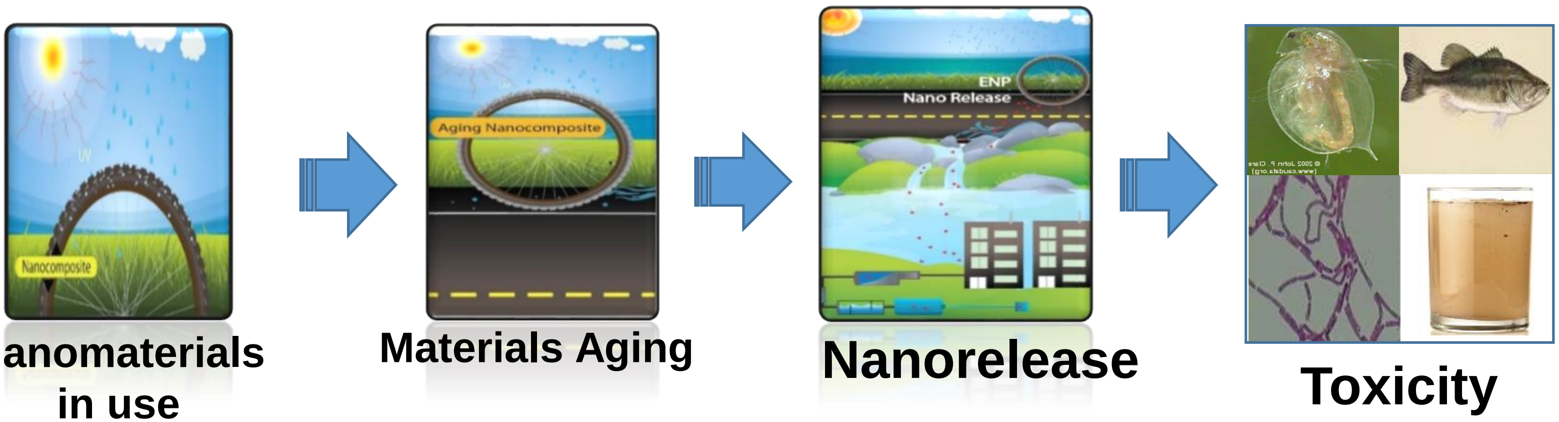
The Impacts of Nanocomposites Across their Life Cycle



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Applications of Nanotechnology

- **Energy** – Improved efficiency of energy production and use production, catalysis, storage
- **Material** – New materials, Improved functionality of materials, → coatings, composites Lubrication, abrasives, paints, tires, sport ware


- **New processes** green nanotechnology, e.g., catalysis, adsorbents
- **Electronics** & **Optics** chips, screens

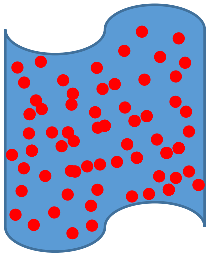

- **Food** – additives, package
- **Cosmetics** – skin, lotion, sun screen
- **Medicine** – diagnostics, drag delivery
- **Environmental Remediation** – Pollution prevention: Reducing use of chemicals Improved information and communication, absorption, water filtration, disinfection and sensor/detection






Nanomaterials in Consumer Products

Reactive ENMs



Ag^{o} clothing

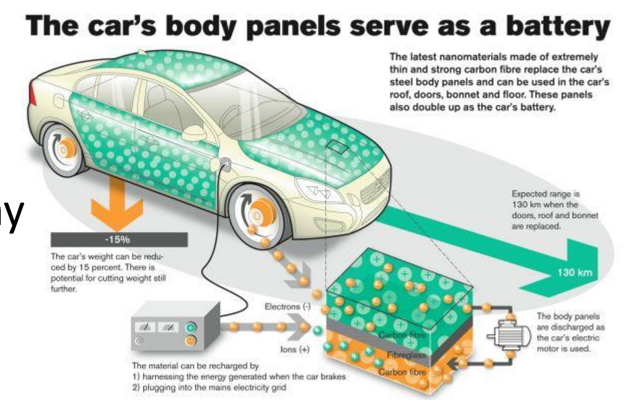
CeO_2 in Polishing agents

“Free” ENMs

Embedded ENMs

TiO_2 in sunscreens

nanoclay



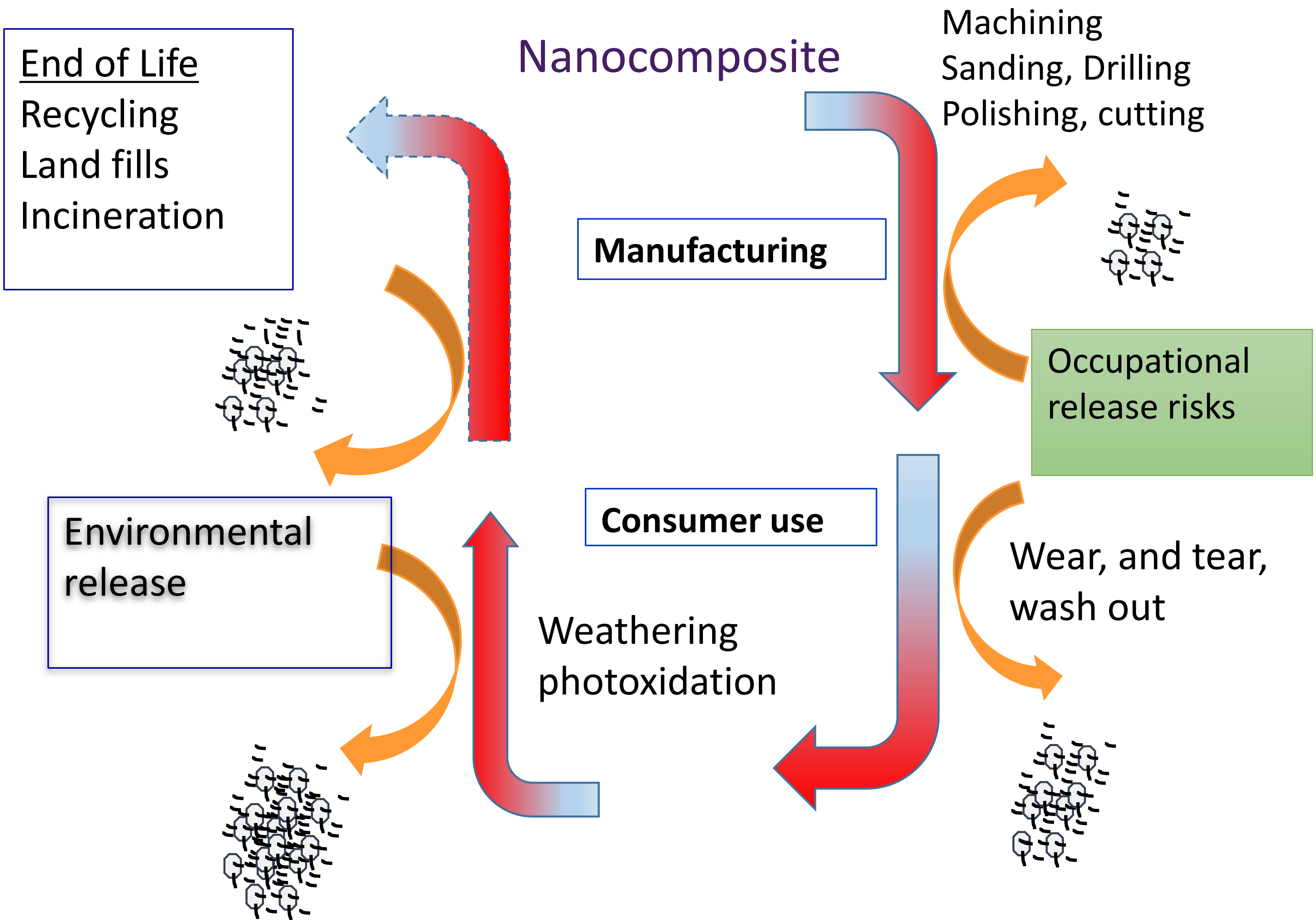
Passive ENMs

Microplatics and nanoparticles in the Environment

Microplastics in the Ocean

Exfoliating microplastics bead for facial rubs

Life Cycle Release of Nanomaterials



Environmental, Safety, and Health (ESH) Impact of Nano-products Across the Life Cycle

Nanomaterials may enter the environment if released during synthesis, formulation, use stage, and product end-of-life,

Manufacturing of Feed Nanomaterials

Shipping Handling

Introduction of other potentially harmful feed materials

Resource

Synthesis Manufacturing

Nano-products

End of Use

Release to the Environment

LCA of Feed Materials

Manufacturing

Open Loop
No recovery or recycling

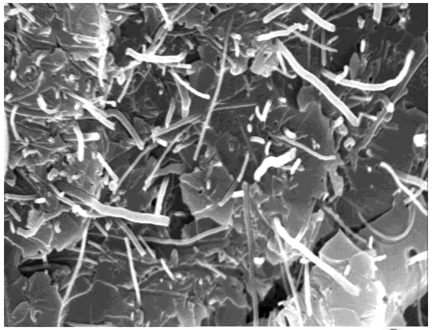
LCA of Products & Emissions

Potential Environmental Impacts of Nanomaterials

1) Increase use of Resources

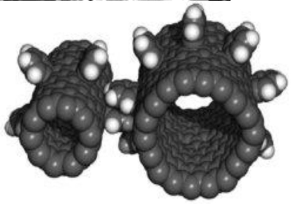
- ➢ Increased exploitation and loss of scarce resources
- ➢ Higher requirement to materials and chemicals
- ➢ Increased energy demand in production lines

Polypropylene with CNF



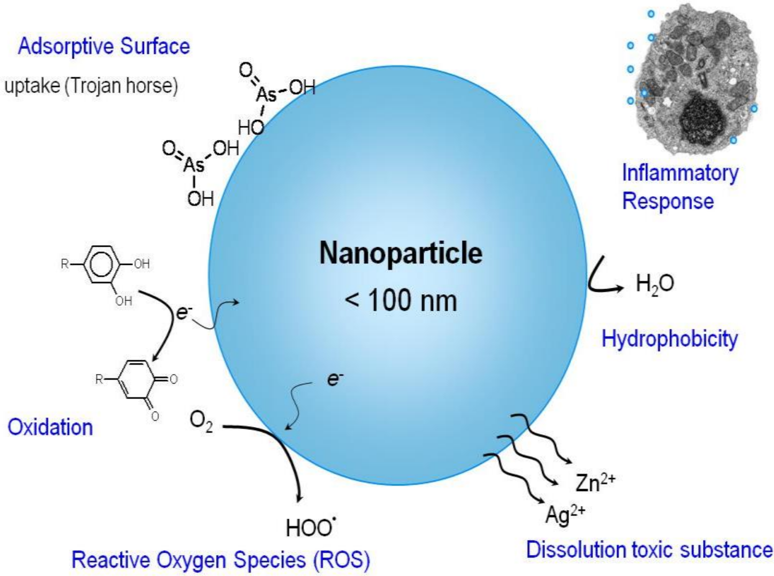
2) Waste generation

- ➢ Increased waste production in top down production
- ➢ One way system: little disassembly, recycling or incineration problems



3) Toxicity

- ➢ Toxicological risks to humans and the environment
- ➢ Potential released from products or E

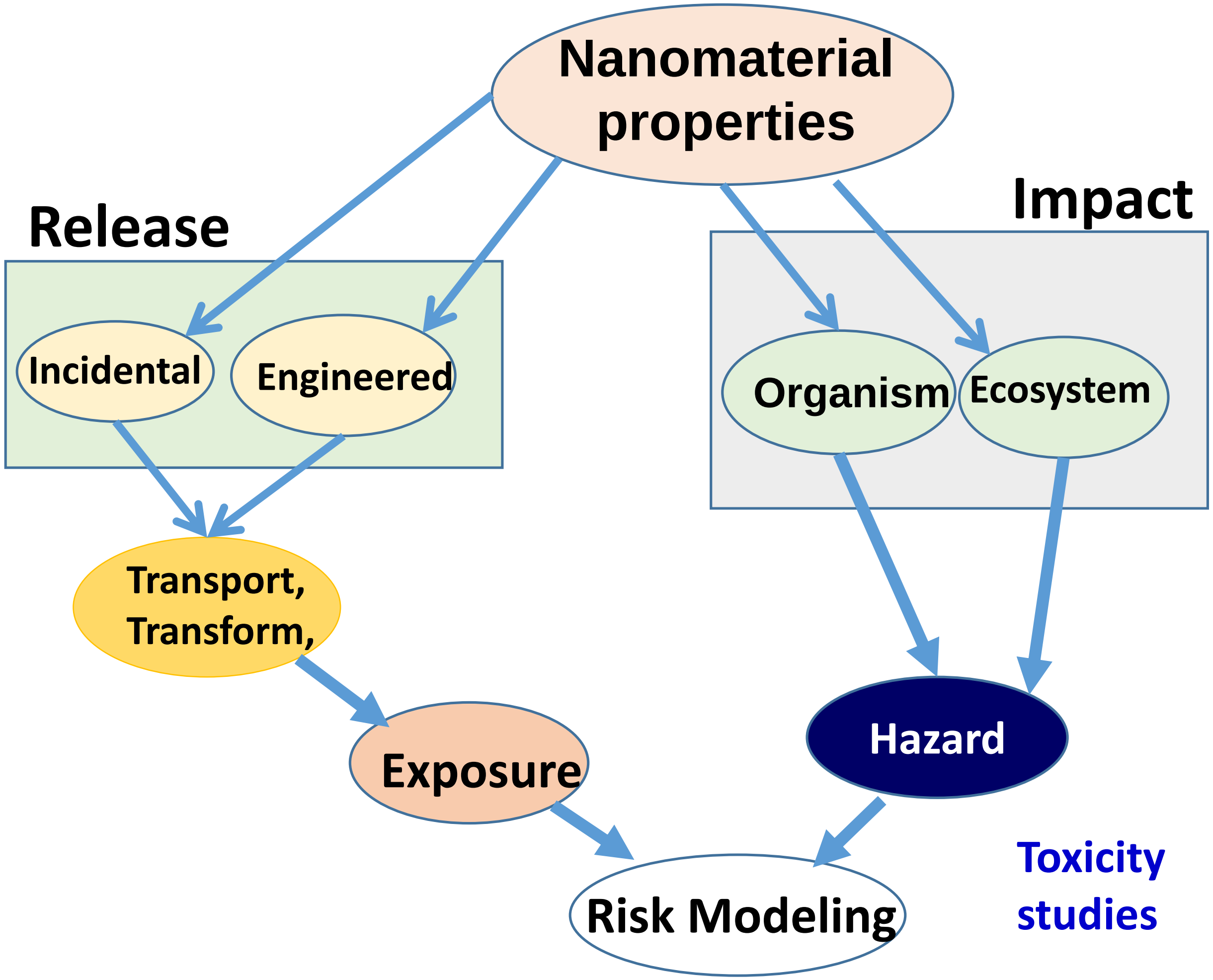


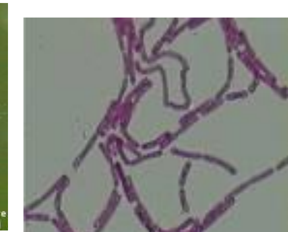
Nanomaterial Implication EPA's Research

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)

