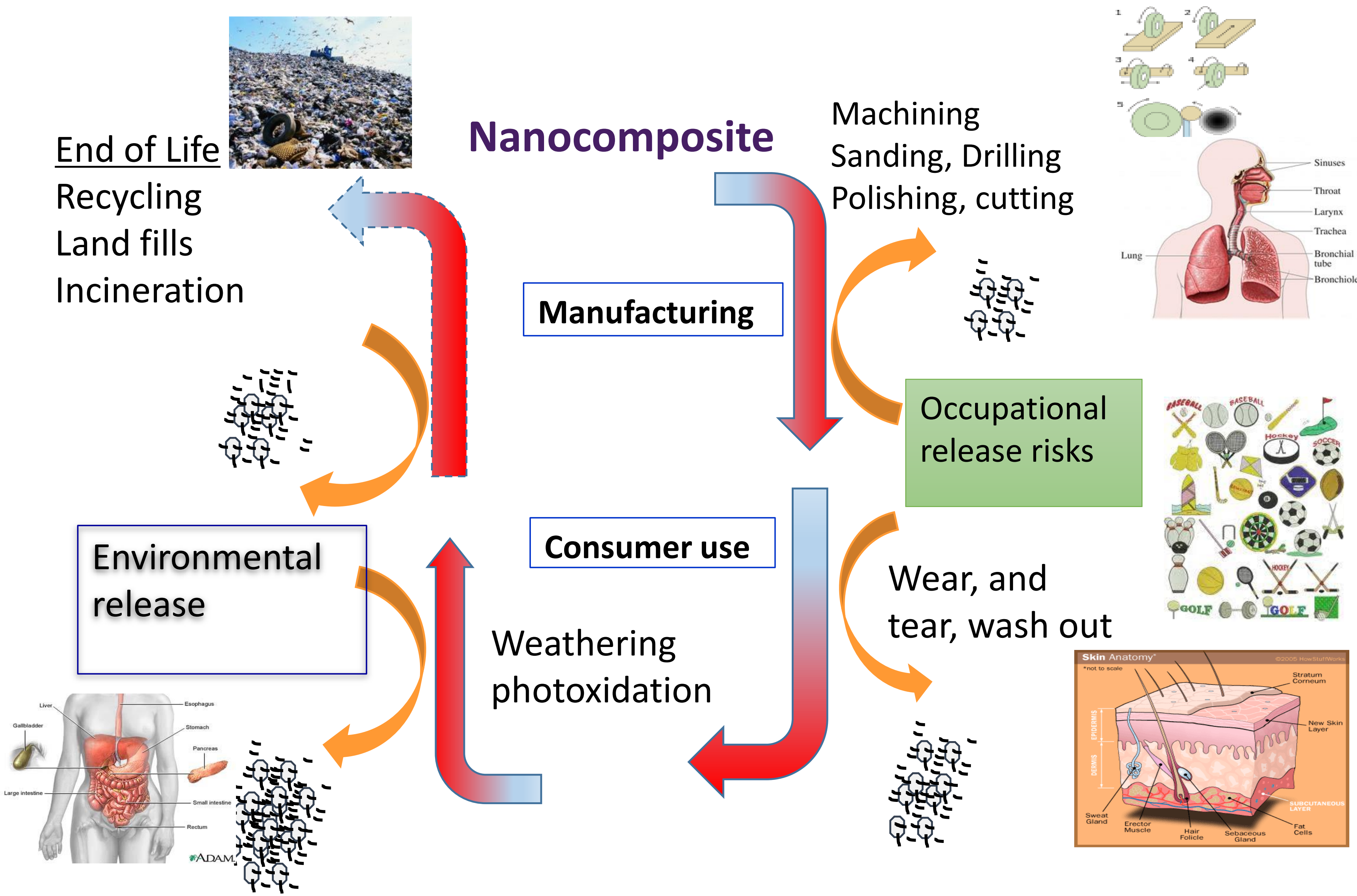
May 15, 2018

Life Cycle Specific Exposure of Nanomaterials

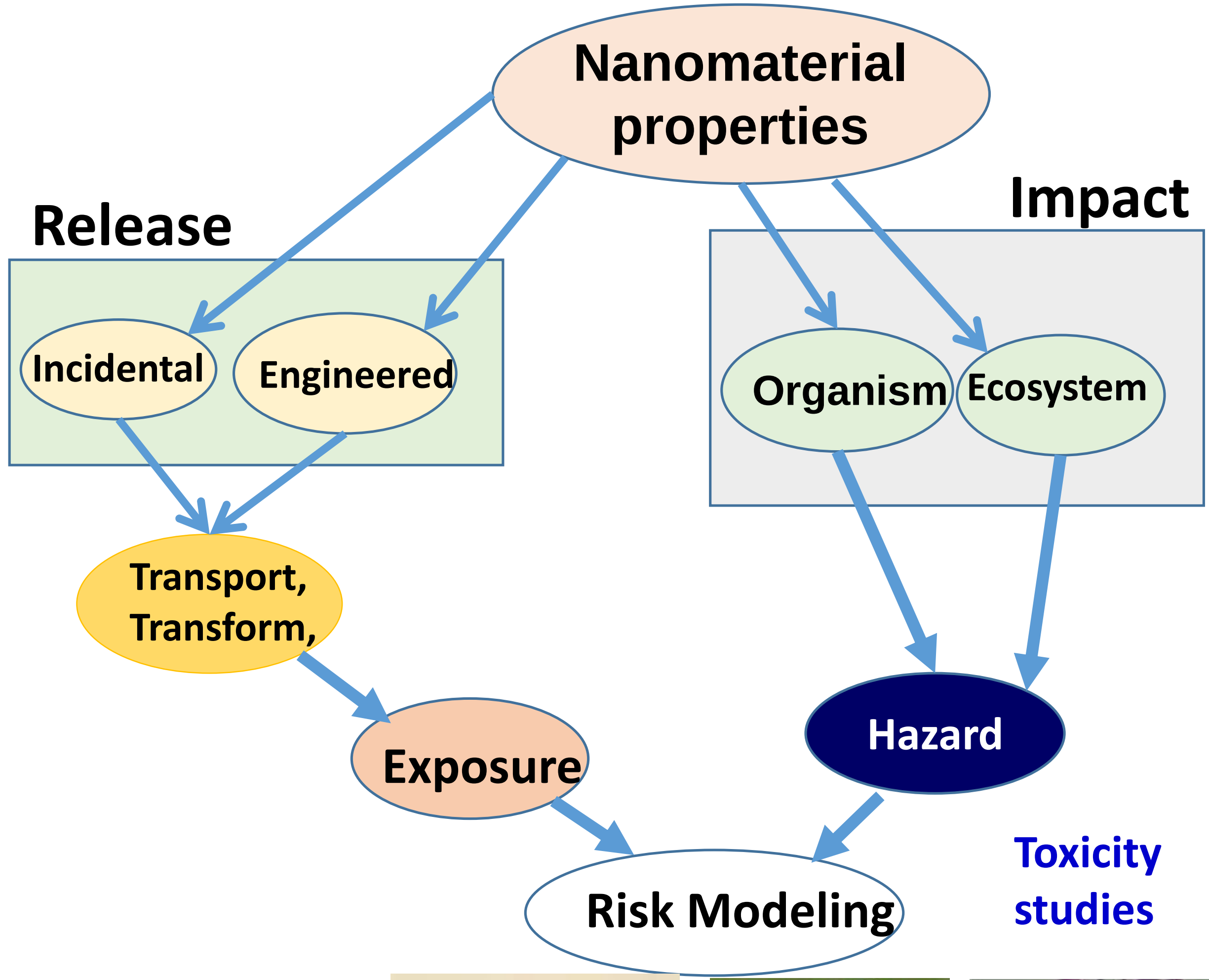


Nanomaterial Implication EPA's Research

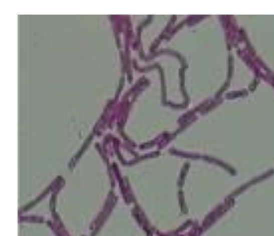
Distribution in soils, water, air
- Transport, transformation and fate
- Reactivity
- Unique challenges?

Impacts on ecosystems and particular species
- Either direct (toxicity)
- Indirect (changes local conditions or prey)

Toxics - Impacts on human health -
- Exposure--Inhalation, ingestion, contact
- Dose-Response
- Bioaccumulation, biotransformation, bioavailability



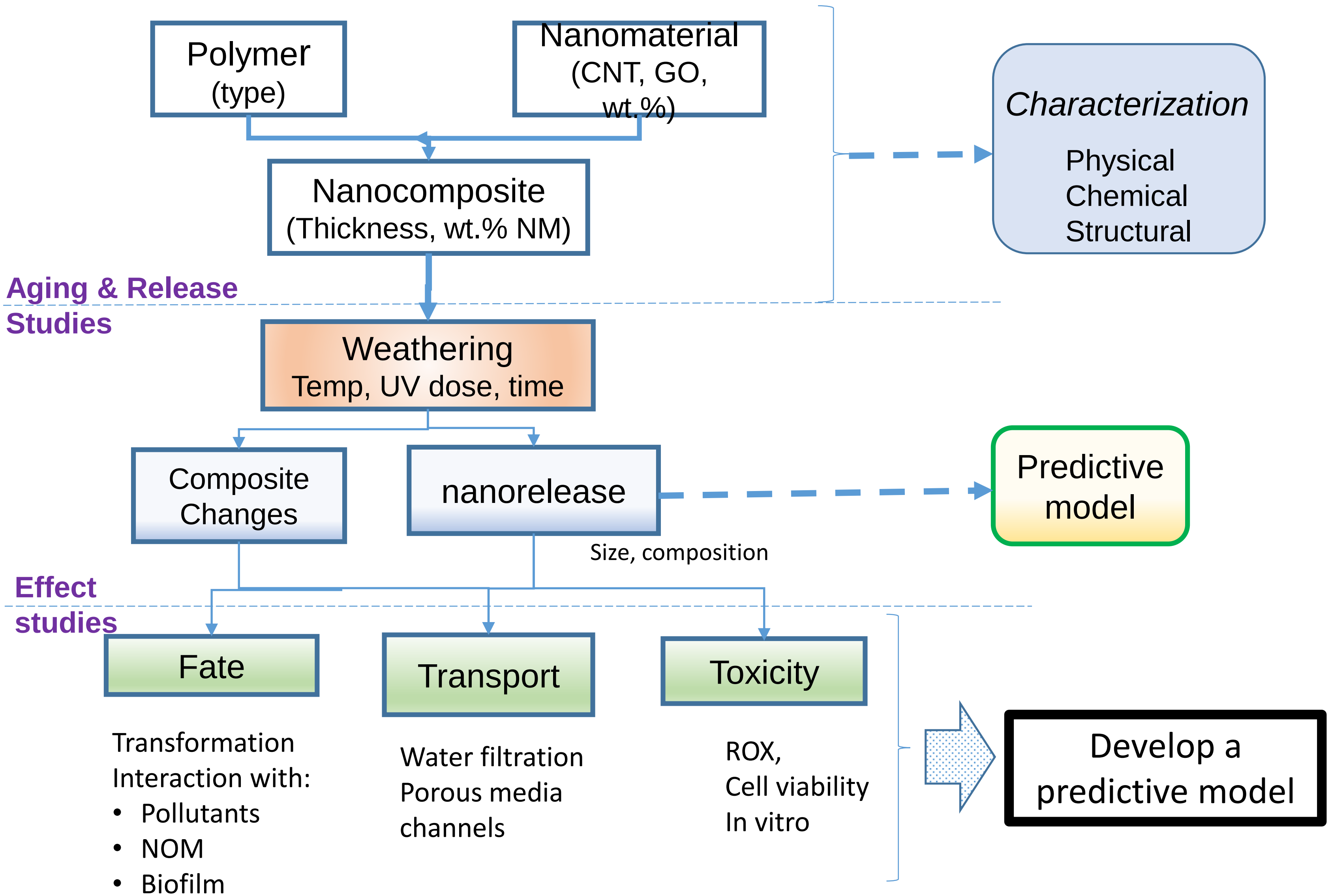
Toxicity studies



Analysis of ENM in different matrices is critical!