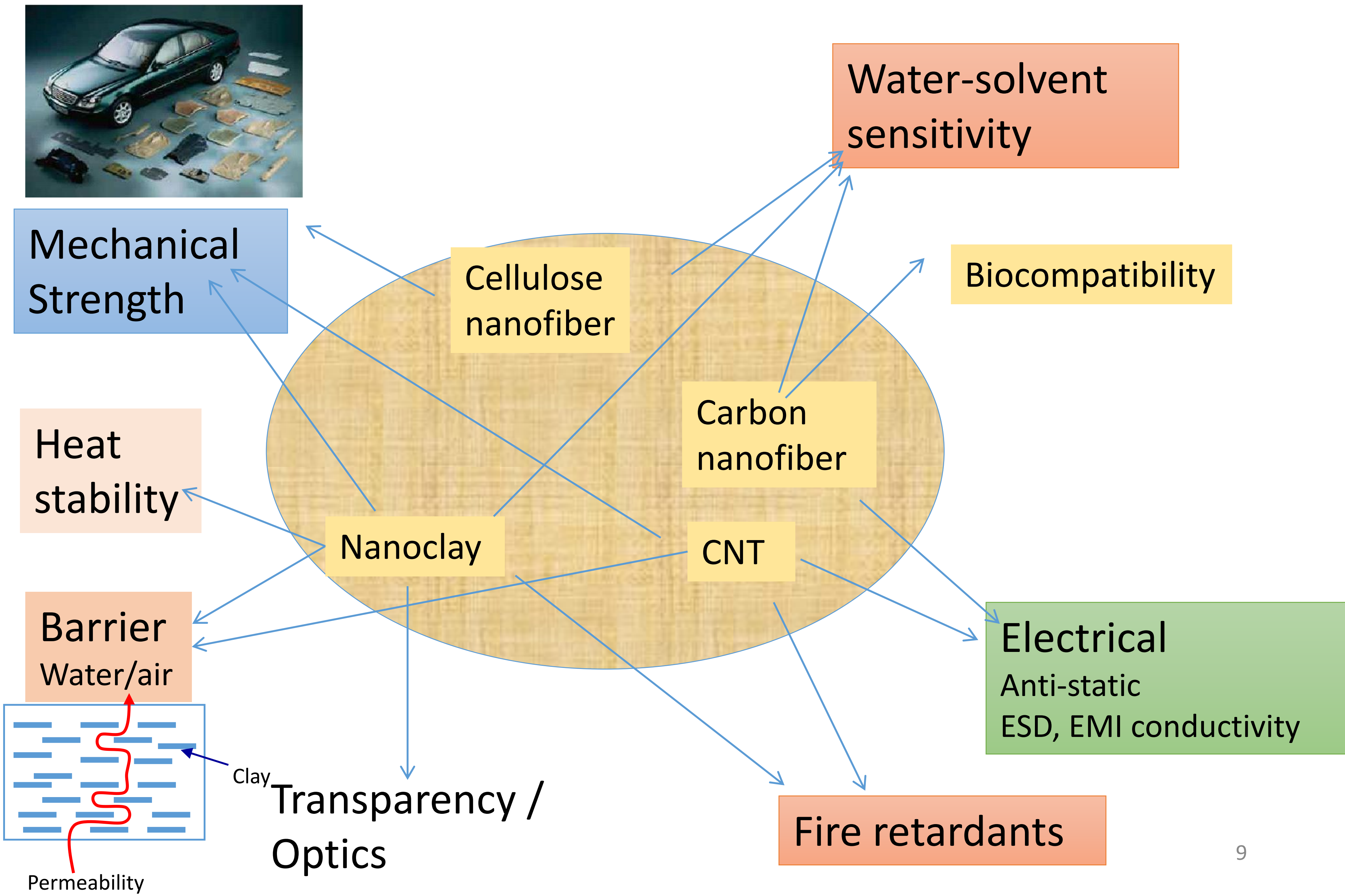
Toxics - Impacts on human health -
- Exposure--Inhalation, ingestion, contact
- Dose-Response
- Bioaccumulation, biotransformation, bioavailability



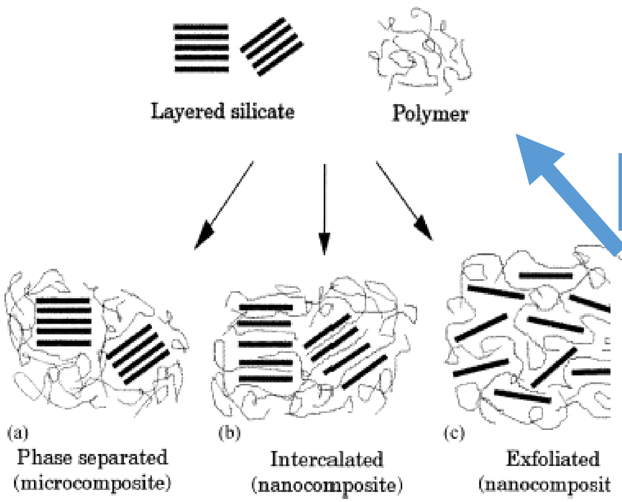


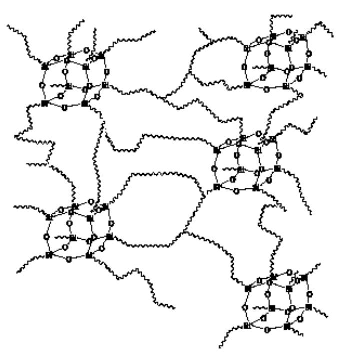
Analysis of ENM in different matrices is critical !

Enhanced Materials with Nanoadditives

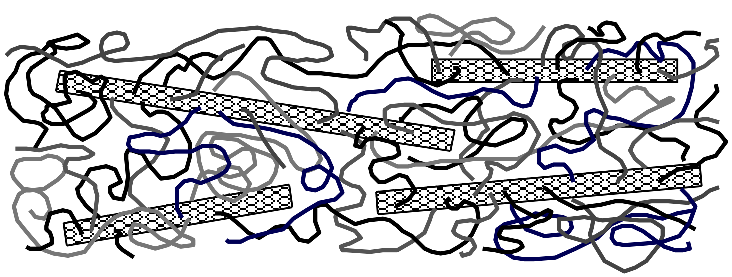


Polymer Nanocomposites





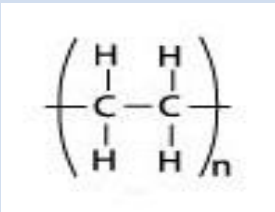
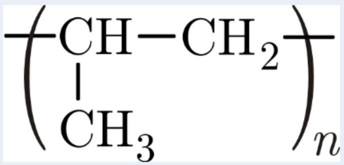
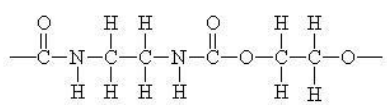
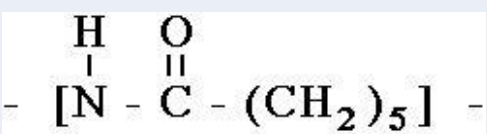
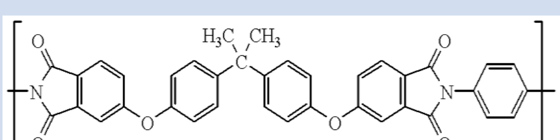
POSS



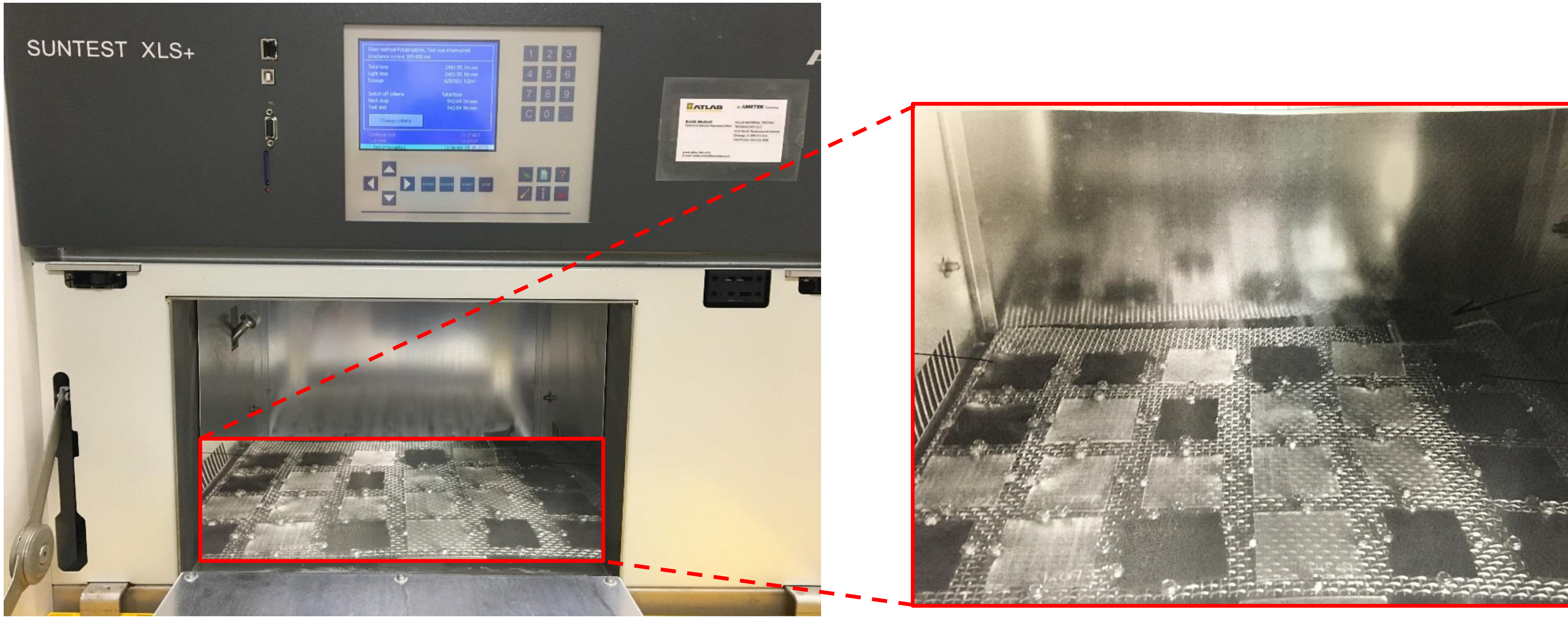
Carbon Nanotubes

- Polymerization develops 3D structure with nano-reinforcement
- How does weathering age composites?
- Does it reverse the process to separate the nano-reinforcement from polymer ?

Composites tested for weathering

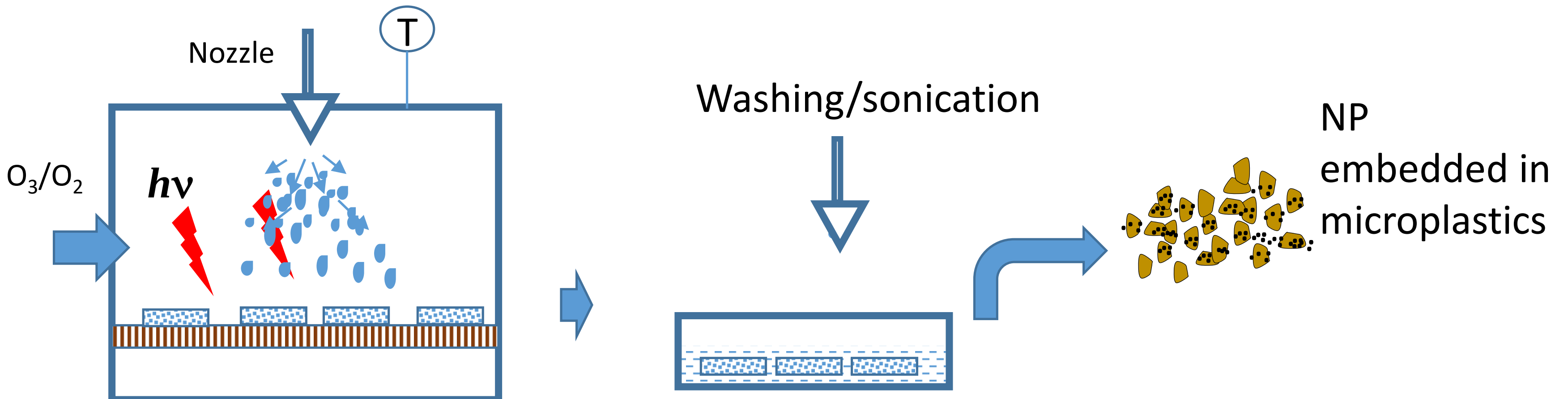
Polymer		Additive	Properties/Use
	Polyethylene	Nano-clay (2 – 6%)	Excellent chemical resistance, robust and flexible. <u>Usage</u>- packaging, plastic bags, plastic films, geomembranes, bottles.
	Polypropylene	CNF / CNT	high temperature resistance, good chemical resistance, translucent. <u>Usage</u>- trays, funnels, pails bottles, instrument jars
 Polyurethane	Polyurethane	CNT	- hardness, tensile strength, compression and impact resistance. <u>Usage</u>- rigid and flexible foams, insulation, boating
	Nylon 6 (Polyamide)	CNT	high strength, amorphous, heat and flame resistant. <u>Usage</u>- automotive, healthcare, additive manufacturing
	Ultem® 1000 Polyetherimid	CNT	high-strength amorphous excellent heat and flame resistance, used for additive manufacturing

Solar Aging System



- A cycle of weathering: 120 min (Sunshine : 98 min and Rain: 12 min)
- The cycle continuously repeats during the aging process
- Humidity: 8-20% for Sunshine and over 60% for Rain
- Irradiation: 700 W/m^2 and Wavelength: 300-800 nm
- Chamber Temperature: 33-37 ^{o}C
- Black Substance Temperature: 65 ^{o}C
- Sampling time: 756, 1512, 2268, and 3024 h

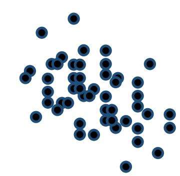
Studying Photo-initiated Oxidation of Nanocomposite



Accelerated weathering chamber

<u>Challenge:</u>
Uniformity
Reproducibility→
Standard Methods

Aging:
Characterization
Kinetics
Mechanism
Prediction

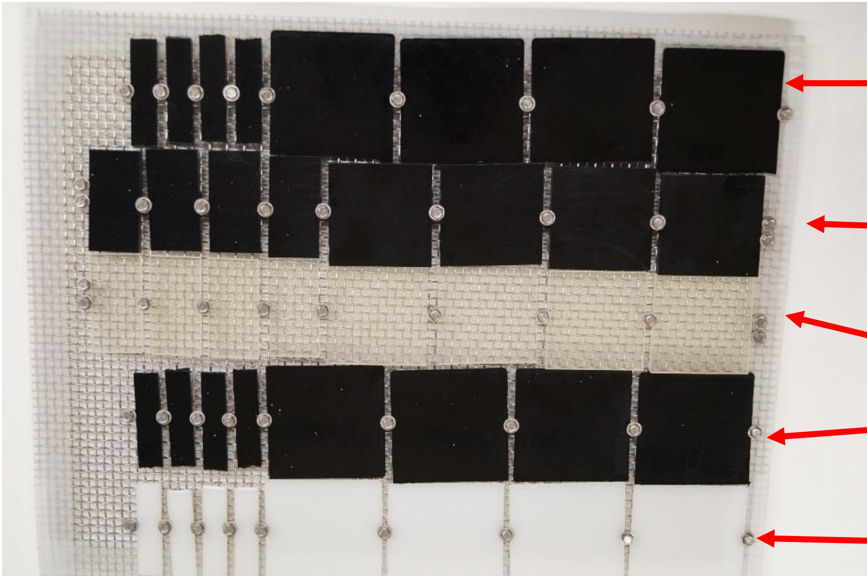


NanoRelease?