Hazard Assessment of NM

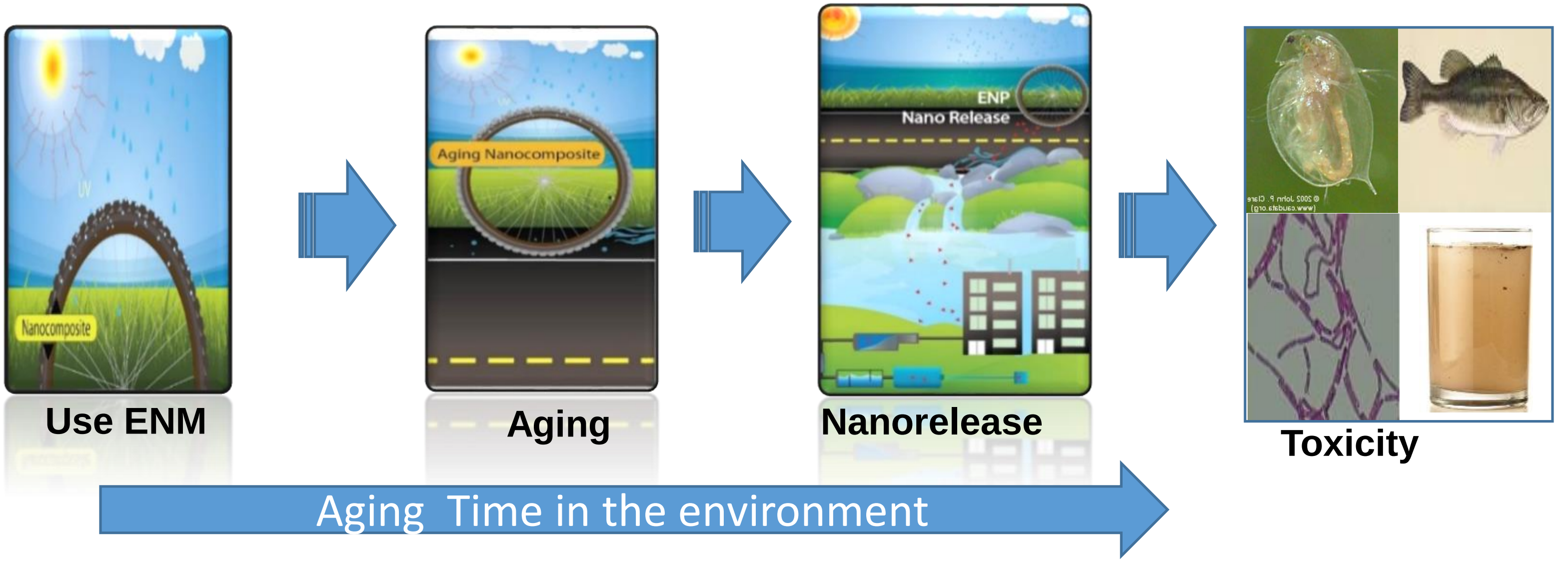
Consumer nanomaterial research

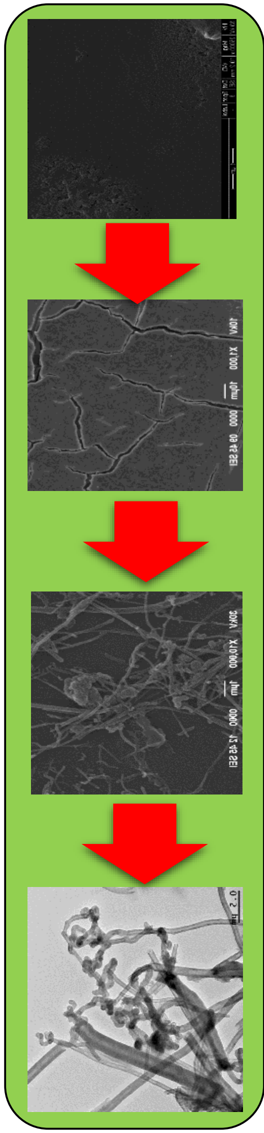


Objectives of weathering study

- To reduce the risk of product failure
- Meet product codes, compliance requirements
- Discover and mitigate failure modes
- Demonstrate durability and performance
- Test to various climates, predict service life
- Improve product or reduce cost
- Assess possible risk to human and the environment

Polymers and nanoparticles in the environment

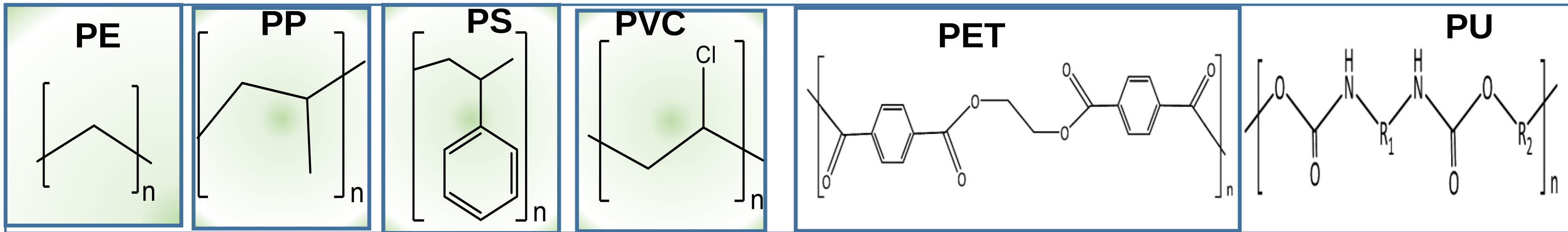




- Persist in the environment ~ 10^3 years
- Release persistent organic pollutants (POP)
- Accumulate POP such as PAHs, PCBs, DDT
- Release chemical additives -

Factors influencing Nanorelease from composites

C-C Backbone	Hetroatoms in Backbone



29.6 18.9 7.1 10.4

NanoFillers

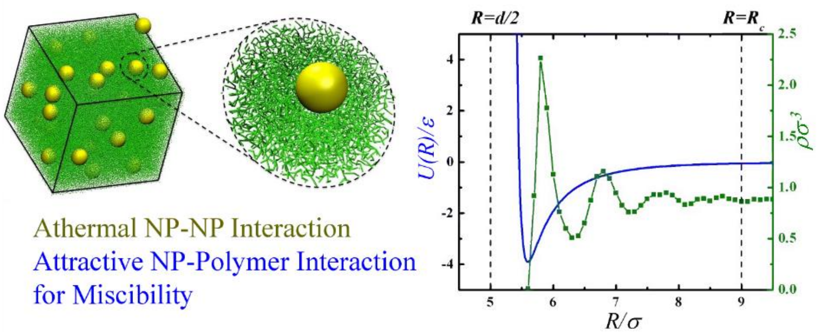
- Metals
- Metal oxides, SiO_2, Fe_2O_3, clay
- Carbon based:
  - CNT, CF, graphene
  - functionalized CNT

stress conditions

Physical Stress
Environmental Stress
→ Weathering

Diffusion of NP in Polymer and Mass transfer for Surface Release

Diffusion of Nanoparticles in Polymers



- Weakly interacting mixtures of nanoparticles (NPs) and ring/linear polymers
- NPs of diameter ***d*** are well dispersed at $\varphi_{NP} \sim 0.1$

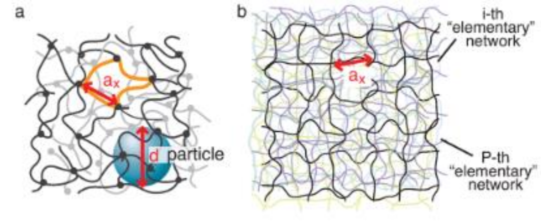
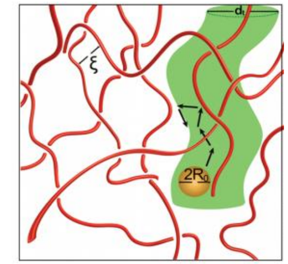
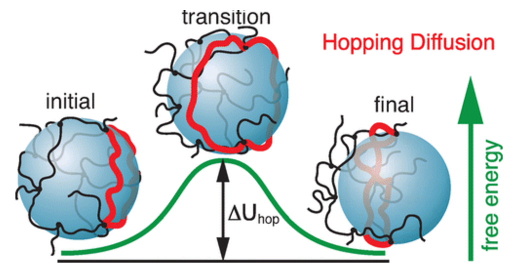
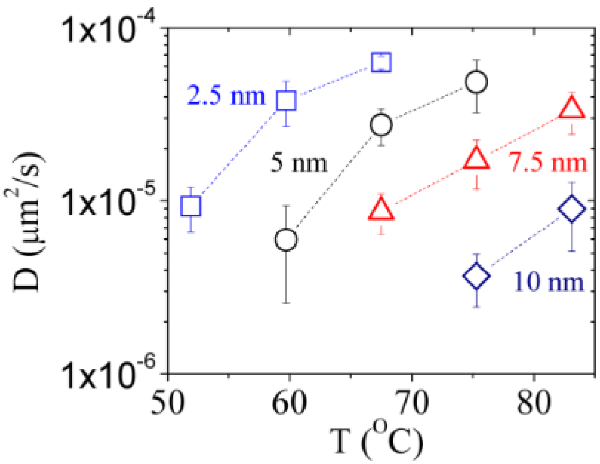


Figure 1. Unentangled polymer network modeled by overlapping "elementary" networks. (a) Schematic visualization of a particle of size





Diffusion → surface release

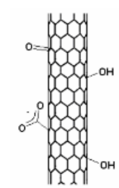


50 – 500 μm

For semi-crystalline polymers below the glass transition temperatures

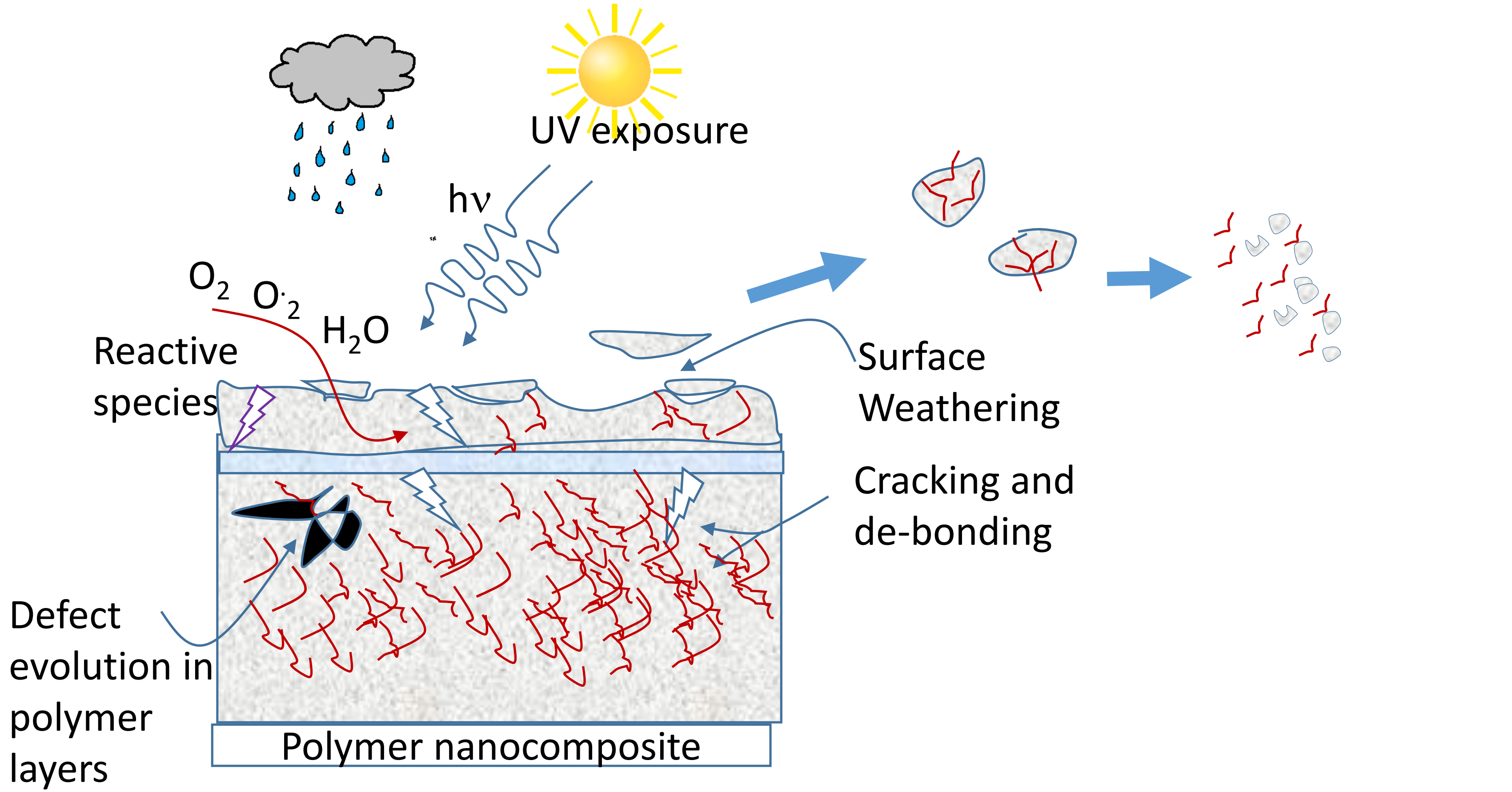
$$t_D \sim \frac{L^2}{D}\text{ , D} - 10^{-5}\ \mu m^2/s$$

$t_D - 1.7 \times 10^5$ h



Grabowski et al., Macromolecules 2014, 47, 7238-7242

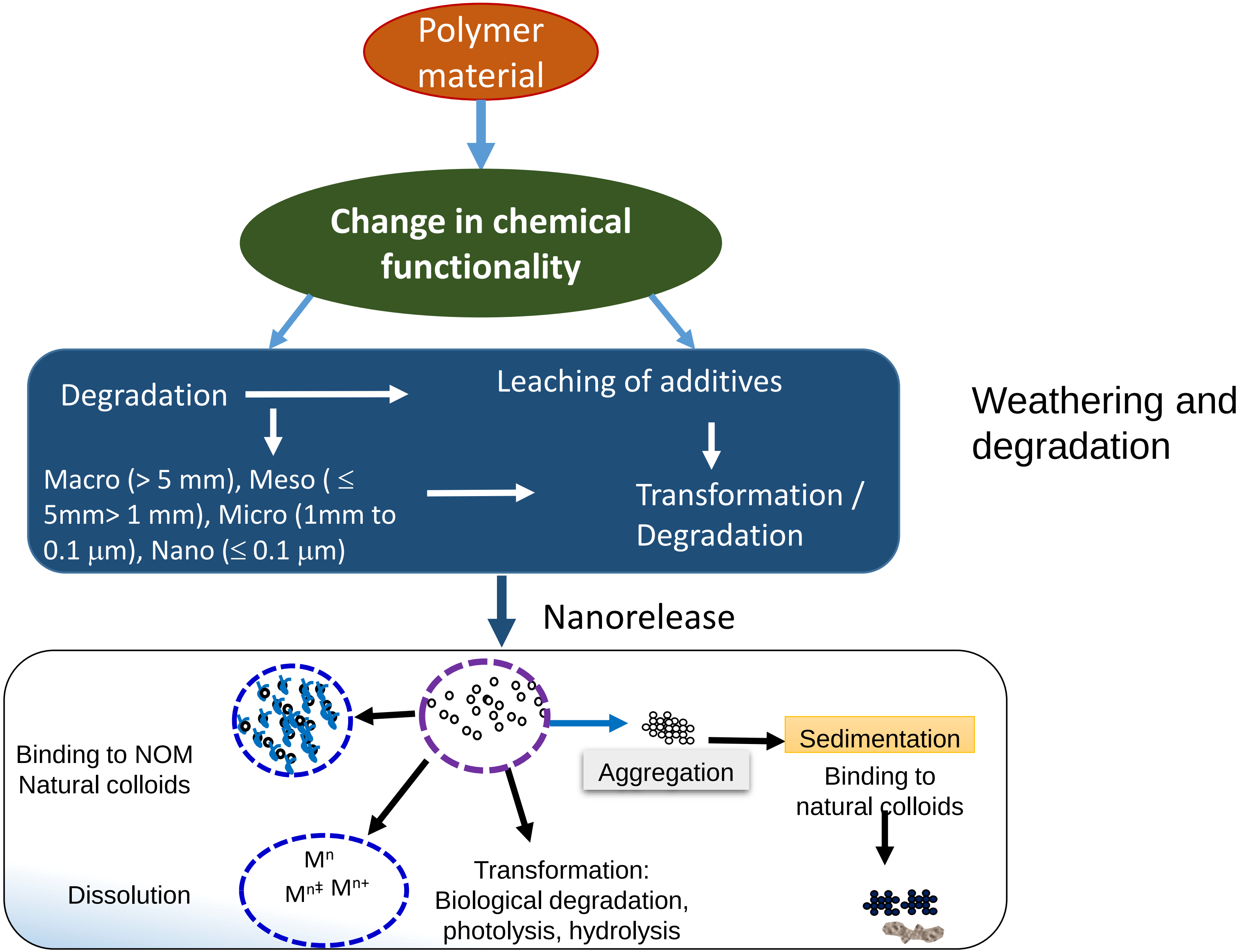
Mechanism of Nanorelease matrix degradation



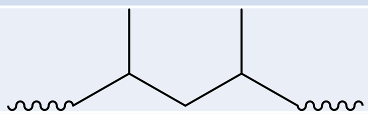
<u>Main mechanism for nanorelease</u>

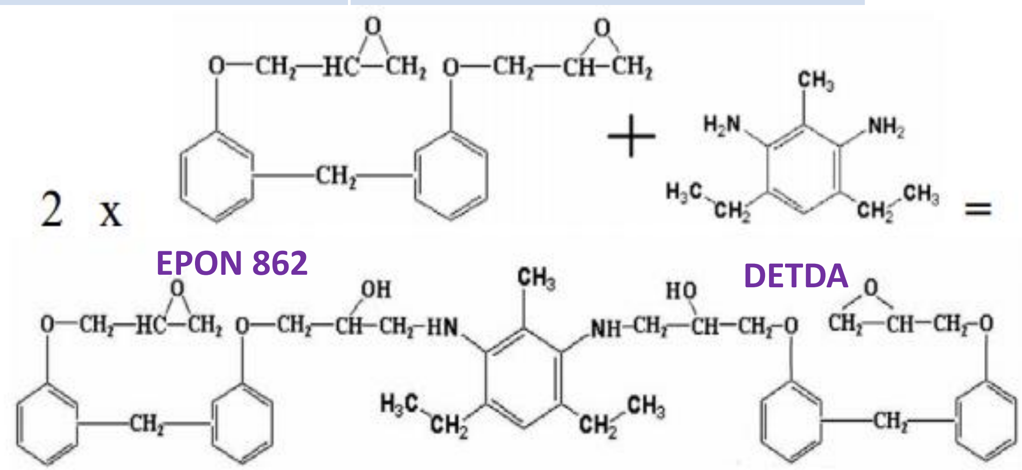
Polymer structural degradation → Surface erosion → Microplastics release → Nanoparticle release

Conceptual model illustrating degradation pathways for polymer



Materials Tests

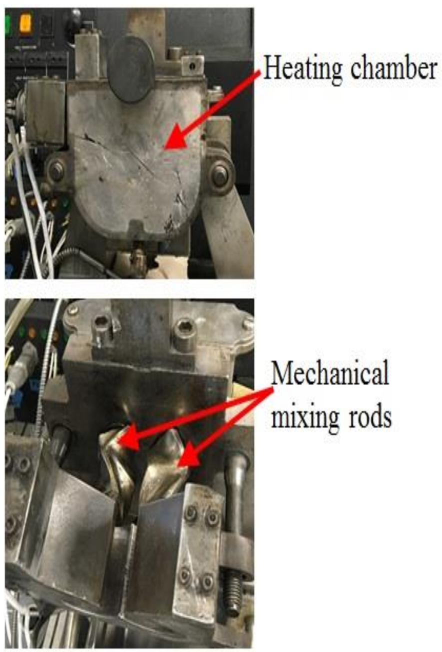
Polypropylene (PP) (Pristine)	PP-MWCNT 4 Wt.%	Epoxy
PP01, L = 0.25 ± 0.01 mm	L = 0.35 ± 0.03 mm	Neat
PP02, L = 0.39 ± 0.02 mm	L = 0.50 ± 0.01 mm	Epoxy-CNT
PP03, L = 0.69 ± 0.04 mm	L = 2.07 ± 0.06 mm	Epoxy-CNT-COOH
		Epoxy-CNT-NH2
T_g = -13 ^oC		Epoxy-Graphene

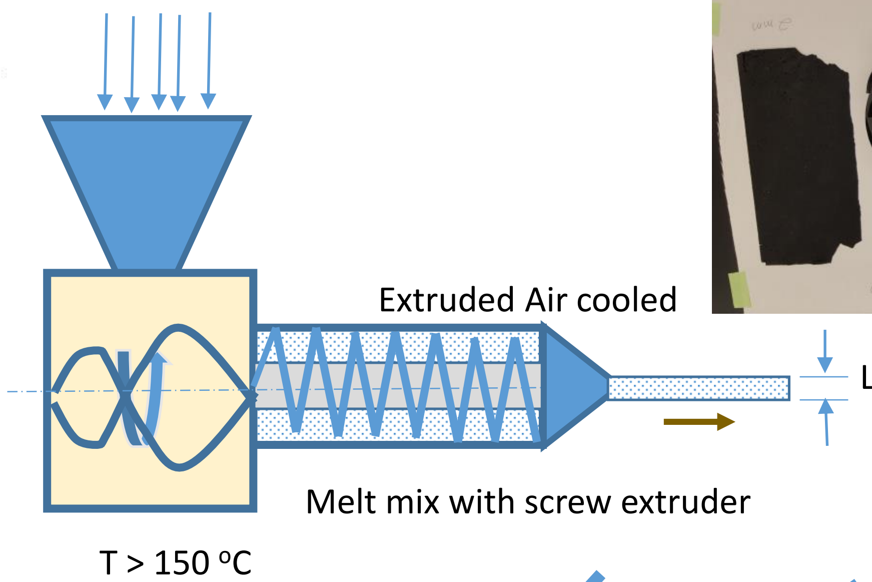


T_g = 60 - 110 ^oC

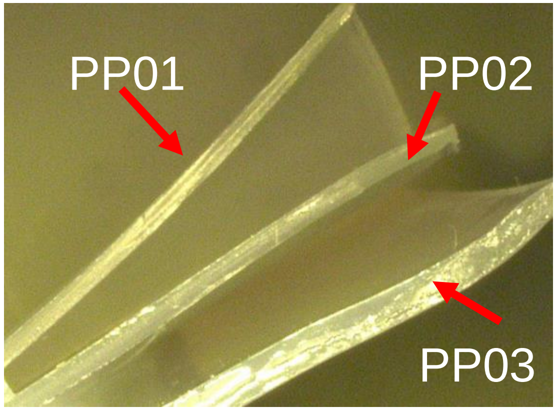
Preparation of polypropylene (PP) and PP-MWCNT film