<u>Analysis:</u>
Thermal
Mechanical
Spectroscopic
Imaging
XRD

<u>Analysis:</u>
Spectroscopy (UV)
ICP-MS
SP-ICP-MS
Imaging
???

NanoRelease Weathering Project



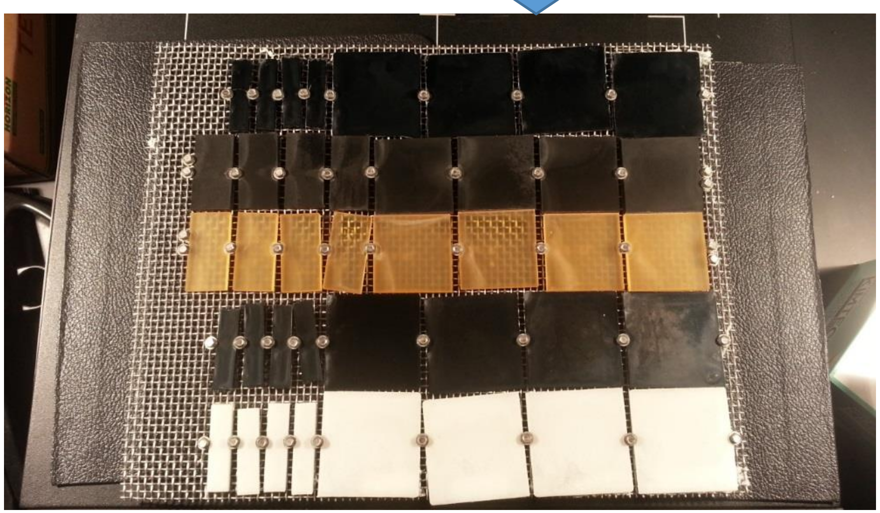
Polyimide with 2% CNT wafer

Epoxy with 4% CNT

Epoxy

Polyimide with 4% CNT wafer

Polyimide wafer



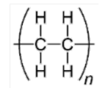
Aged wafers

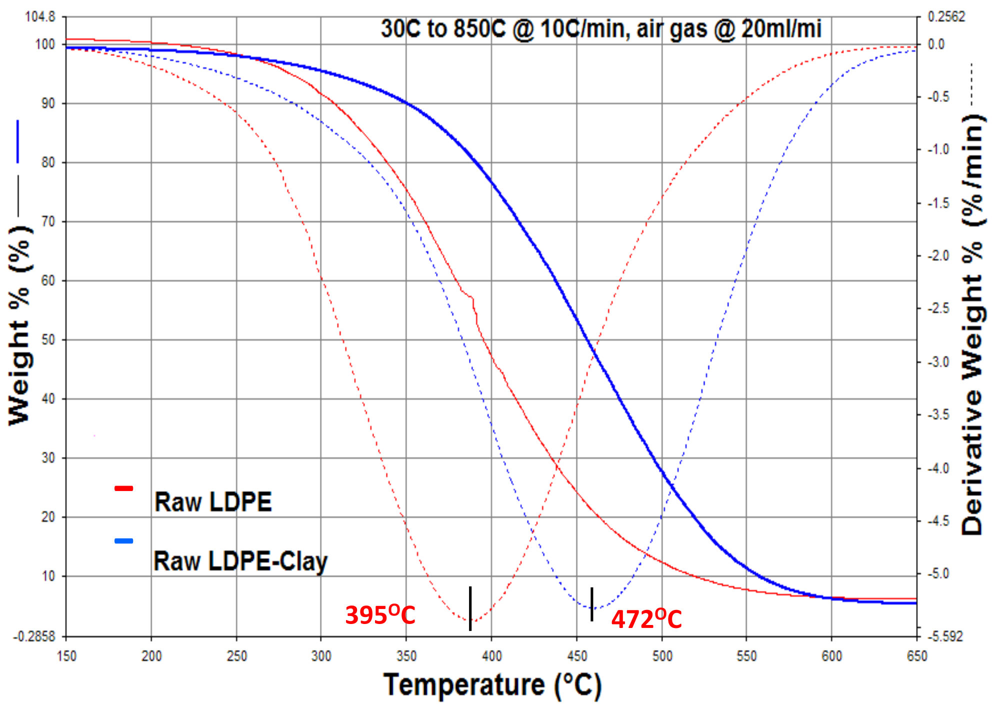
Measuring Weathering of Nano-Composites

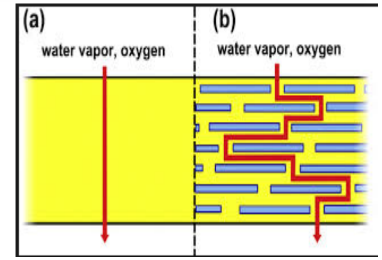
Thermal Analysis

- **Thermogravimetric analysis**(TGA)
- **Differential Scanning Calorimetery** (DSC)

Nanoclay in polyethylene Improved Thermal stability



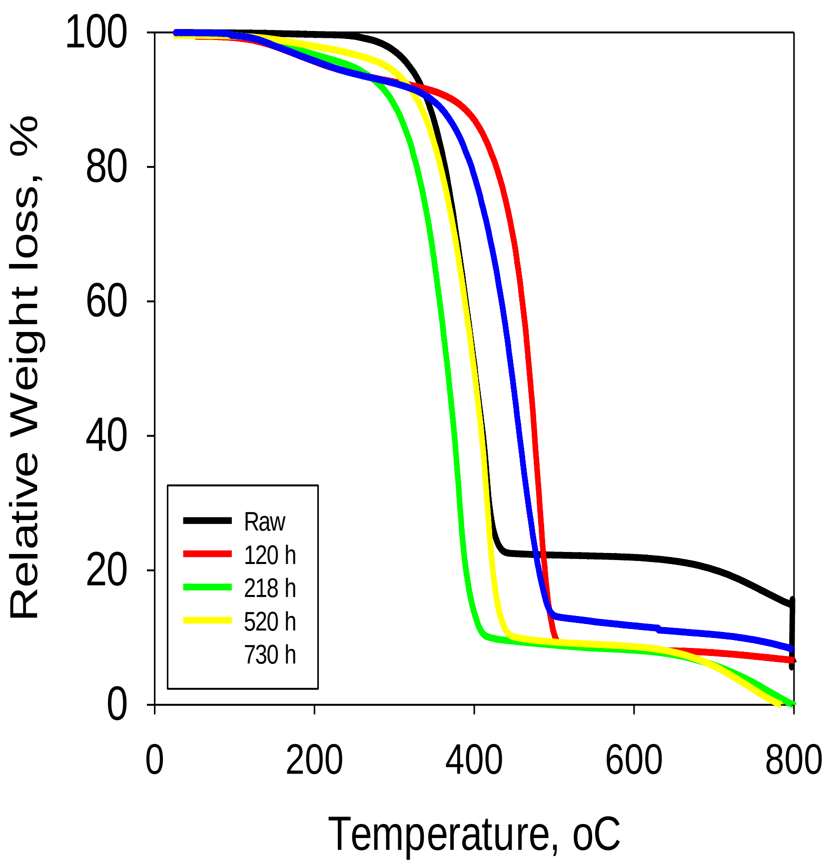


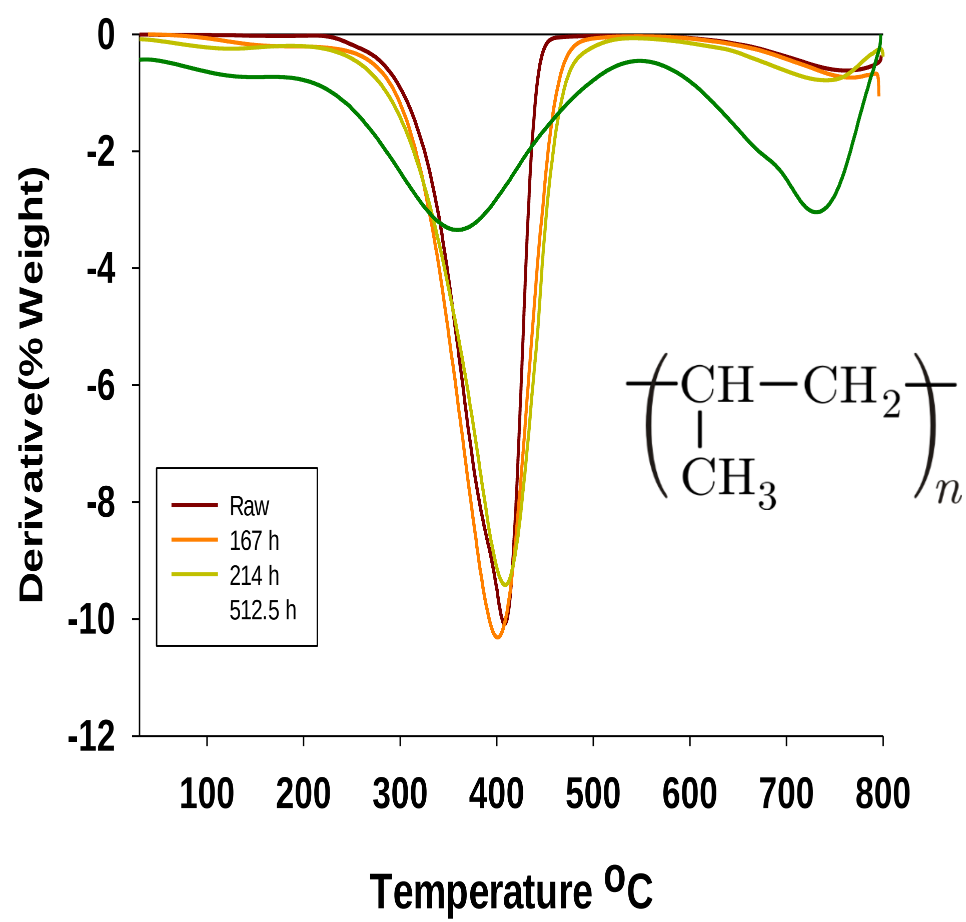


Barrier - Quality
Bio-Sensor – Safety
Gas sensor

30^{O}C hold for 1min, to 850^{O}C @ 10^{O}C/min, Air flow 20ml/min.

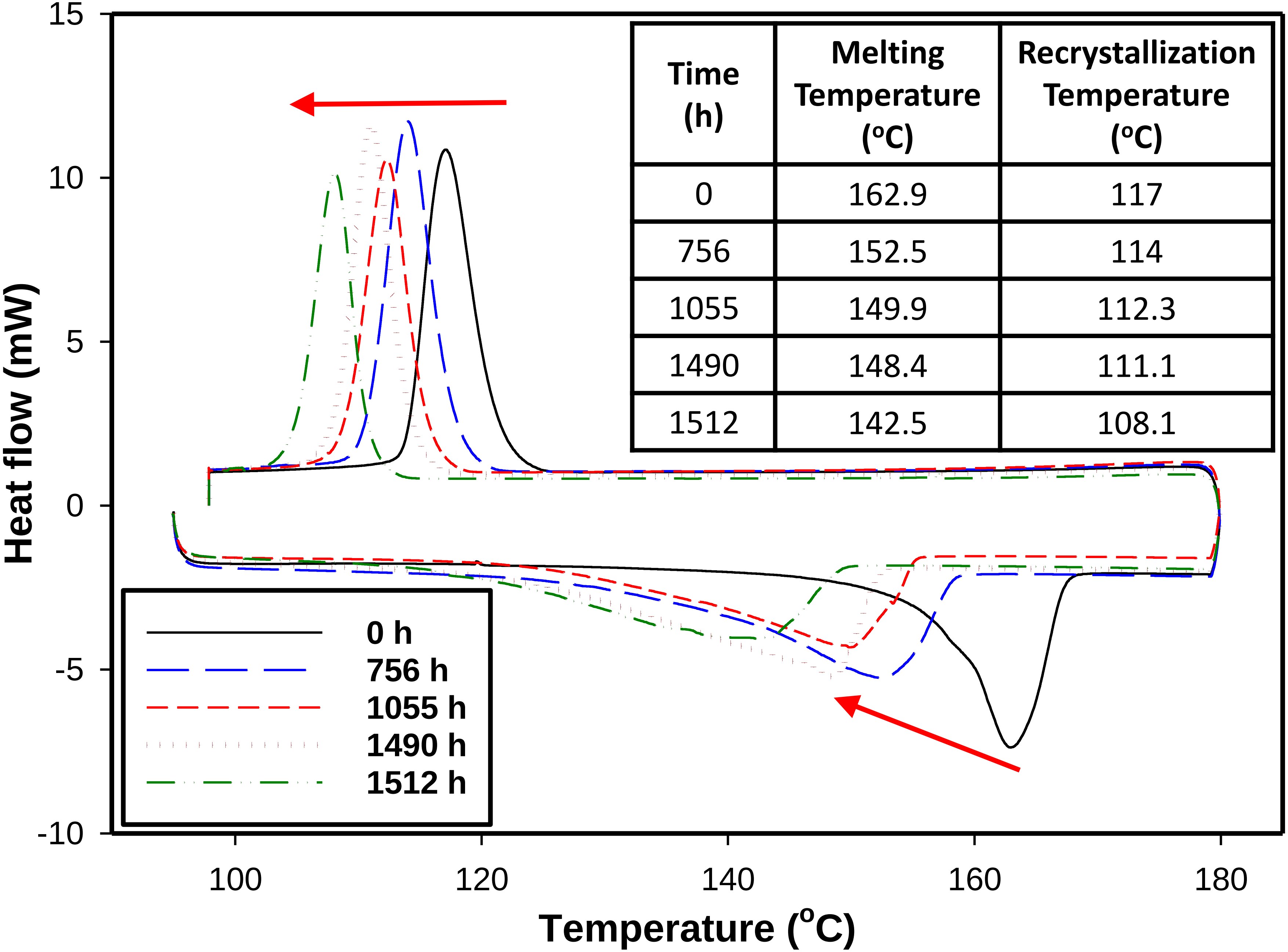
Thermal analysis to measure the Effect of Ozone on composite of Polypropylene with 8% CNF





Initially PP showed some increase in thermal stability initially, before it start to degrade.