Melting and mixing of PP and MWCNTs

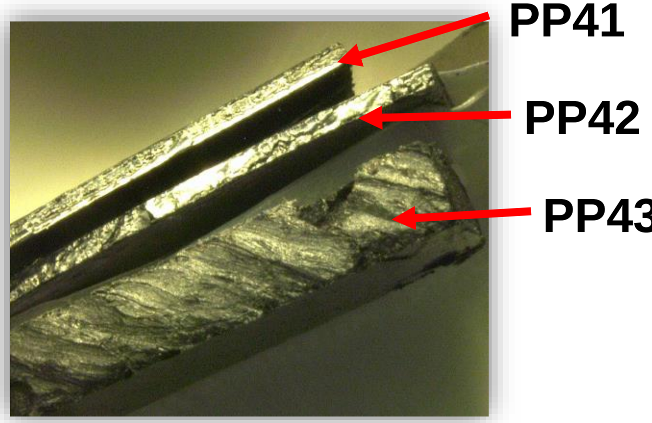




PP



PP-MWCNT

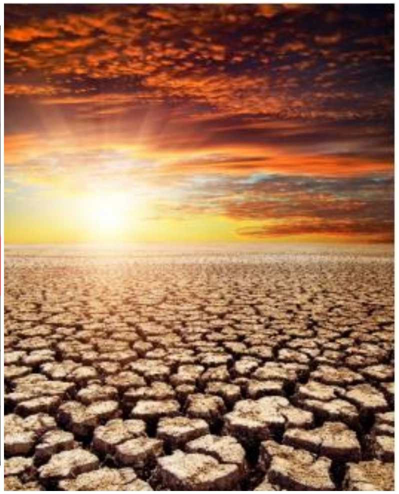


Operating conditions

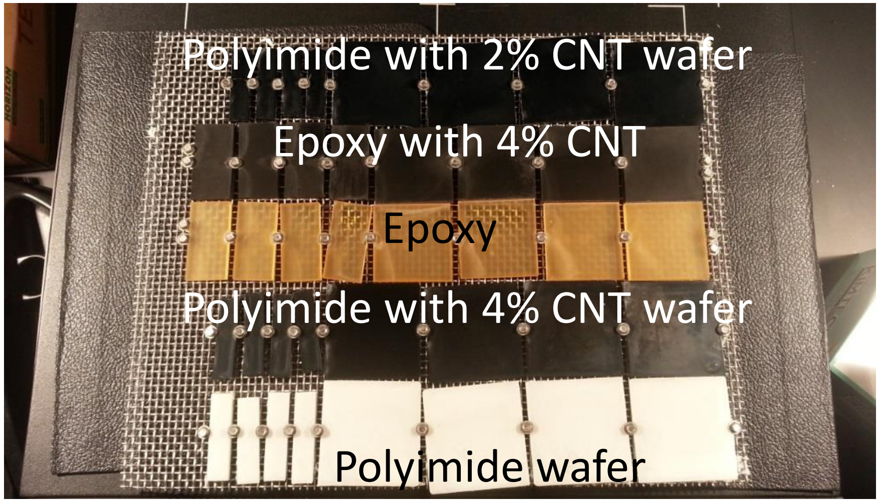
Parameter	Condition
A cycle of weathering	120 min (sunshine: 108 min and rain: 12 min)
Humidity	8-20% for Sunshine and over 60% for Rain
Solar light irradiation	700 W/m^2
Wavelength of solar light	300-800 nm
Chamber Temperature	33-37 ^oC
Black Substance Temperature	65 ^oC

June 21, clear day

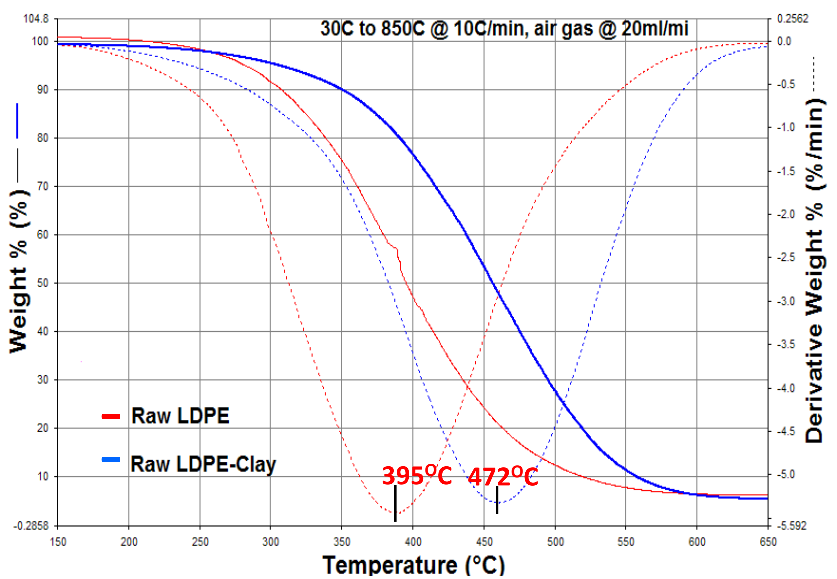
Wavelength range	Arizona	Florida	Frankfurt	Barcelona	CIE No. 85 (Tab. 4)
nm	E (W/m^2)	E (W/m^2)	E (W/m^2)	E (W/m^2)	E (W/m^2)
280-300	0.016	0.017	0.008	0.018	0.010
300-400	**60**	**62**	**48**	**61**	**66**
400-800	566	584	469	542	617
800-4000	420	387	350	373	434
280-4000	1046	1033	867	976	1117



Aging and thermal stability of Composites

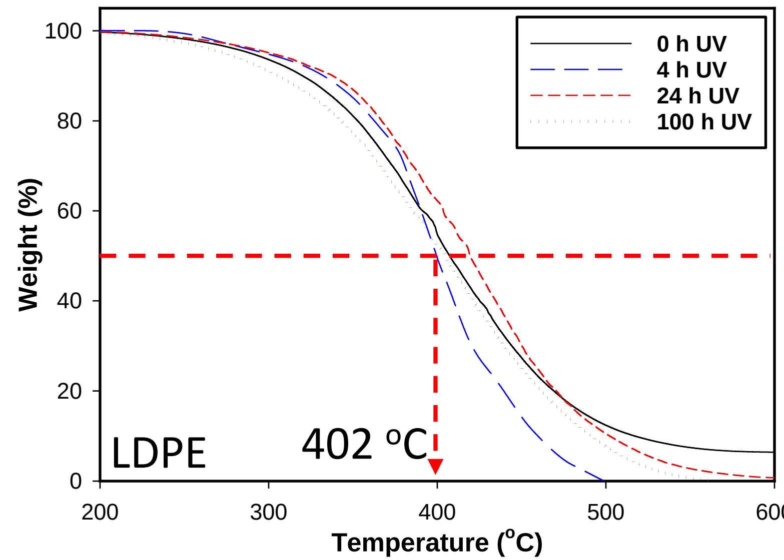


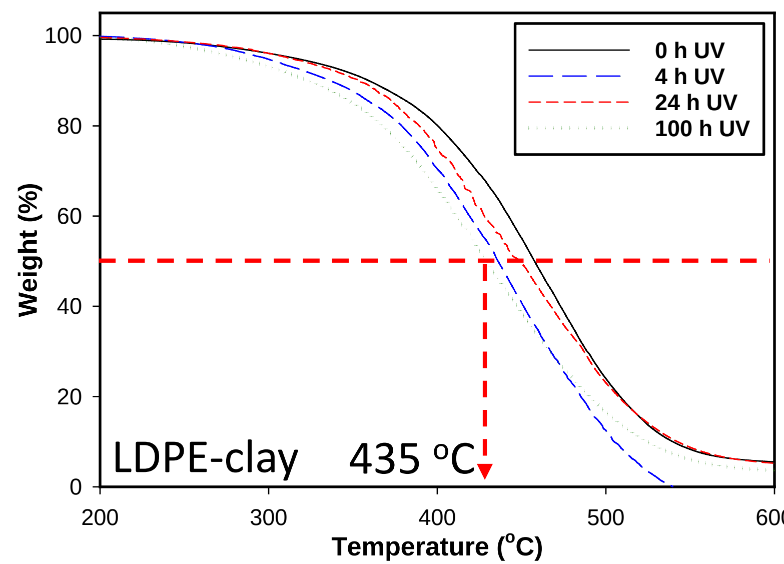
TGA Data for Raw PE and PE-nanoclay



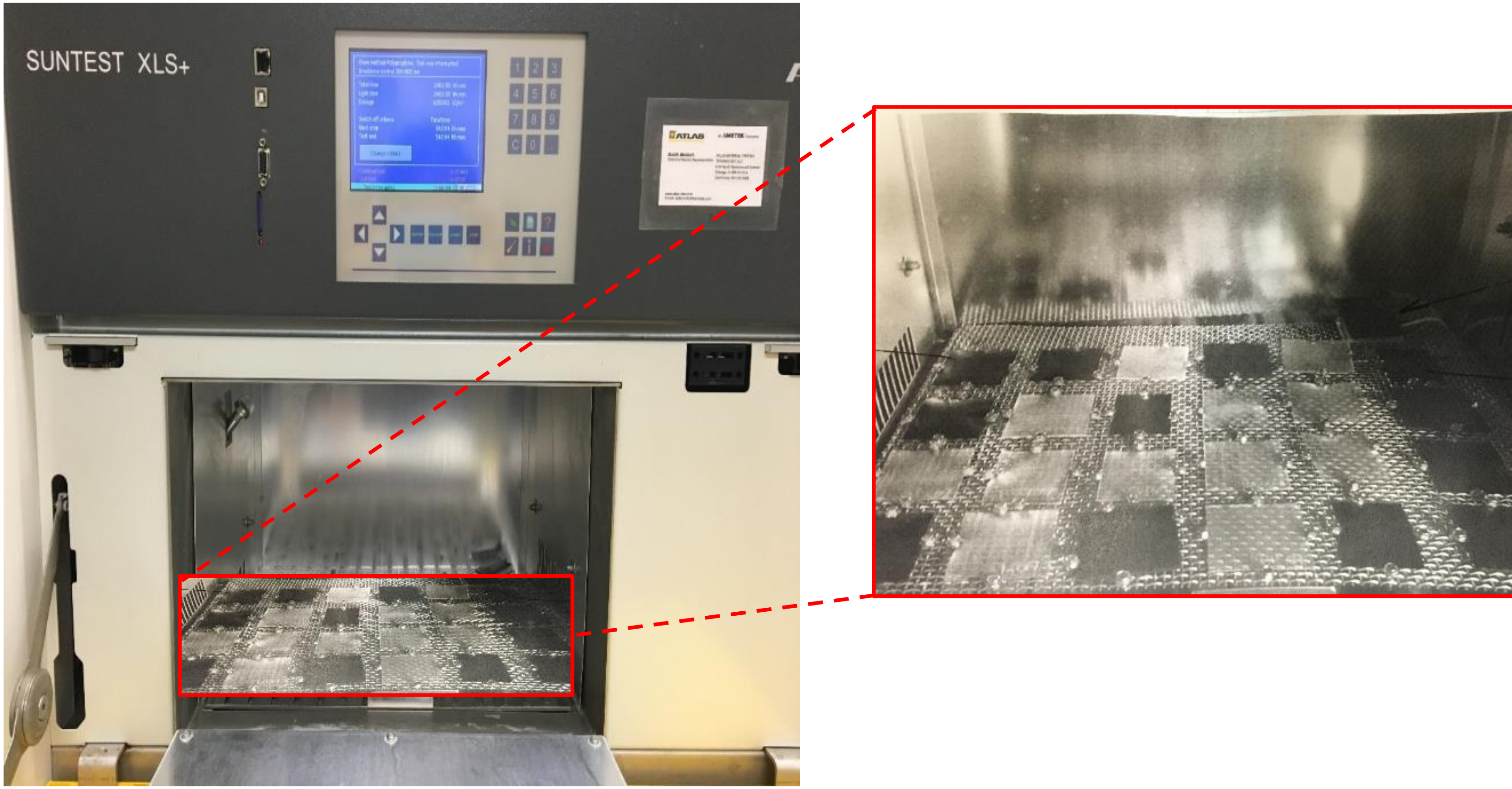
30 °C hold for 1min, to 850 °C @ 10 °C/min, Air flow 20 ml/min.