DSC analysis for Solar aged P01 samples



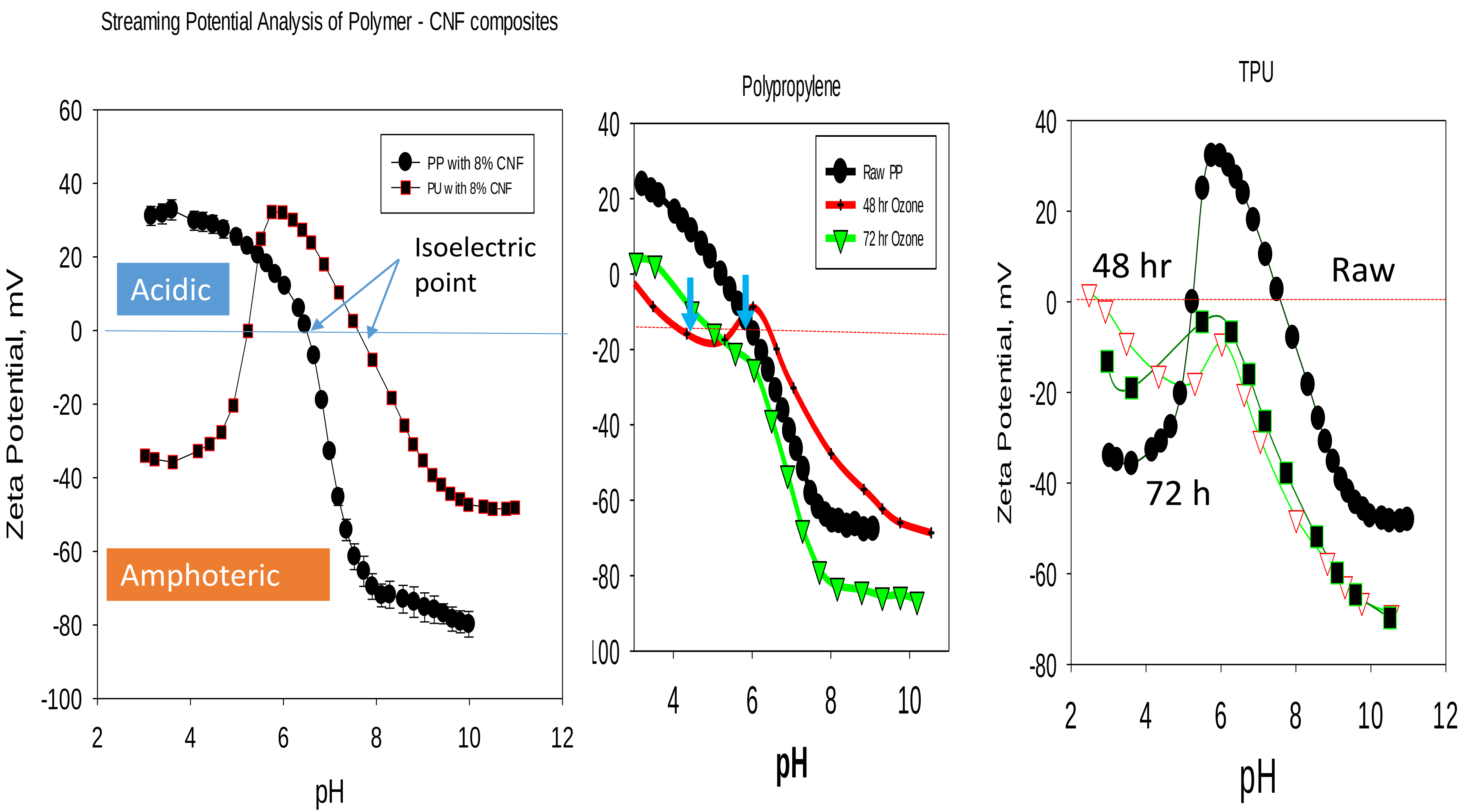
Time (h)	Melting Temperature (°C)	Recrystallization Temperature (°C)
0	162.9	117
756	152.5	114
1055	149.9	112.3
1490	148.4	111.1
1512	142.5	108.1

Measuring Weathering of Nano-Composites

Physical and Structural Properties

- **Surface Charge – Streaming potential**
- **Atomic Force Microscopy (AFM)**
- **X-ray Diffraction Analyzer**

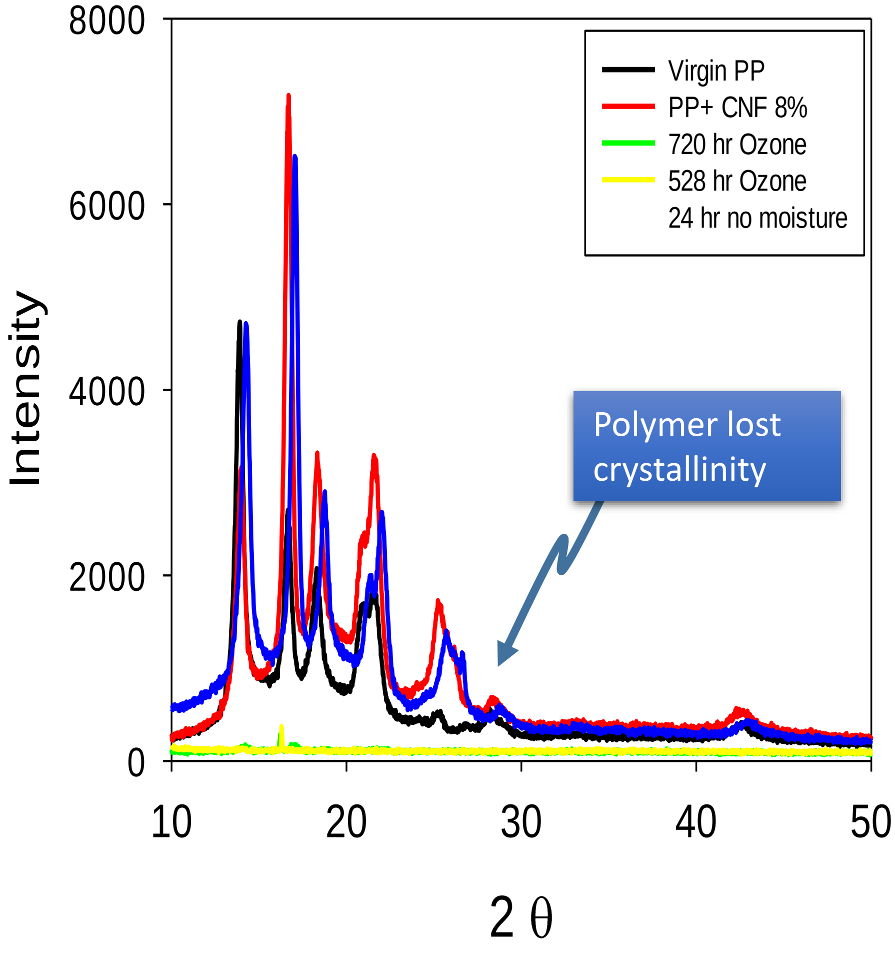
Changes in surface charge during Ozone aging of Nanocomposite polypropylene and polyurethane



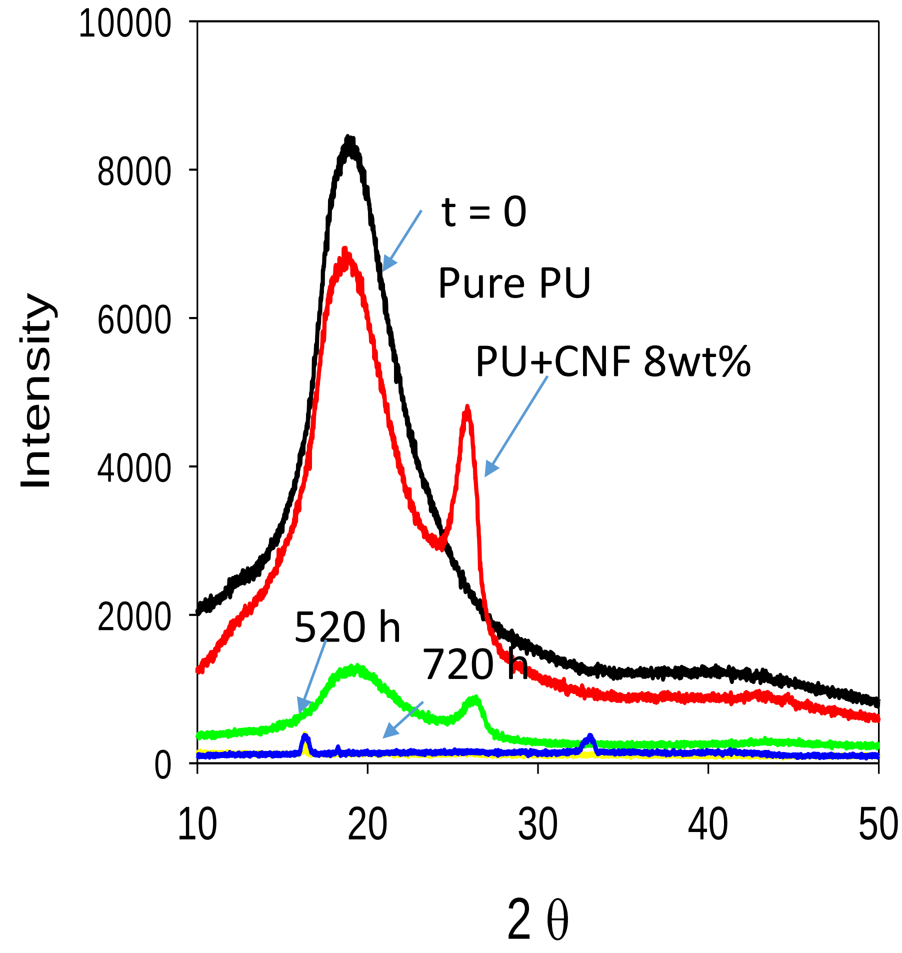
Changes in surface charge after 24 h & 48 h

X-ray diffraction analysis of weathered CNF composites

XRD measurement of Polypropylene during Weathering

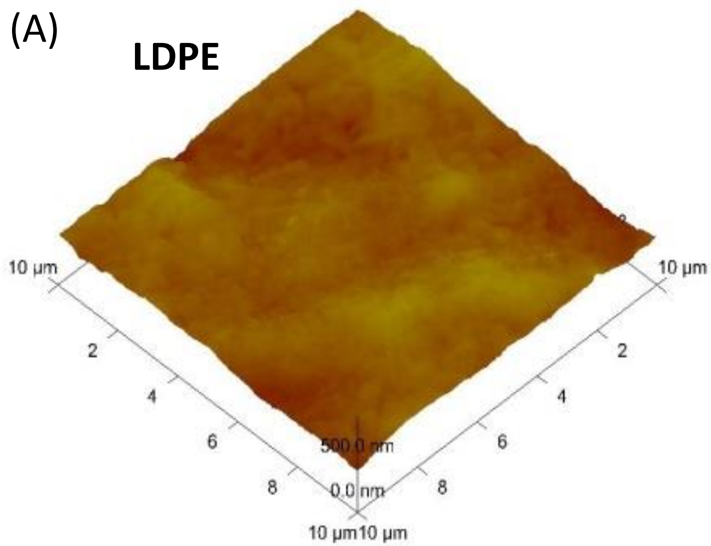


Loss of Polyurethane crystalline structure during Ozone weathering



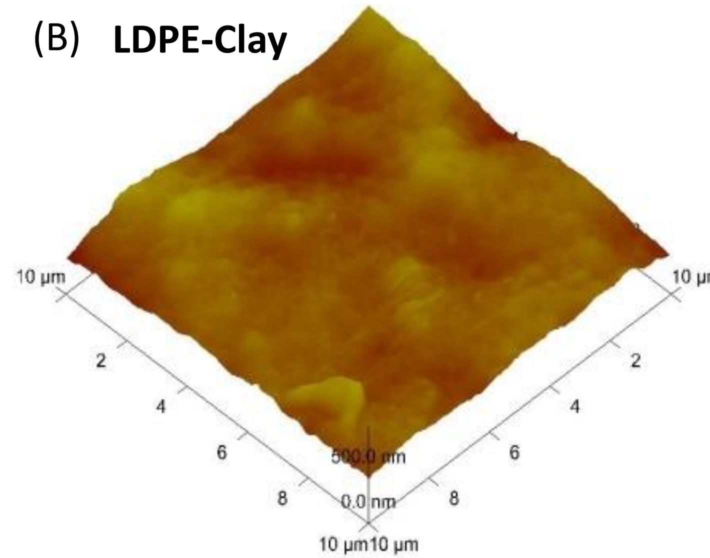
Atomic Force Microscopy images of pristine and aged Polyethylene Nanoclay filled PE food packaging films

(A) **LDPE**



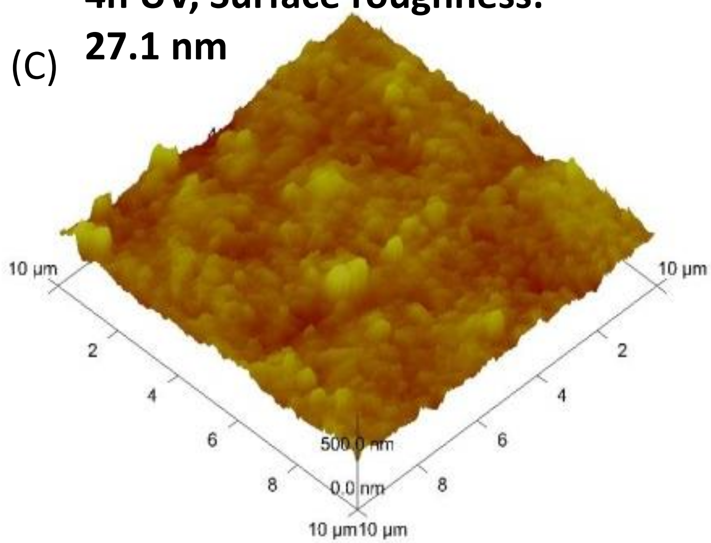
4h UV, Surface roughness: 27.1 nm

(B) **LDPE-Clay**



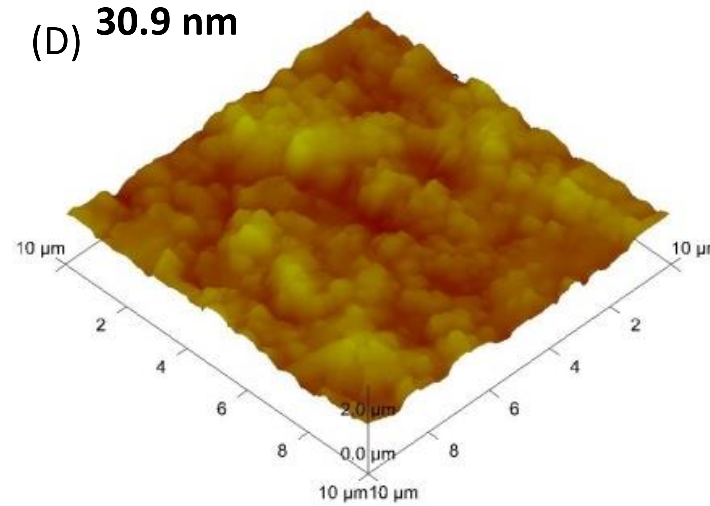
4h UV, Surface roughness: 30.9 nm

(C)



100h UV, Surface roughness: 38.7 nm

(D)



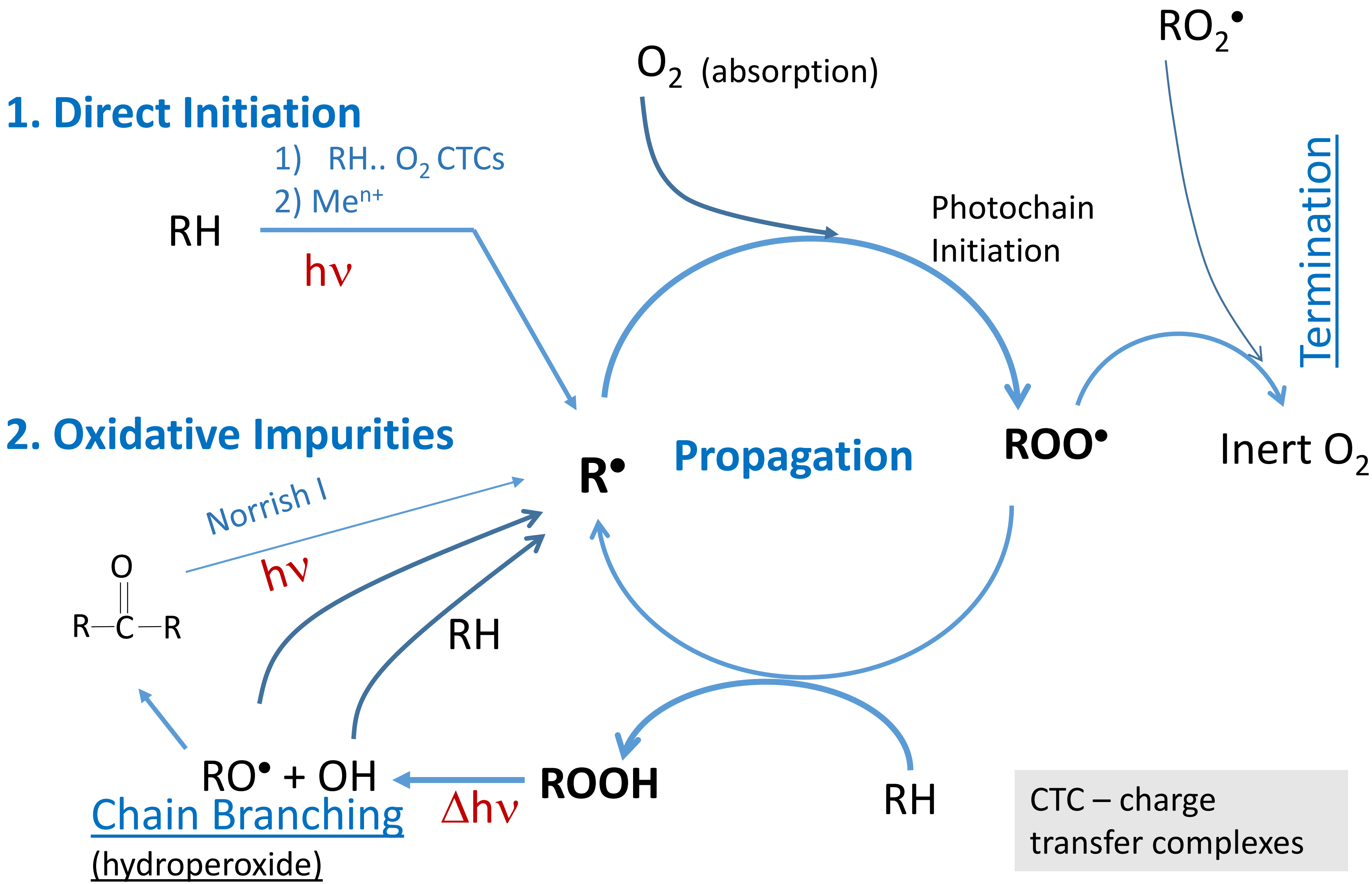
100h UV, Surface roughness: 173.0 nm

Measuring Weathering of Nano-Composites

Chemical Properties

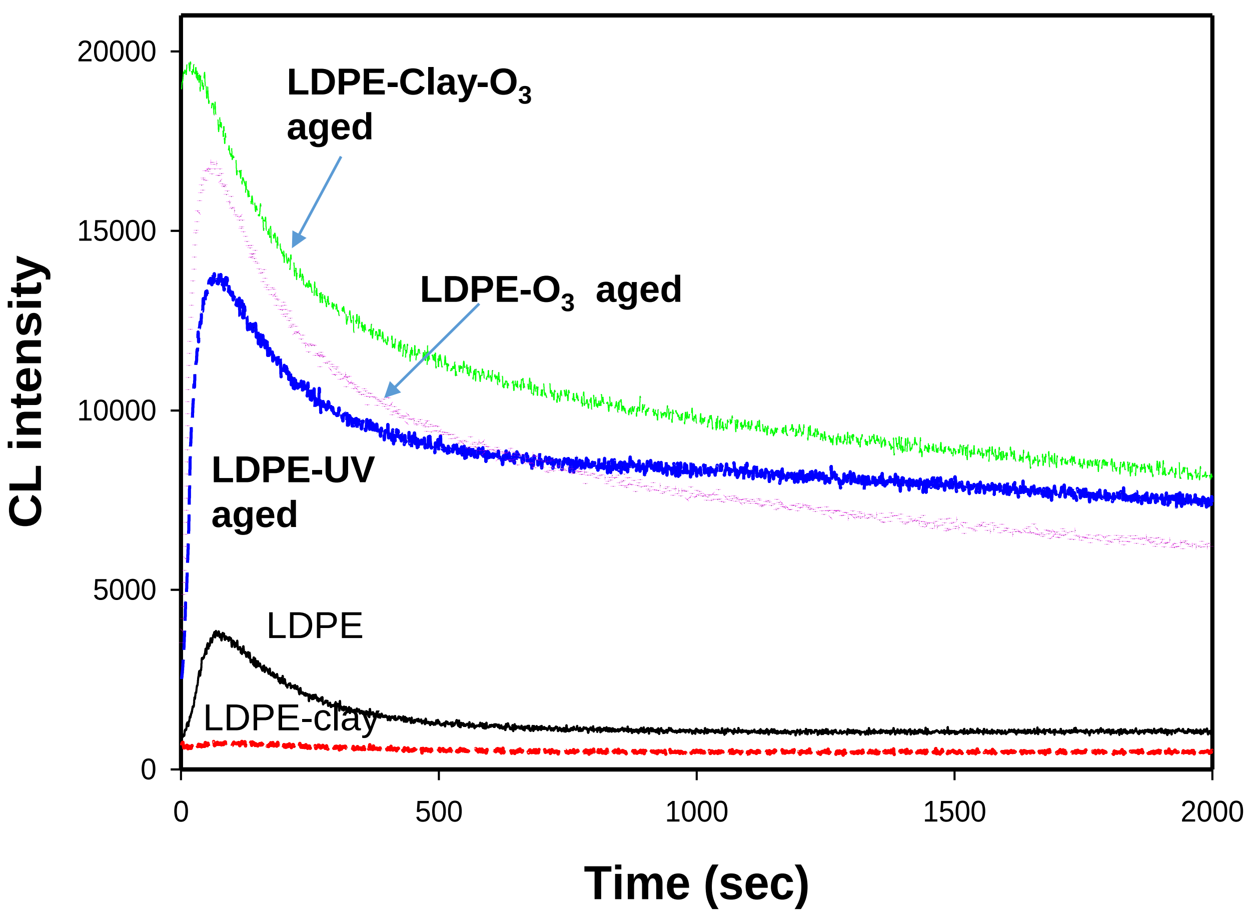
- **Chemiluminescence Analyzer (CL)**
- **Infrared Spectroscopy(FTIR)**

Photooxidation of polymers: Chain and Photochain Mechanism



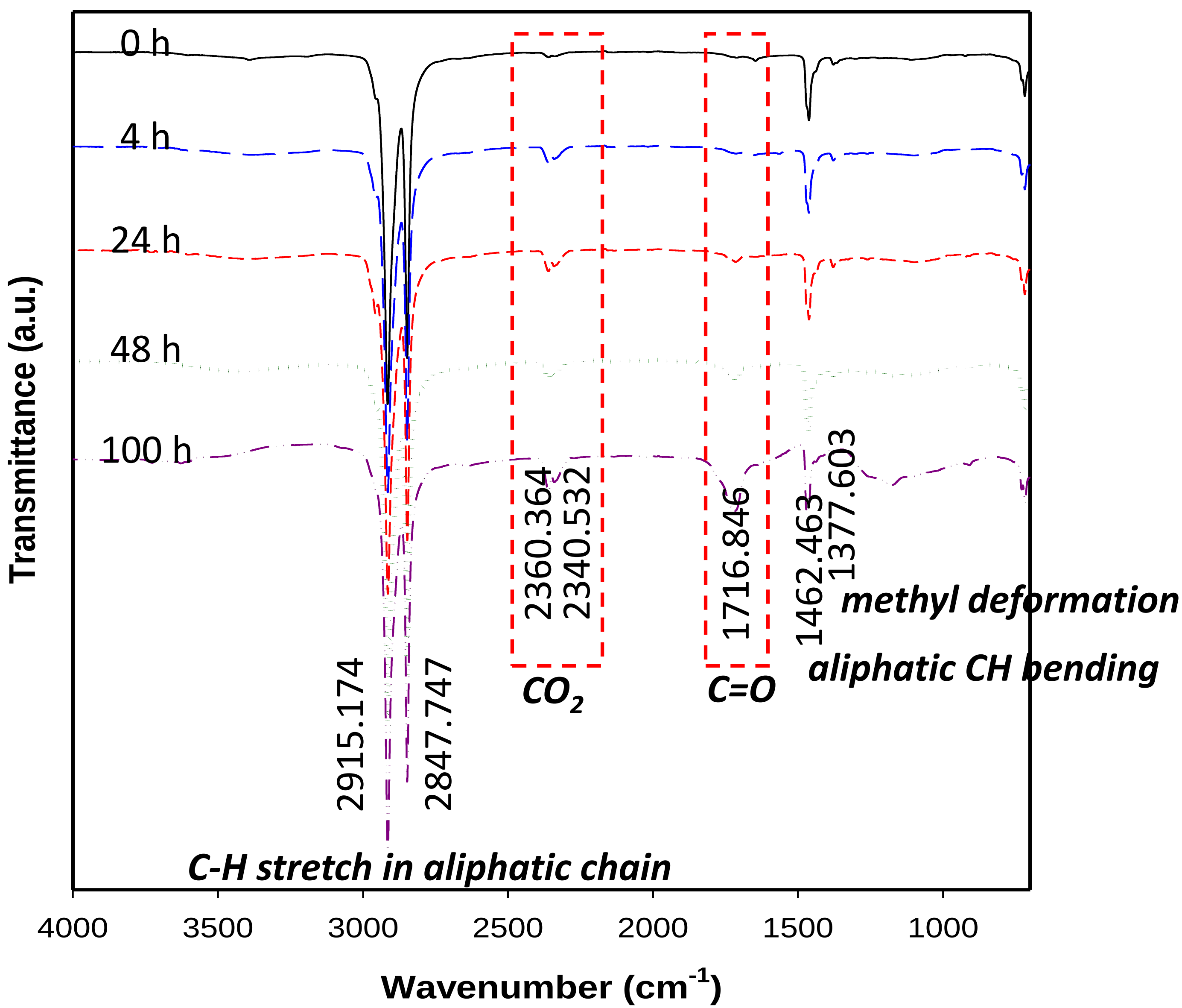
CTC – charge transfer complexes

Isothermal chemiluminescence results for pristine and clay composite LDPE before and after aging

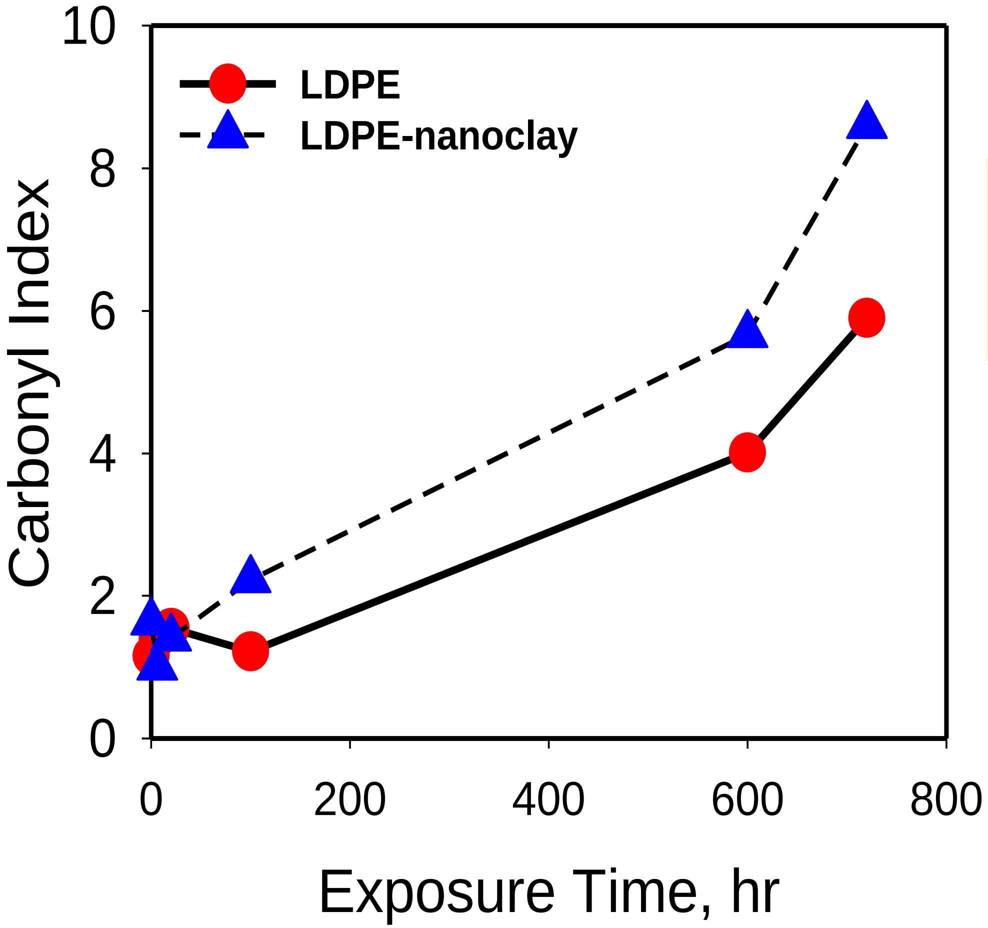


Clay composites showed higher chemiluminescence intensity due to the direct oxidation of the polymer additives giving The rate of oxidative attack is then related to the intensity of the signal and the molar mass of radicals formed.