TGA Data for aged PE and PE-nanoclay



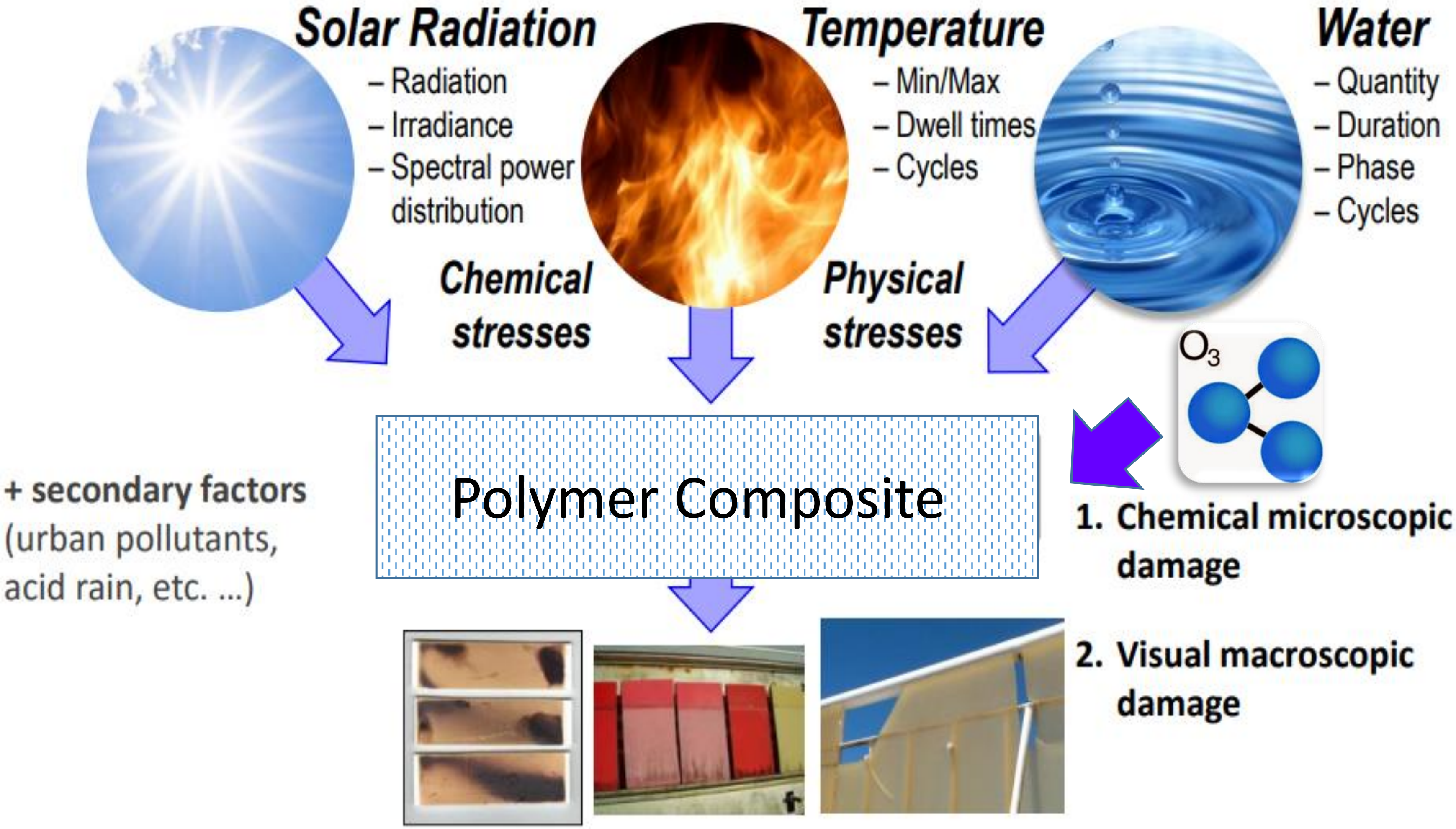


Laboratory Accelerated Weathering System

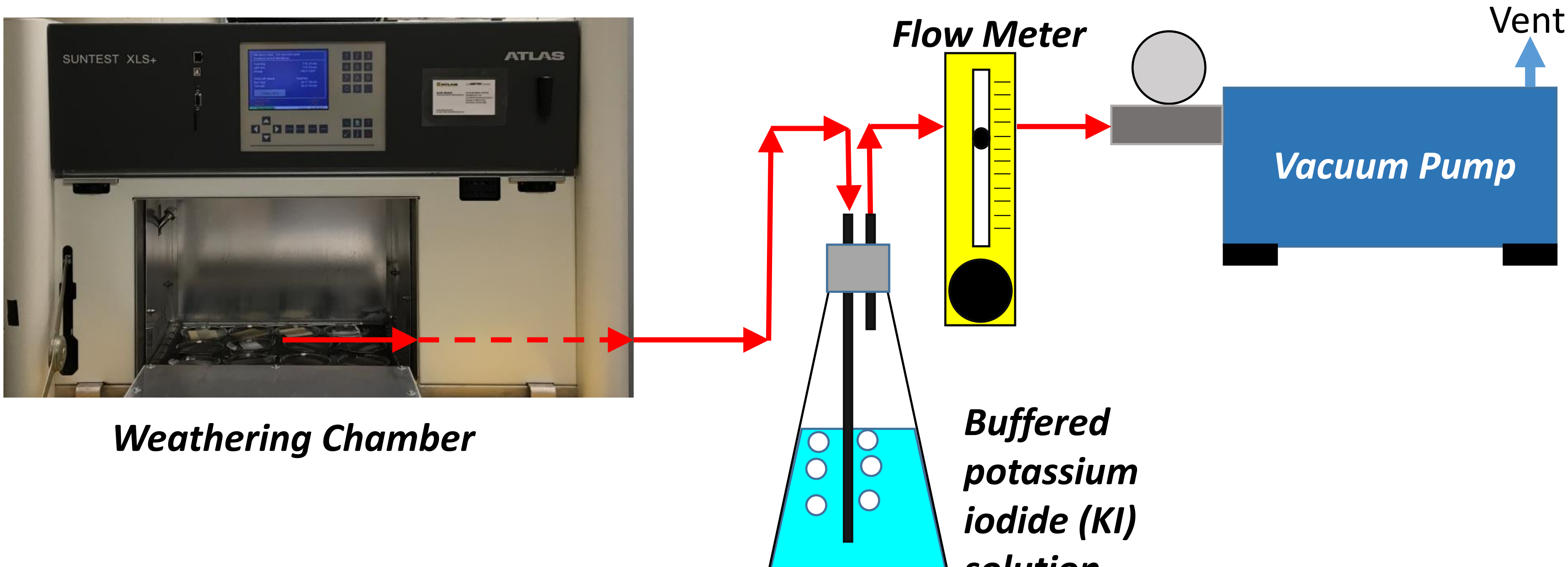


- ❑ Xenon Arc Weathering – simulates terrestrial solar irradiation
- ❑ Irradiation: 700 W/m^2 and Wavelength: 300-800 nm
- ❑ Chamber Temp: 33-37 ^{o}C, Black Substance Temp.: 65 ^{o}C, air cooled
- ❑ Standard method- ISO – 4892-2/2013

The primary weathering factors



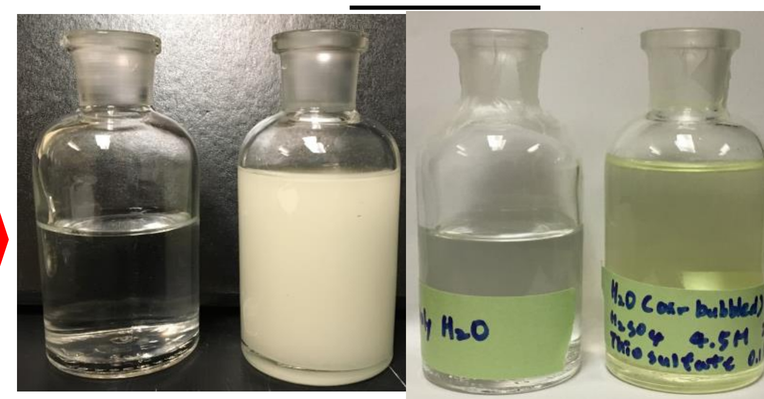
The Formation of Ozone during Weathering



Procedure

1. The air next to polymer samples was taken out and bubbled into KI solution for 15 hr.
2. Perform "**Iodometric Method**" test for O3.
   a. 2.5 mL of 4.5 M H_2SO_4 was added in 100 mL of the bubbled water.
   b. 0.1 M $Na_2S_2O_3$ solution was added to the acidified water (#2).
   c. Observe color changes of the solution from transparent to pale yellow.

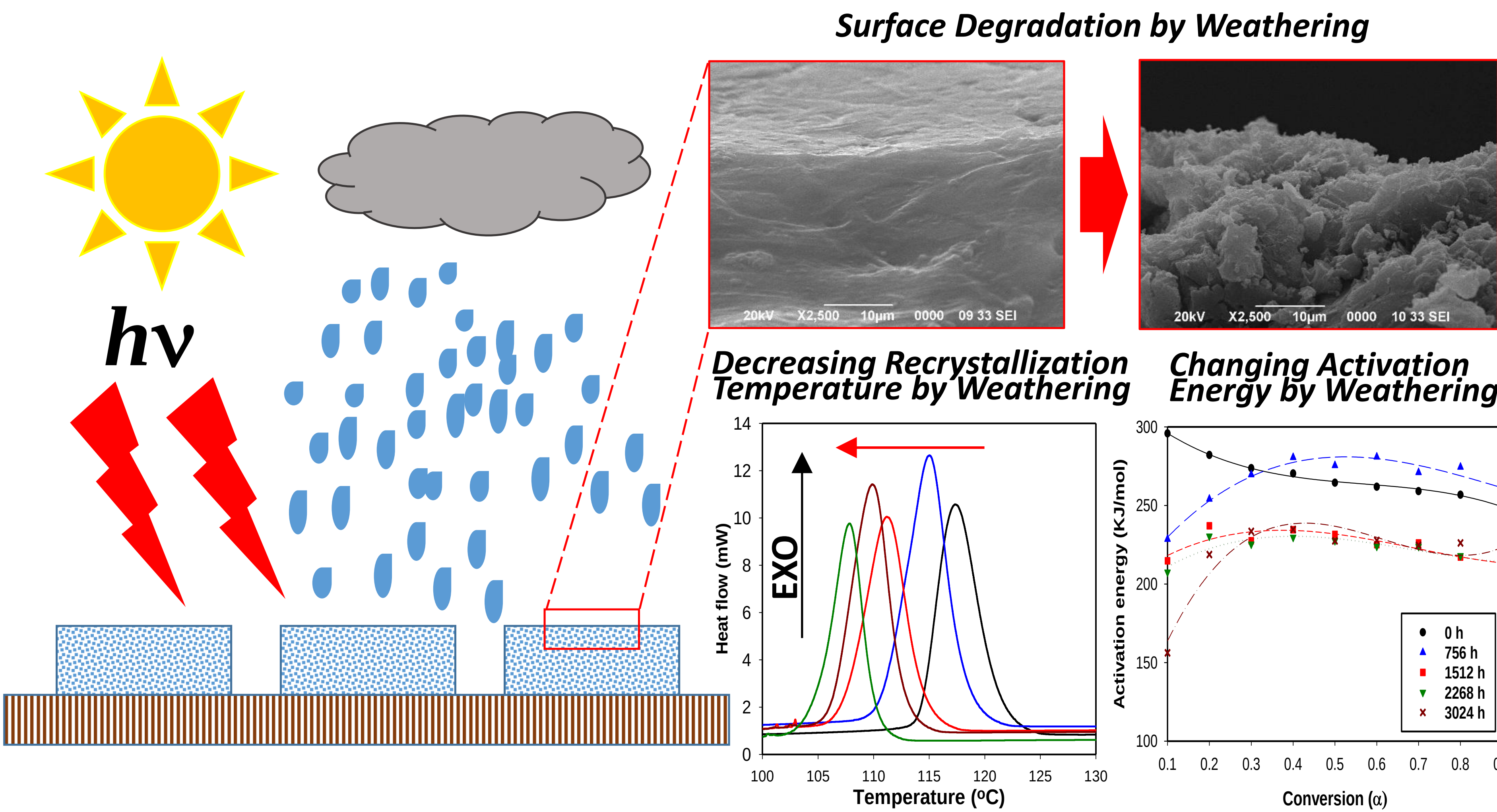
Results



Air bubbled Water

❖ Due to dissolved O_3, color became **pale yellow**.

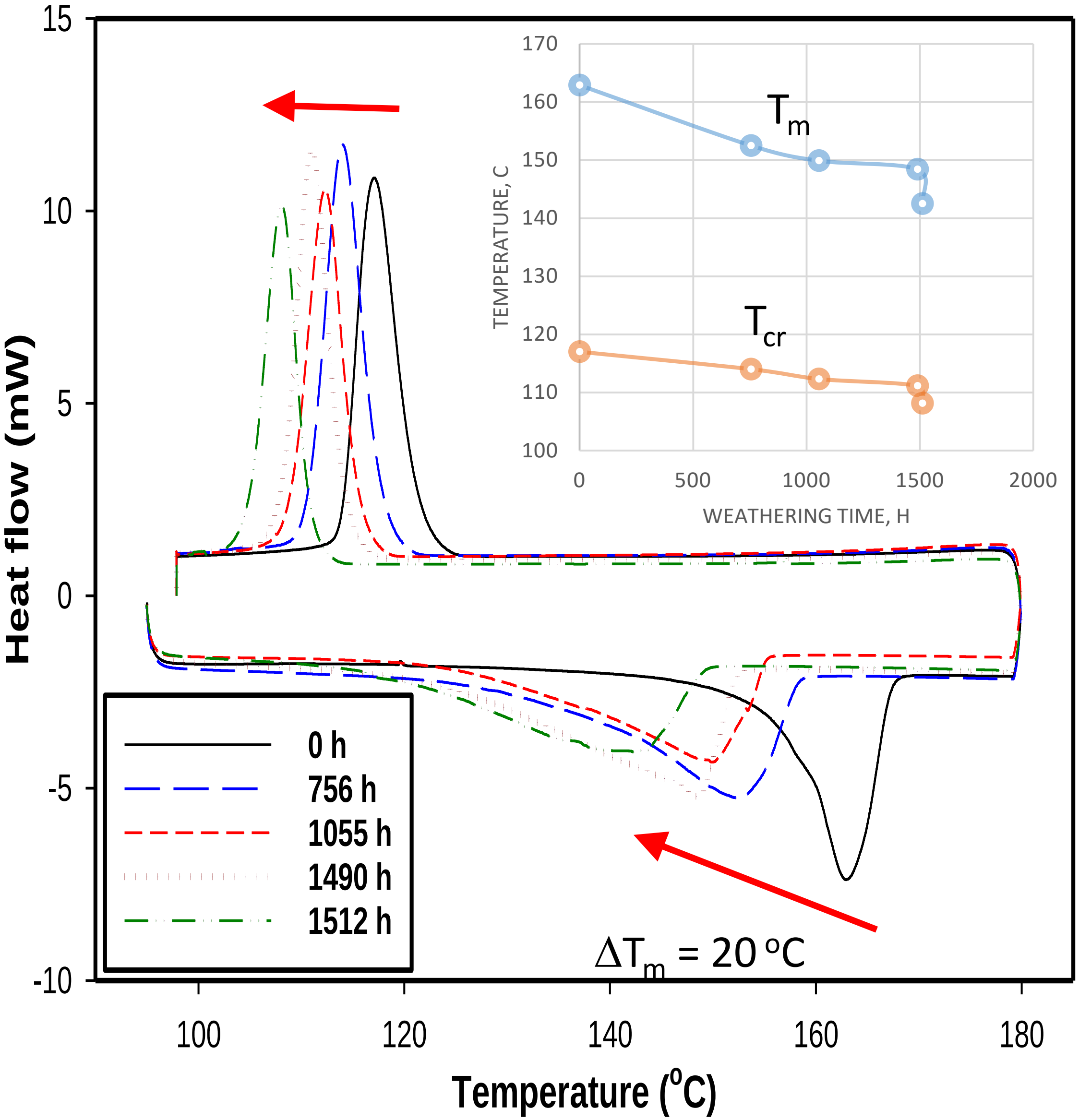
Weathering of Polymer Nanocomposite



Han, Sahle-Demessie, *NanoImpact*, Vol. 9, pp 102-113, January 2018.

Han, Sahle-Demessie, *Carbon*, *Vol 129*, *pp 137-151*, *April*, *2018*

Effects of Weathering on CNT-Polypropylene



Time (h)	Melting Temperature (ºC)	Recrystallization Temperature (ºC)
0	162.9	117
756	152.5	114
1055	149.9	112.3
1490	148.4	111.1
1512	142.5	108.1

$$\Delta \frac{dH}{dt} = \left(\frac{d\ H}{d\ t}\right)_{sample} + \left(\frac{d\ H}{d\ t}\right)_{Reference}$$

Melting point depression due to molecular chain scission and formation of carbonyl and hydroperoxide groups

Han, Sahle-Demessie, *Carbon, Vol 129, pp 137-151, April, 2018*

Reaction kinetics

Radical chain oxidation mechanism

Initiation: $Polymer \xrightarrow{k1} P^*$ (1)

Propagation: $P^* + O_2 \xrightarrow{k_2} PO_2^*$ (2)

$PO_2^* + PH \xrightarrow{k_3} PO_2H + P^*$ (3)

Termination

$P^* + P^* \xrightarrow{k_4}$

$P^* + PO_2^* \xrightarrow{k_5}$ Inactive species (4)

$PO_2^* + PO_2^* \xrightarrow{k_6}$

$$-\frac{d\,[O_2]}{dt} \cong k_2\left({}^{r_i}/_{k_4}\right)^{\frac{1}{2}}[O_2]$$

$\boldsymbol{r_i = aI^{2\gamma}}$ where a and γ = constants depending on the mechanism, and γ is usually between 0.5 and 1.0 for the chain mechanism

Thickness distribution of degradation during photochemical aging

Kinetic equation

Fick's second law with pseudo first order rate constant

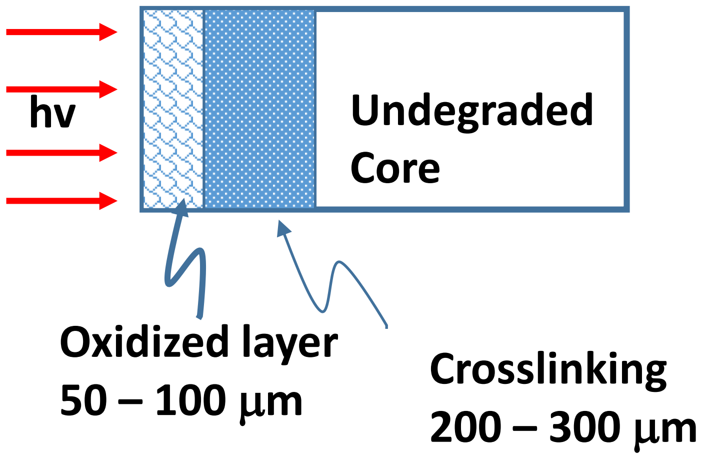
- $$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - kC$$

D= diffusion coefficient for small molecules

k = reaction rate constant

- **Thickness of oxidized layer (TOL)**

$$TOC \cong \Phi^{-1} = \left(\frac{D}{k}\right)^{1/2}$$

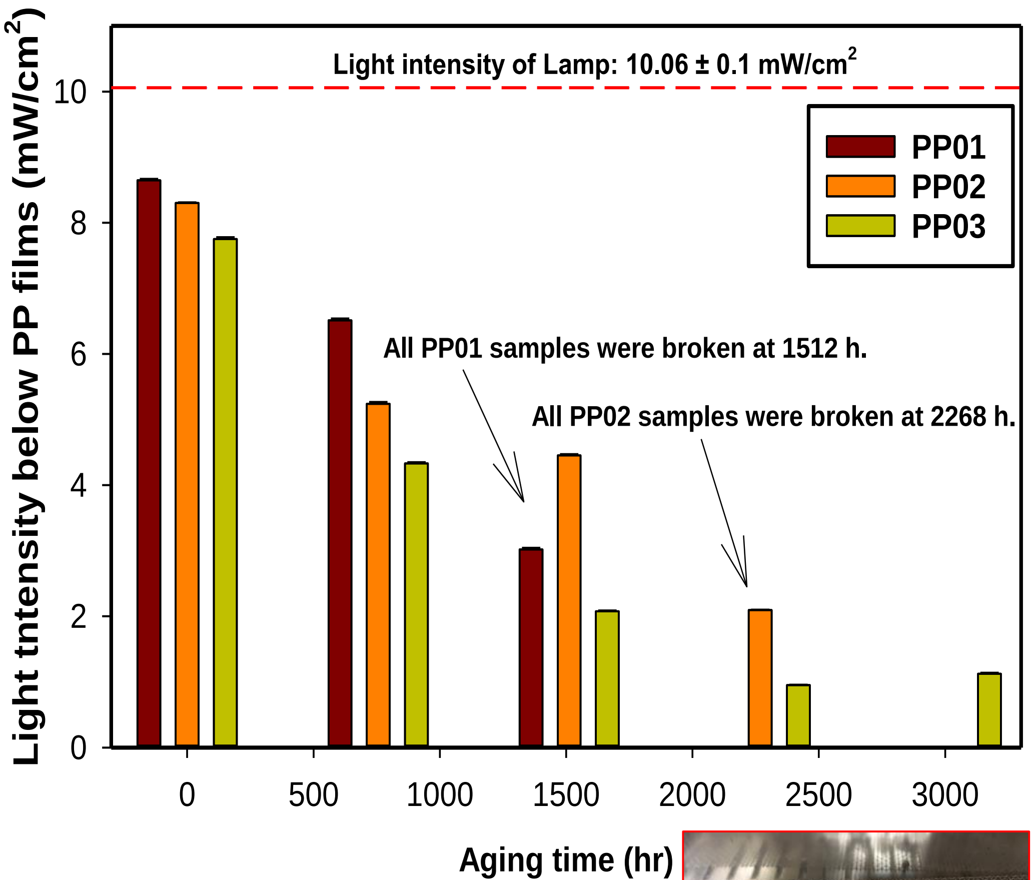


Audoulin et al., J. Material Science, 29 (1994) 560-583

Audoulin et al., Die angewandte Makromelekulare 1998, 25-34

Transmitted UV light through solar aged samples

Intensity of the light source: 10.06 ± 0.1 mW/cm^2



Intensity of transmitted UV light (mW/cm^2)

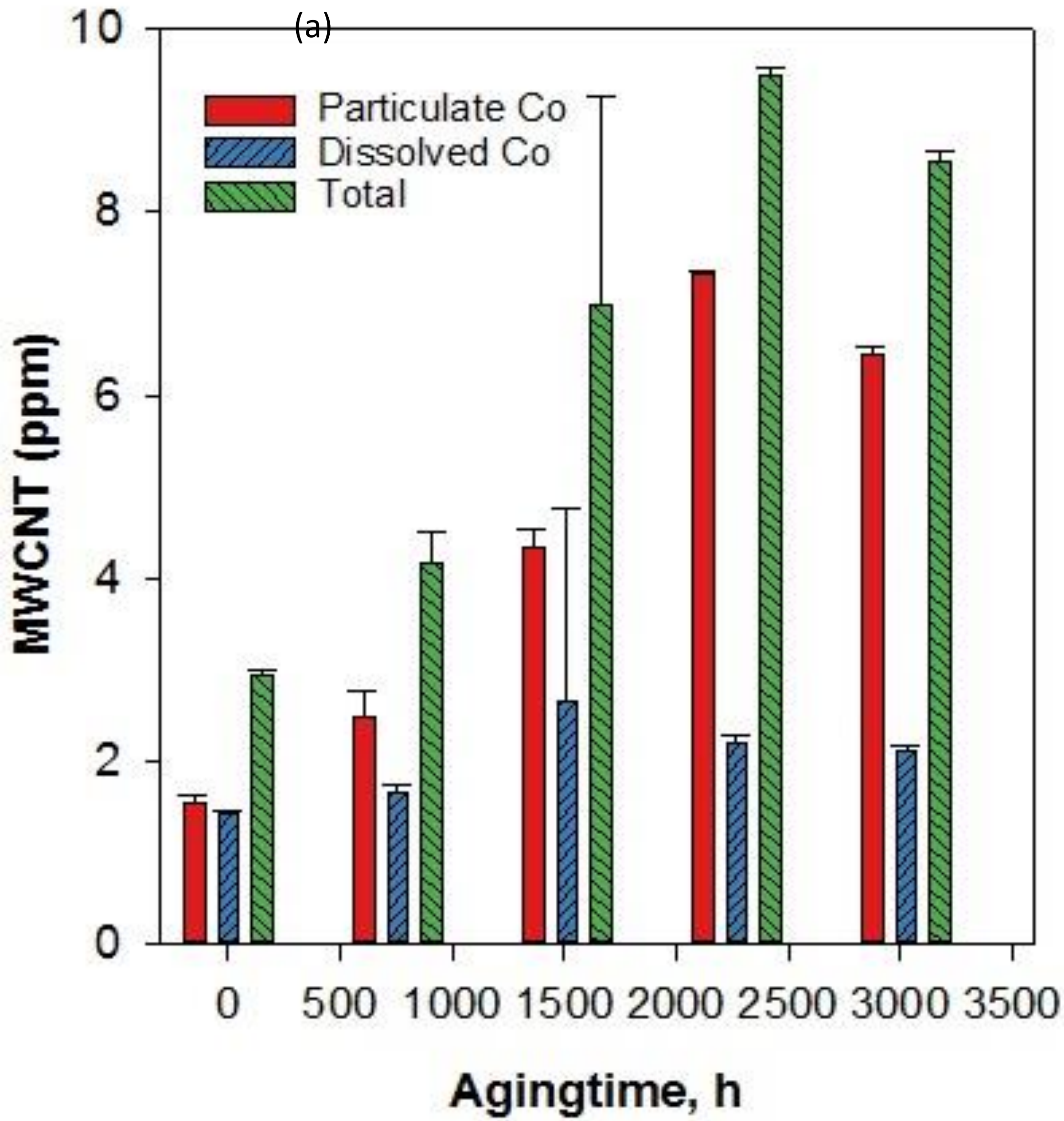
Aging Time (h)	PP01	PP02	PP03
0	8.65 ± 0.02	8.30 ± 0.01	7.75 ± 0.03
756	6.52 ± 0.03	5.24 ± 0.03	4.33 ± 0.02
1512	3.02 ± 0.03	4.45 ± 0.02	2.08 ± 0.01
2268		2.10 ± 0.01	0.95 ± 0.01
3024			1.12 ± 0.02