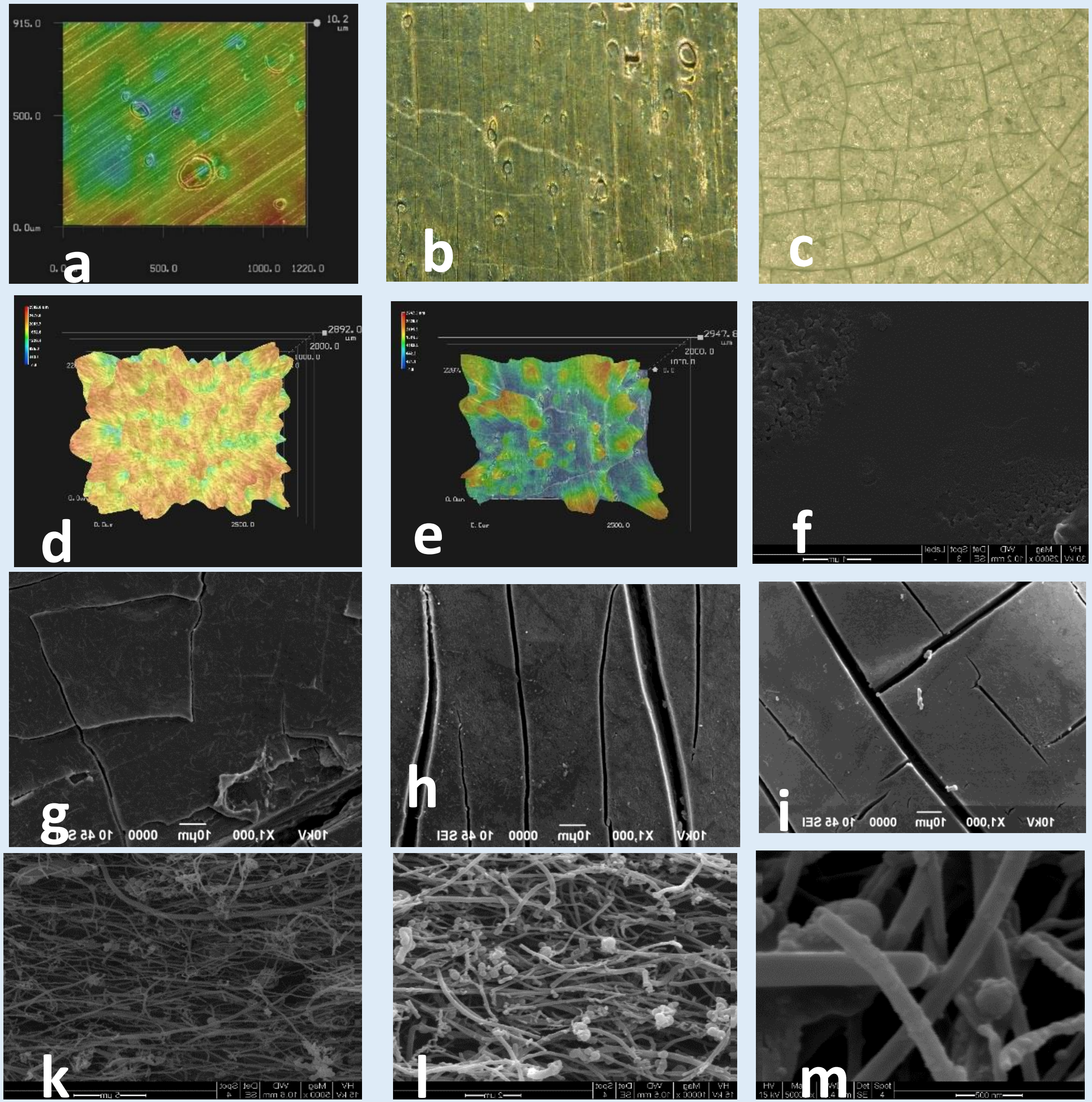
Fourier Transfer Infrared Spectroscopy of aged LDPE



Comparing Carbonyl Index for Ozone exposed pure- and clay-enforced polyethylene



$$Carbonyl\ Index\ (CI) = \frac{Absorption\ at\ 1740\ cm^{-1}}{Absorption\ at\ 2020\ cm^{-1}}$$



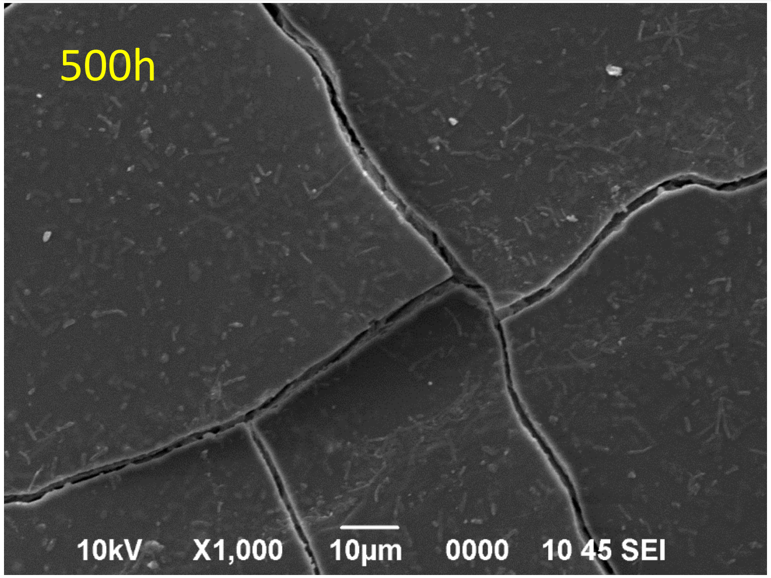
Optical image

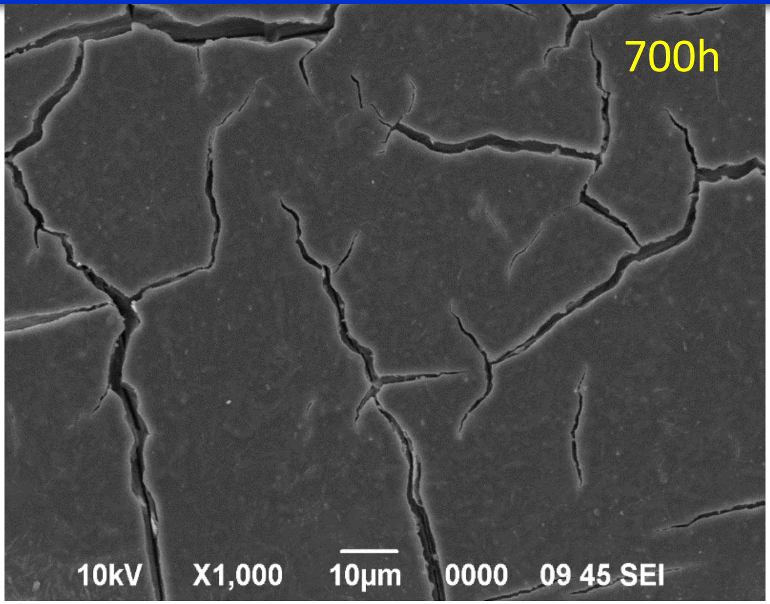
3-D Optical
Surface
morphology

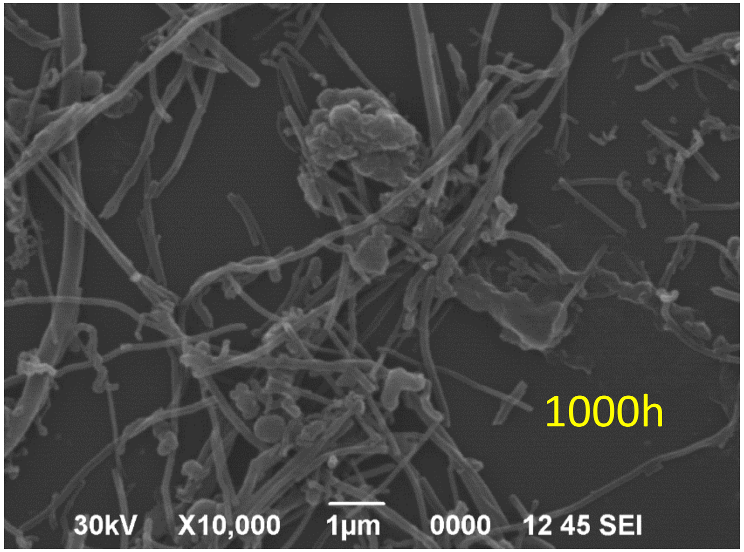
SEM Image
g- 120 h
h, i – 220 h

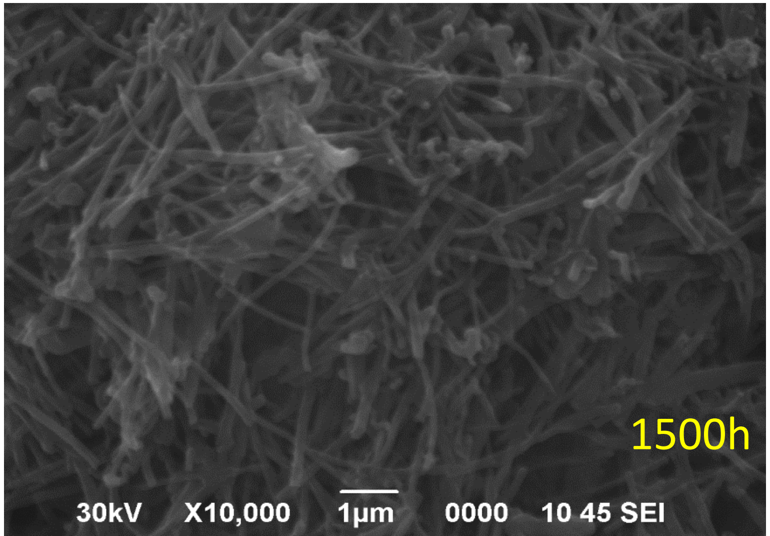
SEM Image
k - 300 h
l,m – 550, 720 h

Scanning Electron micrograph of UV aged Nylon with 2% CNT



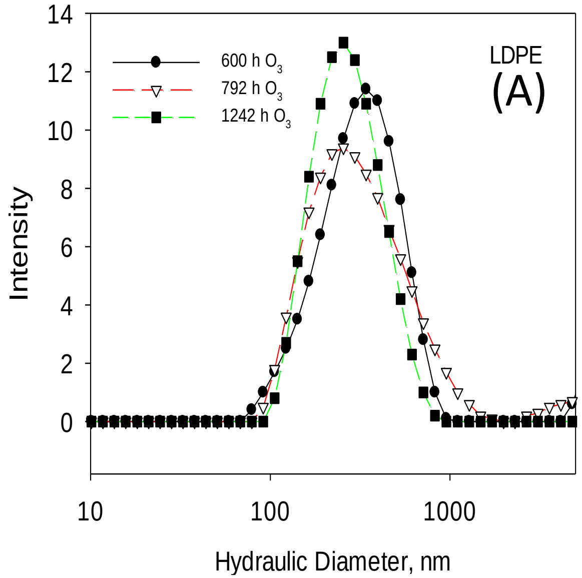


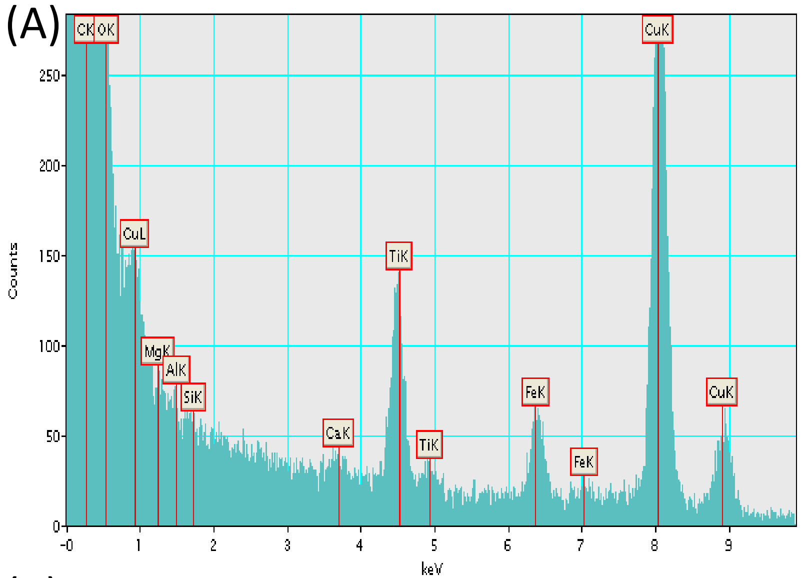


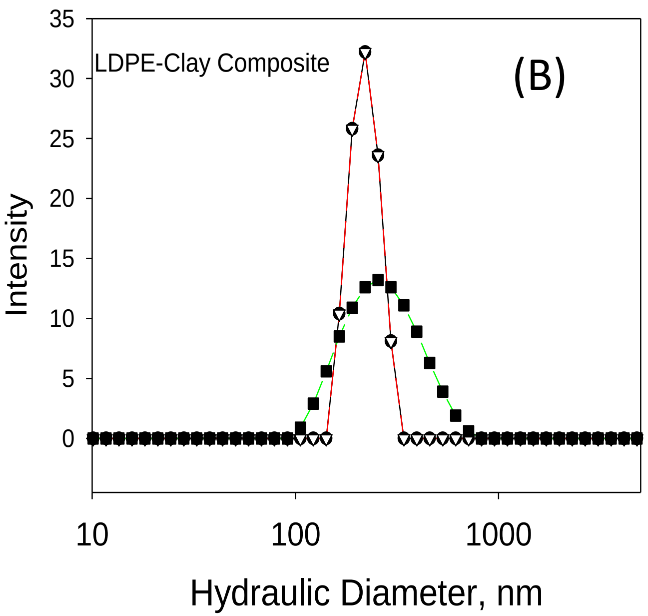


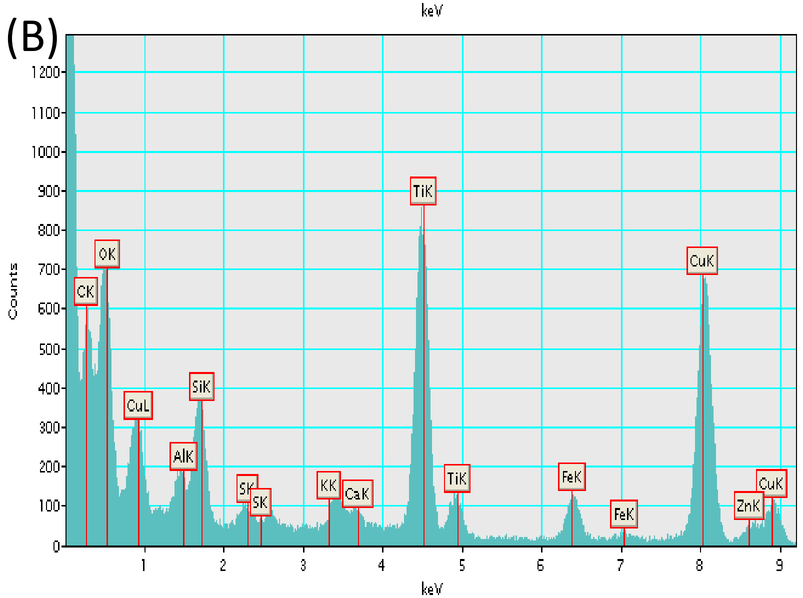
Measuring Release nanoparticles from of Nano-Composites

Composite and Size distribution of Nanoclay released from Polymer Matrix

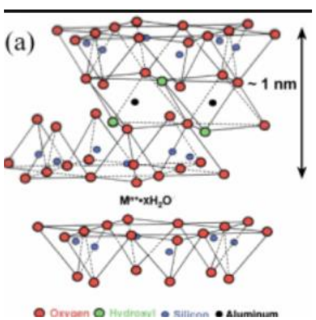




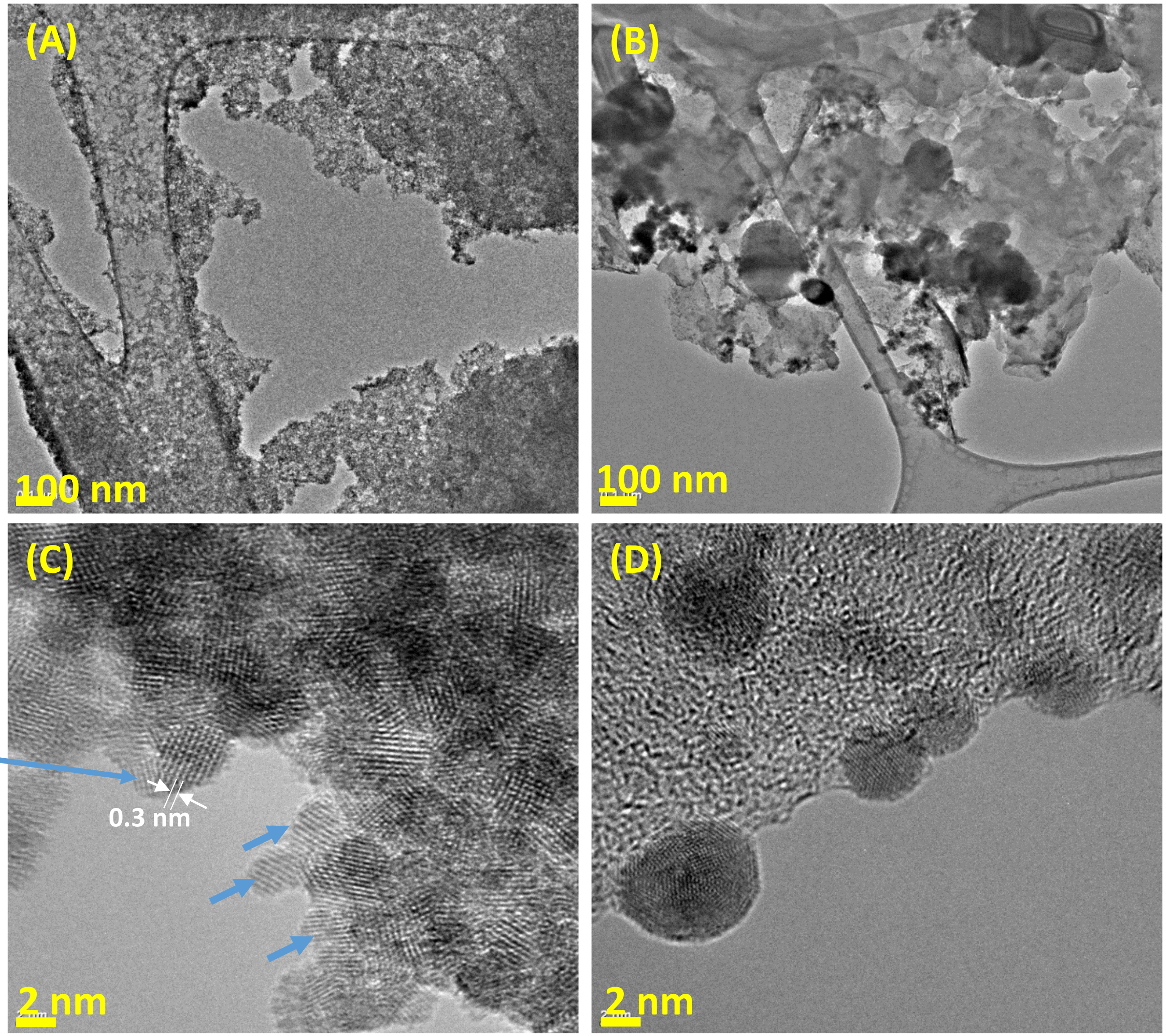




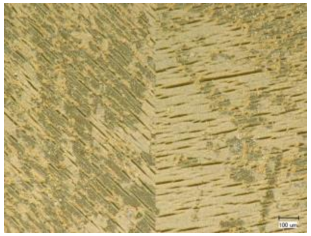
Transmission Electron Microscopy of nanoclay particles released form washed aged polyethylene composite



Layered clay



Composition of Clay NP released from food packaging



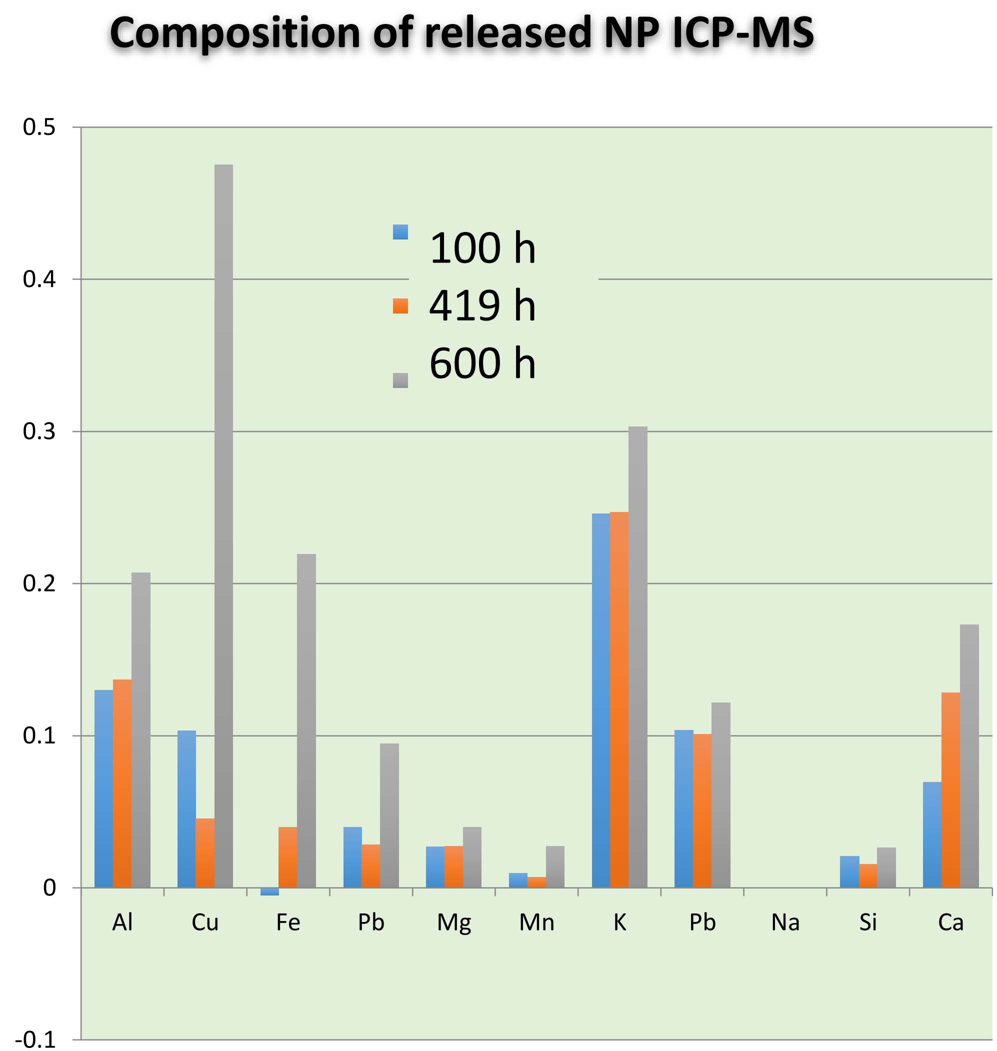
Aged LDPE sample

Measured area sample

Sonicate in ID Water

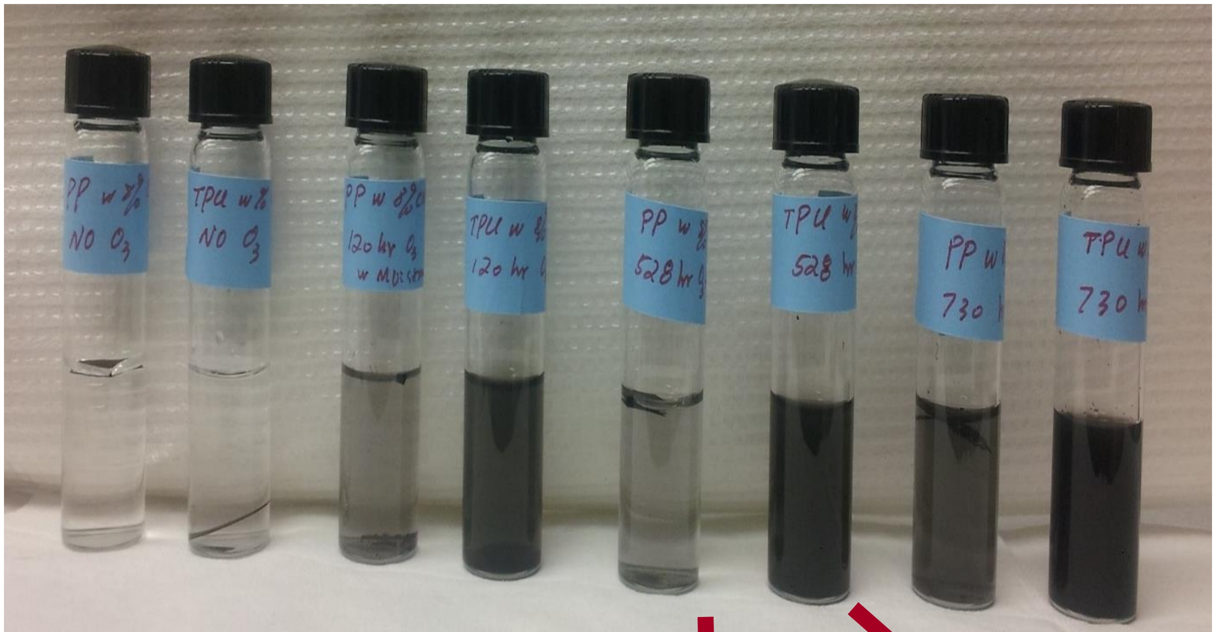
Dry

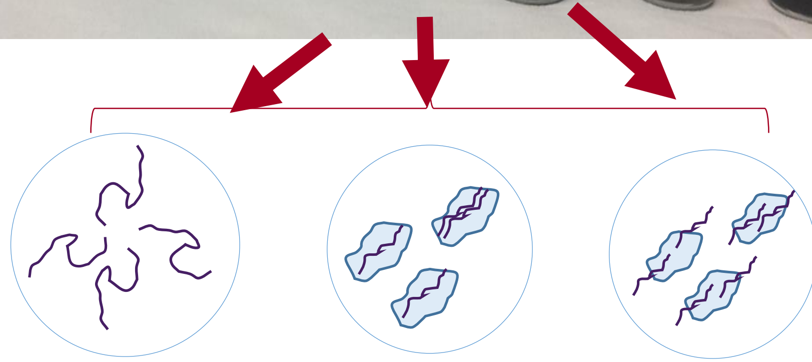
MW Acid digest remaining solid EPA method 3015-8