→ UV transmittance decreased as PP aged showing thermo-oxidative degradation

NanoRelease: Particle size distribution

PP41 =
0.25 mm

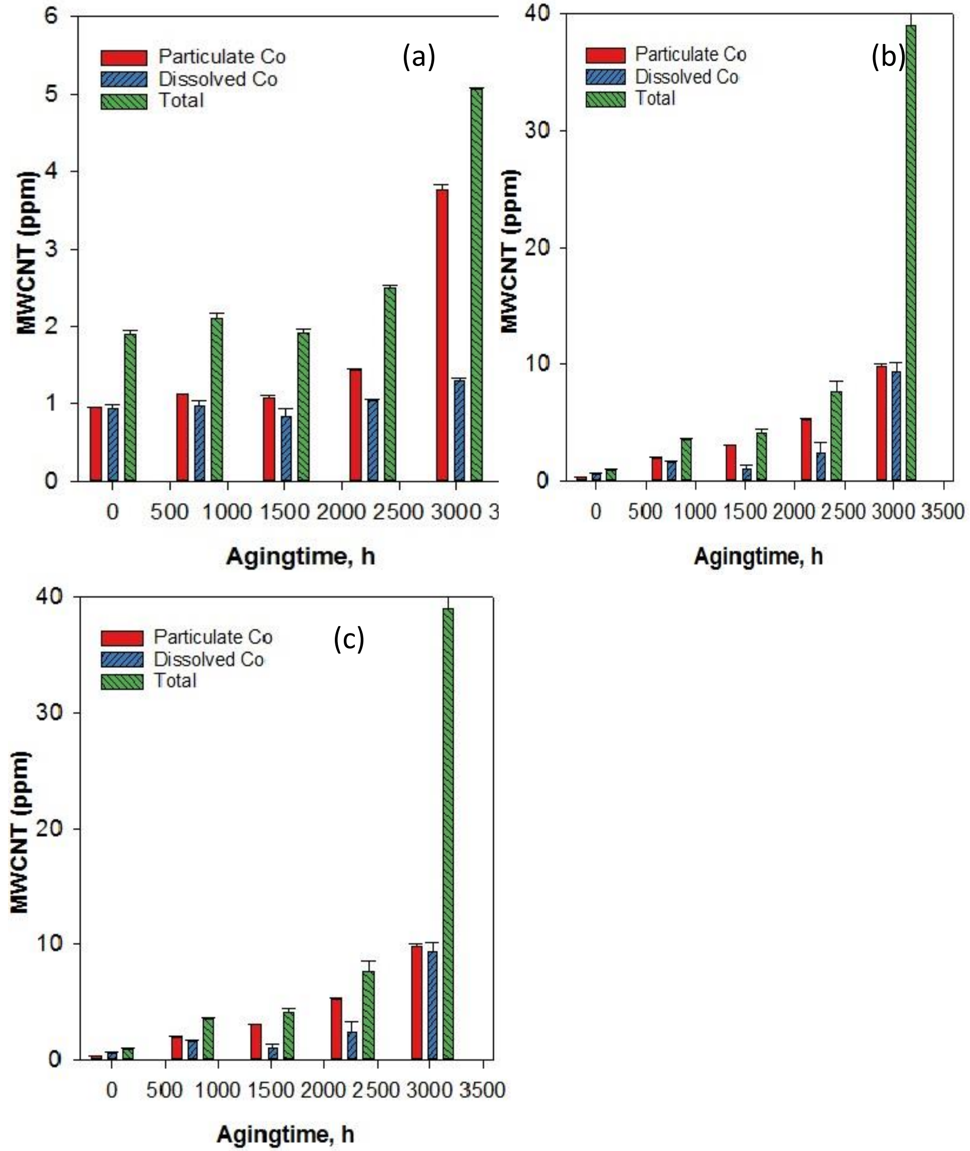
PP42 =
0.50 mm
Filtered



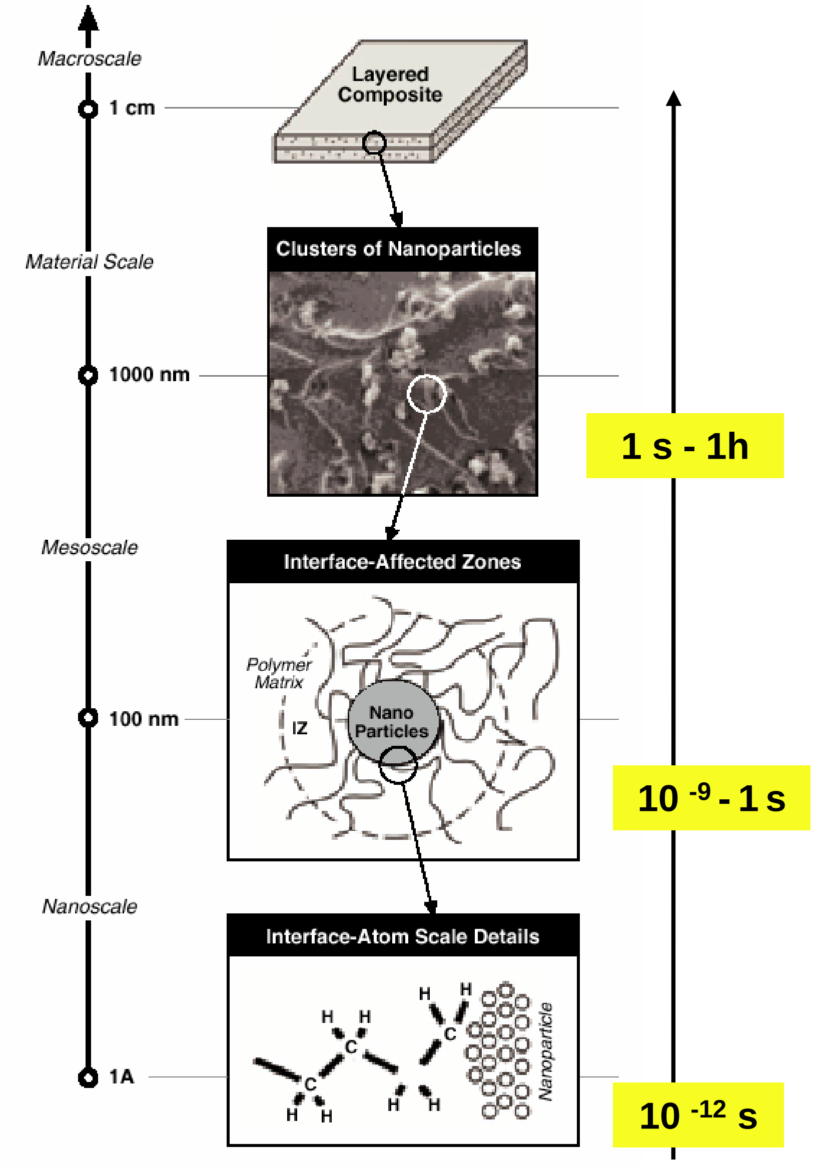
PP42 = 0.50 mm
Unfiltered

PP43 = 2.07 mm

Released MWCNT aged polypropylene-CNT composites determined using sp-ICP-MS

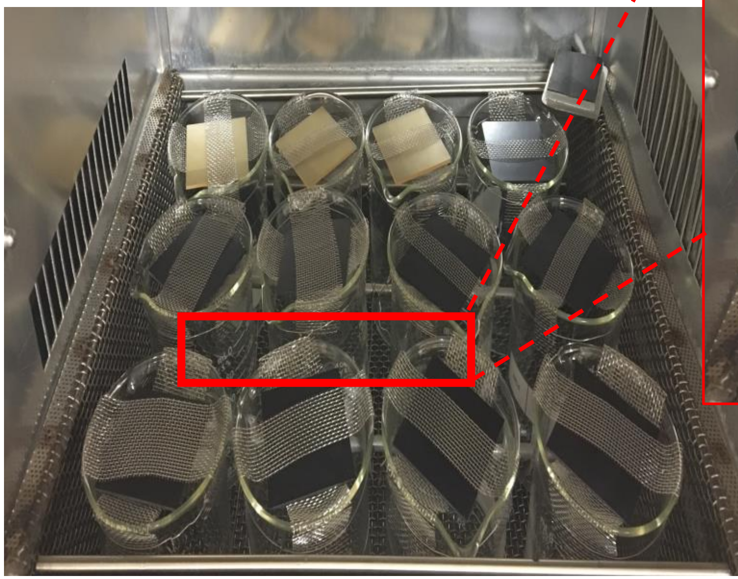


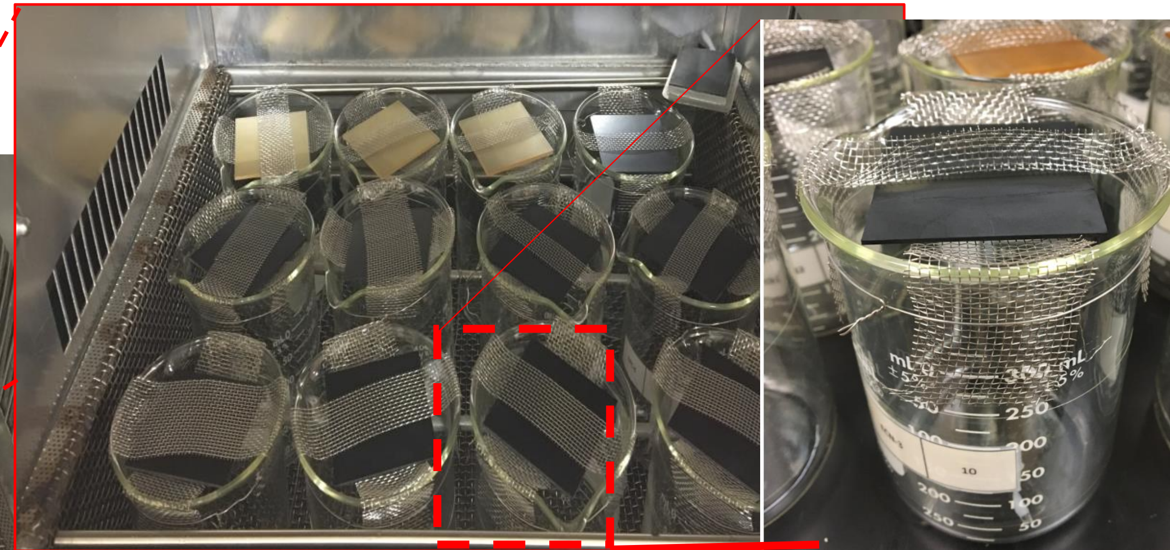
Aging of Nanocomposite as a Multiscale System



- Macroscale composite structures
- Clustering of nanoparticles - micron scale
- Interface - affected zones - several to tens of nanometers - gradient of properties
- Polymer chain immobilization at particle surface is controlled by electronic and atomic level structure

Experimental setup





- ❑ Total Irradiance (MJ/m^2): 6588
- ❑ Solar Irradiance (W/m^2): 700
- ❑ Black Substrate Temperature (^oC): 65
- ❑ Weather: 111 min of daylight and 9 min of raining

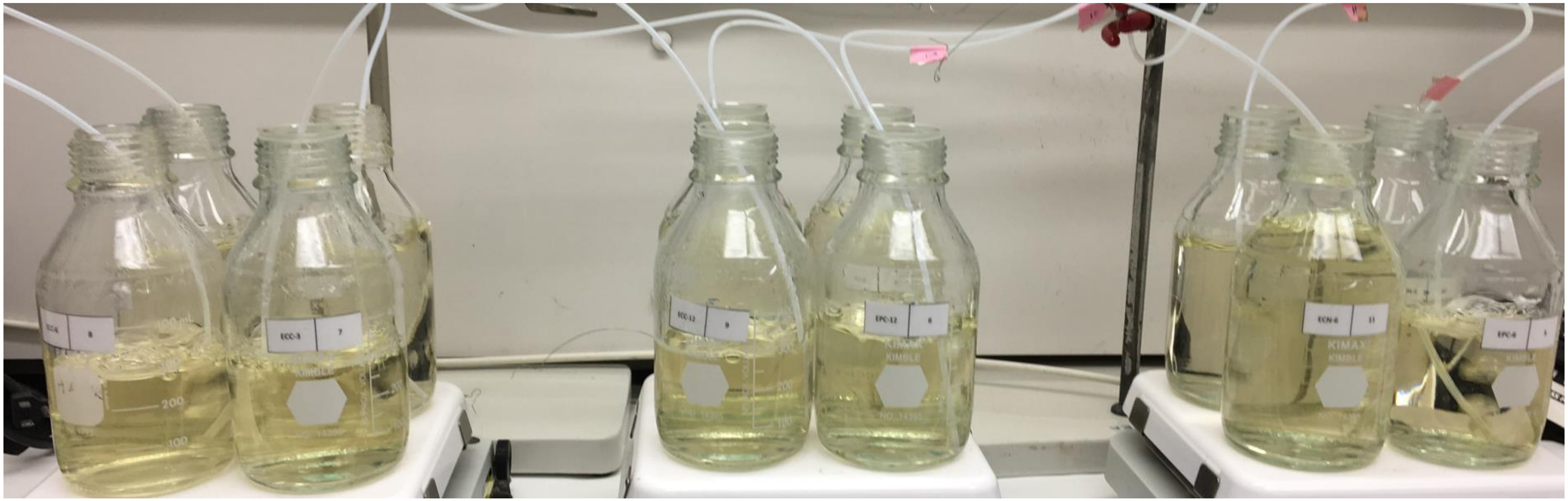
Modified ISO 4892-2:2013 (E)

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)

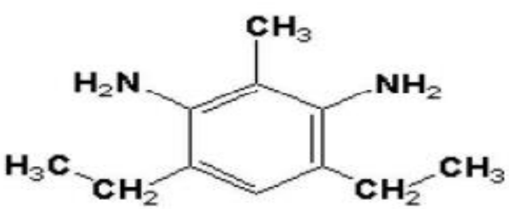
❖ Sample positions are rotated daily for even spraying

Water evaporation setup

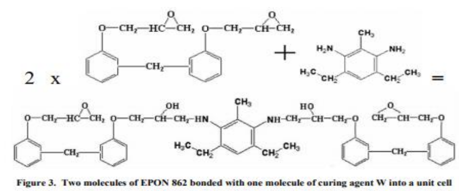


- ❑ Water from the beakers in the SunTest equipment will be collected every day.
- ❑ The water will be transferred to bottles for each sample.
- ❑ The transferred water in the bottles will be evaporated.
- ❑ Water temperature in the bottles is 60-65 ^{o}C.

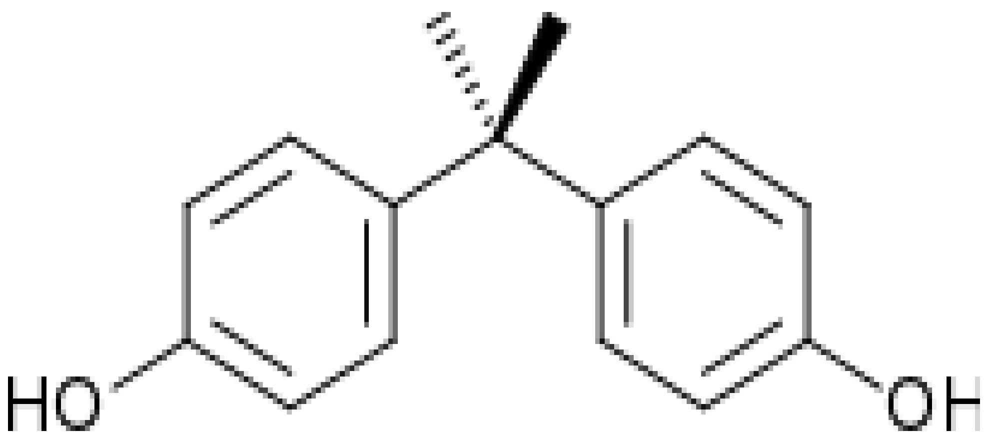
Wash water samples collected in individual Sample-beaker



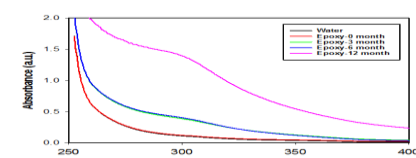
EPON 862



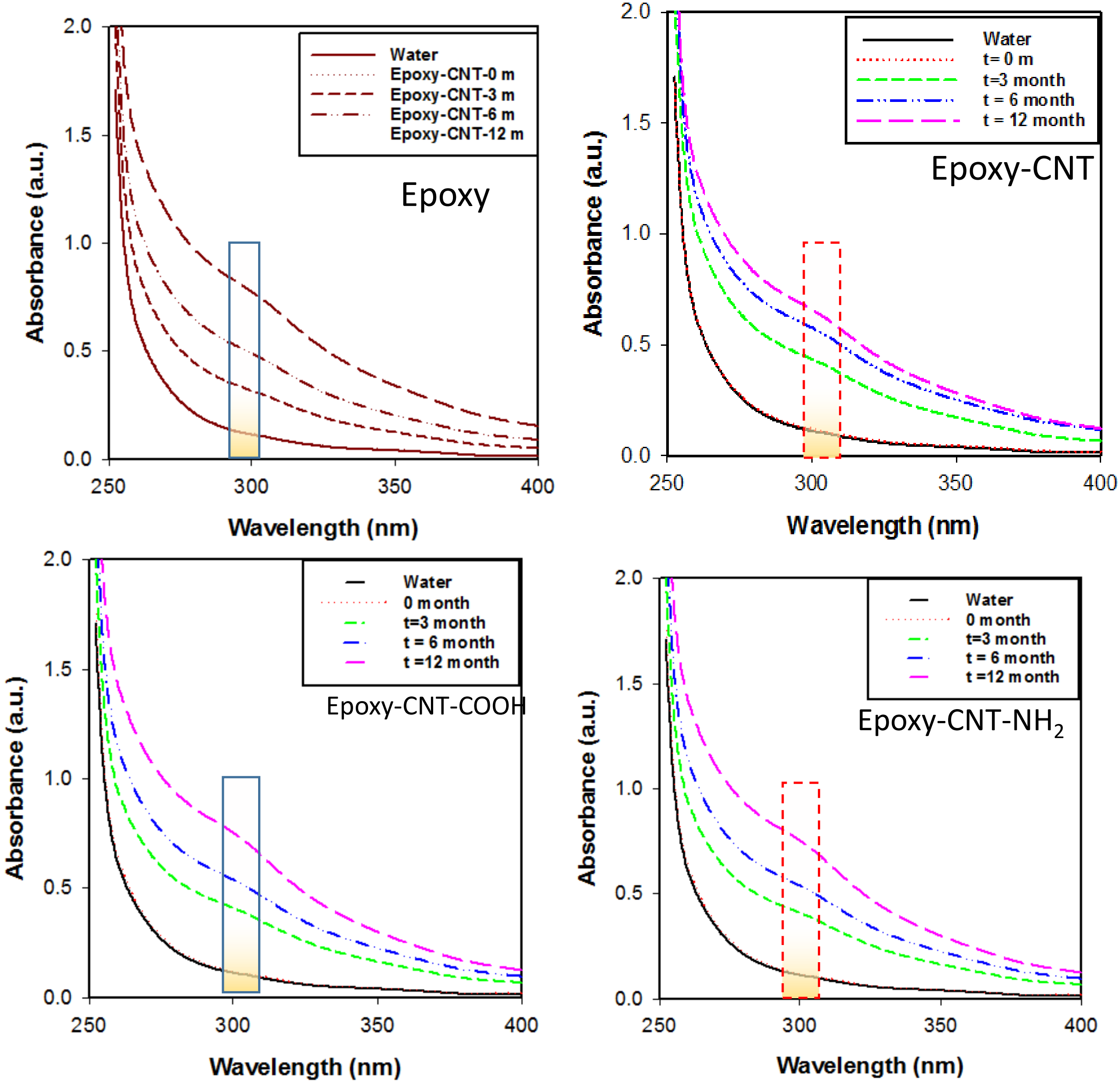
Curing agent



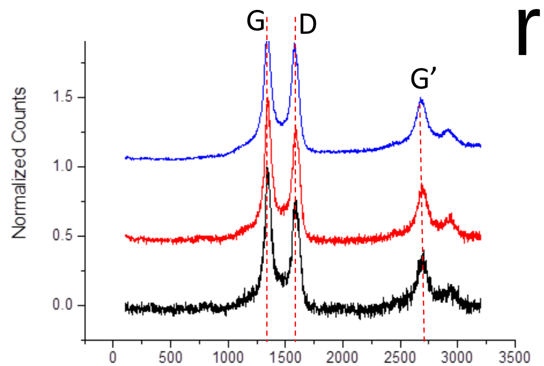
Bisphenol A – common leachate organic from epoxy based polymers – LC-MS-MS

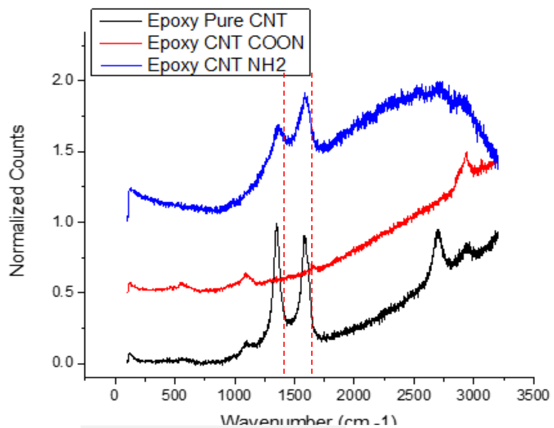


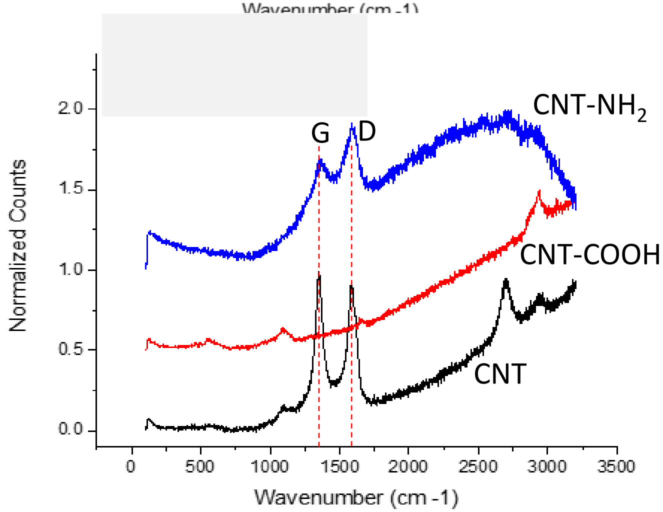
UV-vis spectroscopy nano-release



Raman Spectroscopic characterization of released MWCNT







514 nm Ar-ion laser
G band – at 1580 cm-1 in-plane vibration of C-C bond
D band – activated by the presence of disorder in carbon
G' band – overtone of the D band

	3 Months			6 Months			12 Months		
	Pure CNT	CNT COON	CNT NH2	Pure CNT	CNT COON	CNT NH2	Pure CNT	CNT COON	CNT NH2
G peak Wavenumber (cm-1)	1580.46	1586.44	1590.91	1575.98	-	1580.46	-	1586.44	-
D peak Wavenumber (cm-1)	1351.74	1359.42	1359.42	1348.67	1339.45	1362.49	1359.42	1356.35	1362.49

The Raman band of the functionalized NTs shifted to higher wavenumber → intertube interaction is less and physical interaction of the polymer

Summary

- Weathering of nan-polymer composites is a combination of UV-photolysis, photooxidation, ozonation, and thermal effects
- Main factors affecting degradation are the polymer matrix, environmental conditions, type of nano-reinforcement,
- The reaction rate is influenced by thickness above which the process in kinetically controlled by diffusion of O_2,H_2O in the polymer.
- Superficial oxidation (200 μm) causes cracks and brittle failure of wafer samples.
- The thickness of the degradation layer is order of magnitude $\sqrt{\frac{D}{k}}$
- Polymer thickness influence particle release per mass

Thank you

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Disclaimer

The findings and conclusions of this presentation have not been formally disseminated by U.S. EPA and should not be understood to represent any agency determination or policy.