Washed/sonicated samples of Weathered Polyurethane and Polypropylene

Sample from Increased Aging oxidation

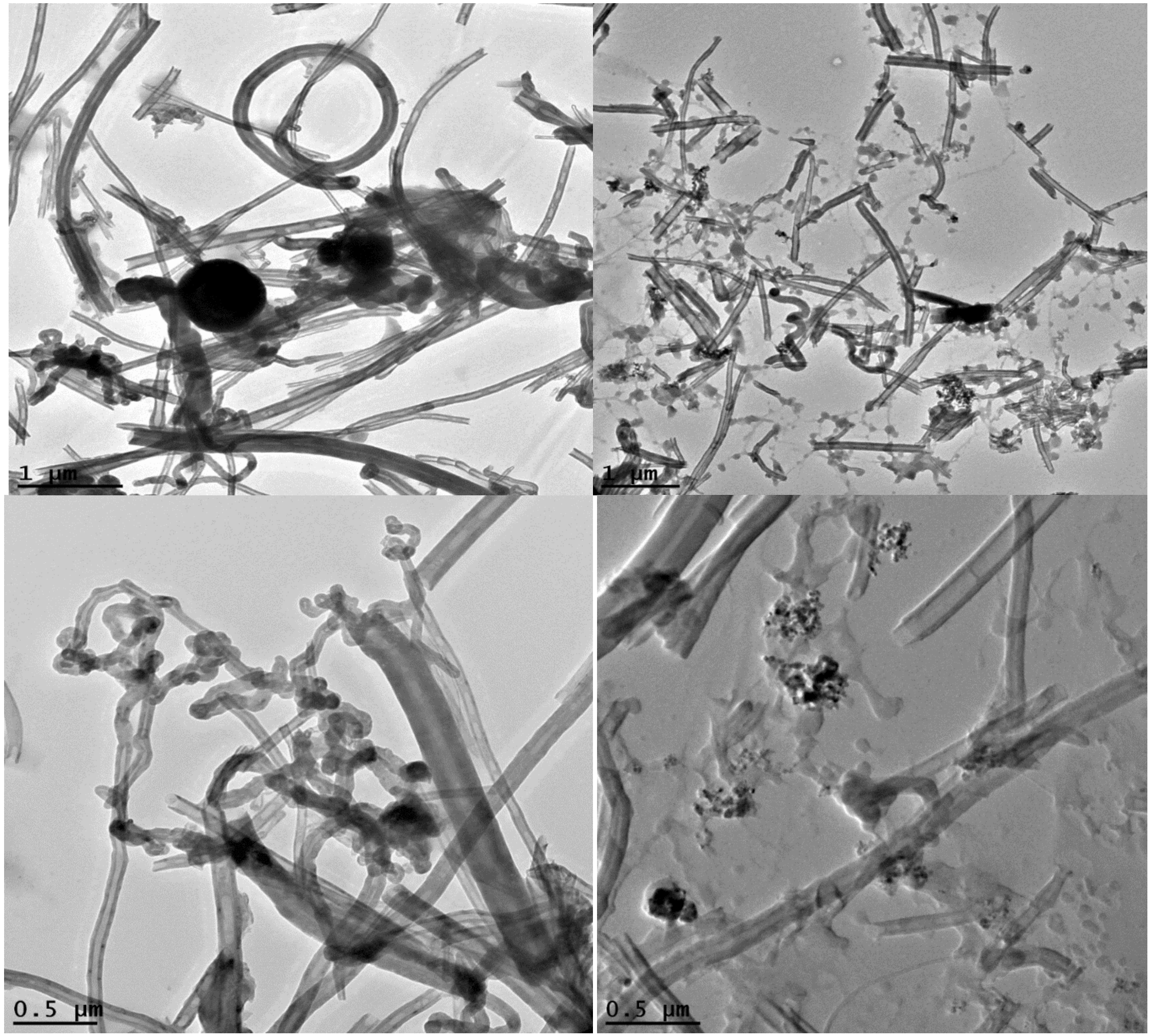




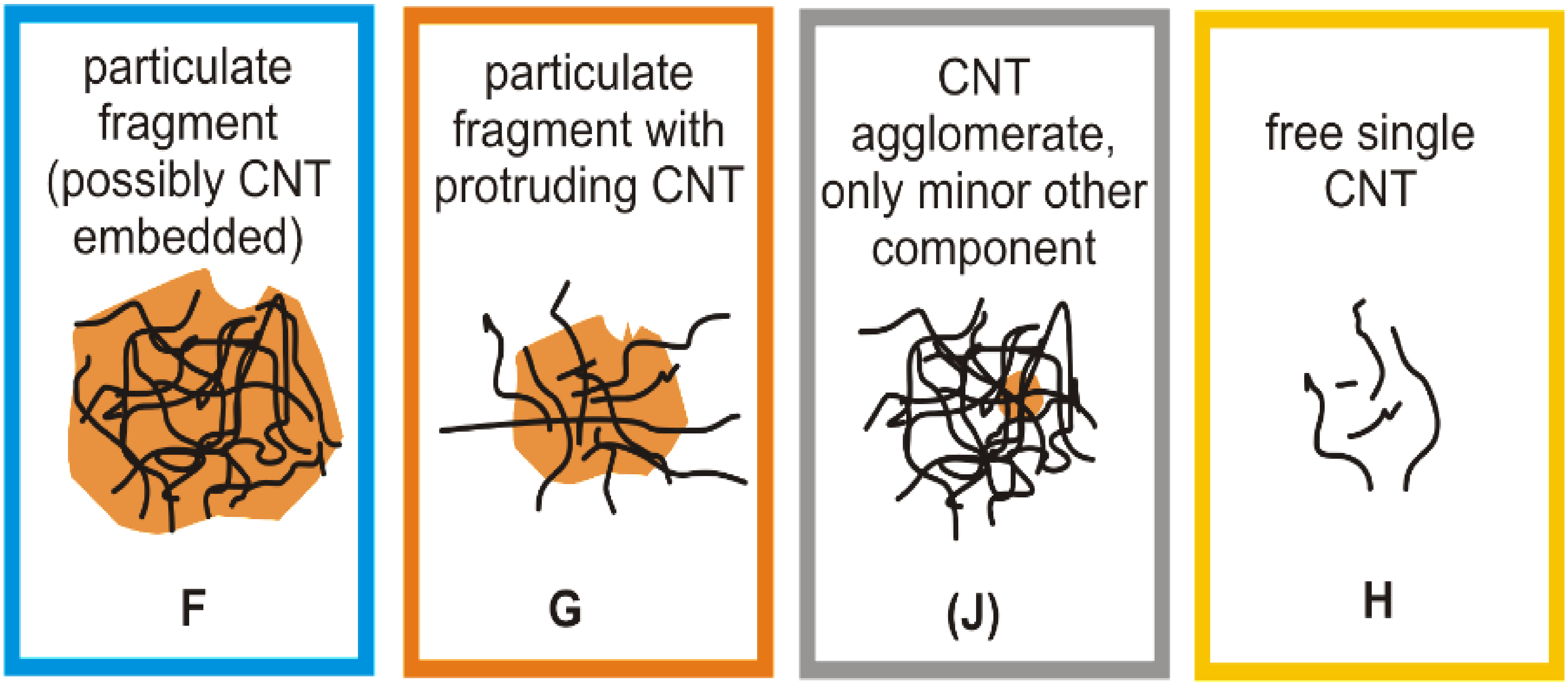
A B C

Does the wash liquid release CNF/CNT?

Carbon nanofiber released into the wash water of aged polypropylene

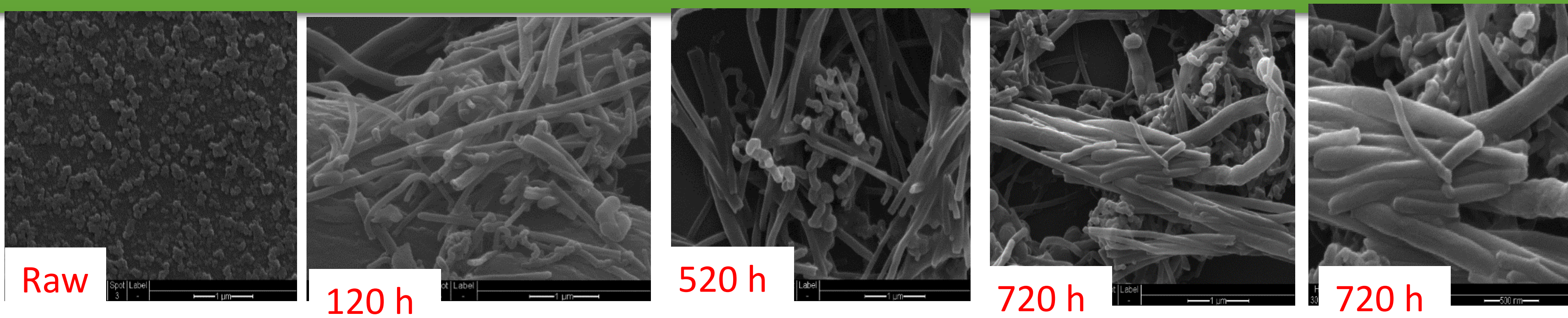


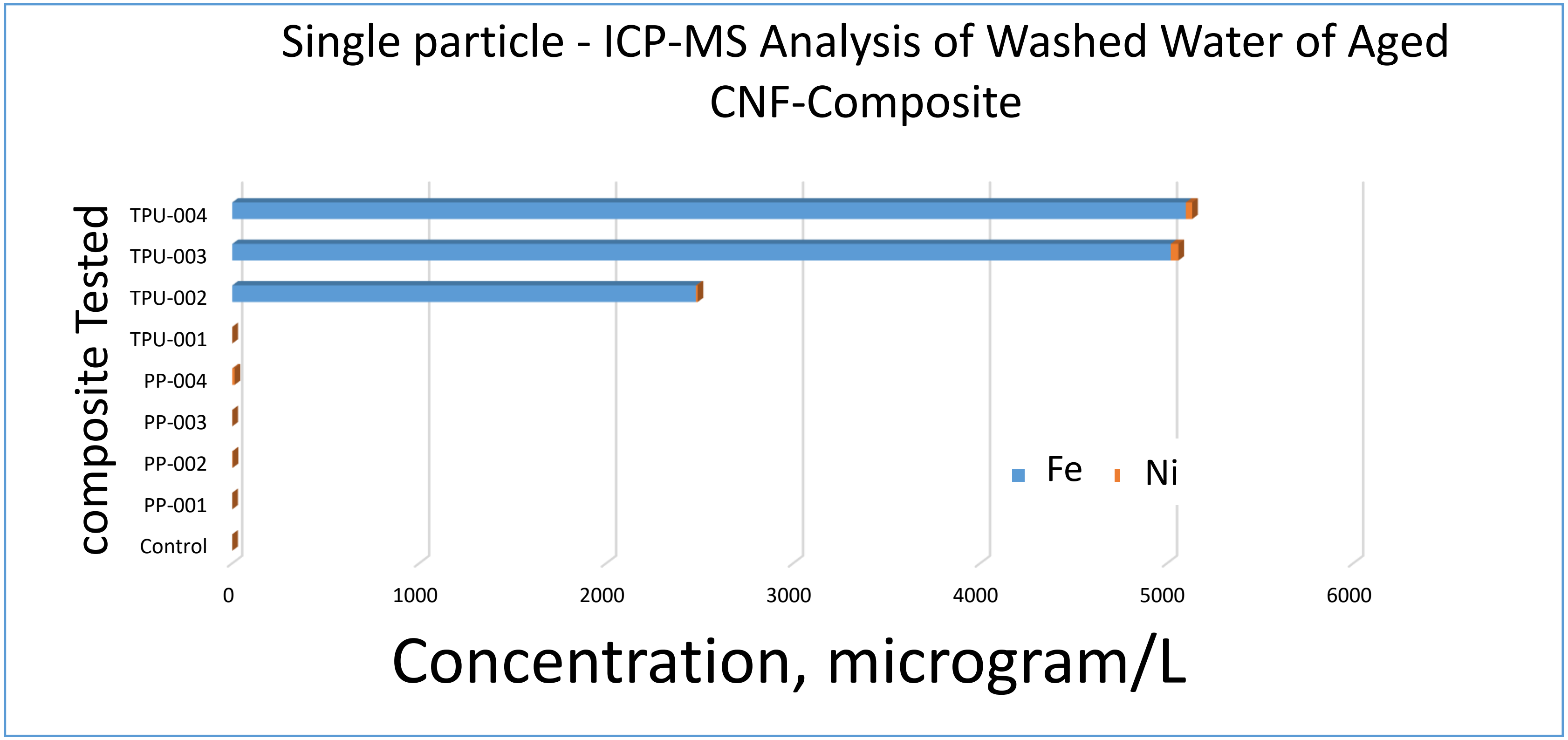
Characteristics of Released Particles



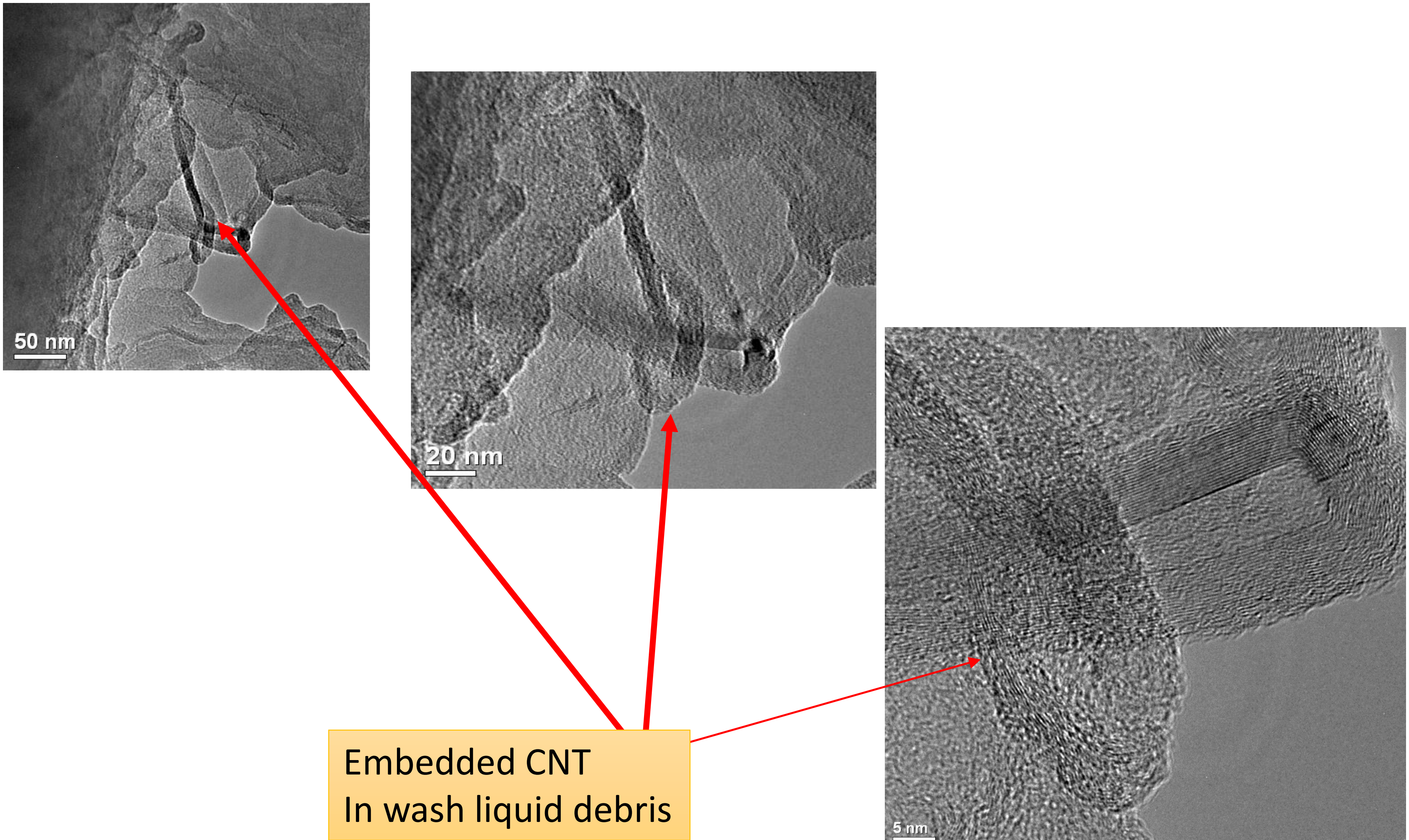
F - H as in the release systematics by Harper et al. 2015

CNF in Water Samples from aged TPU/8%CNF

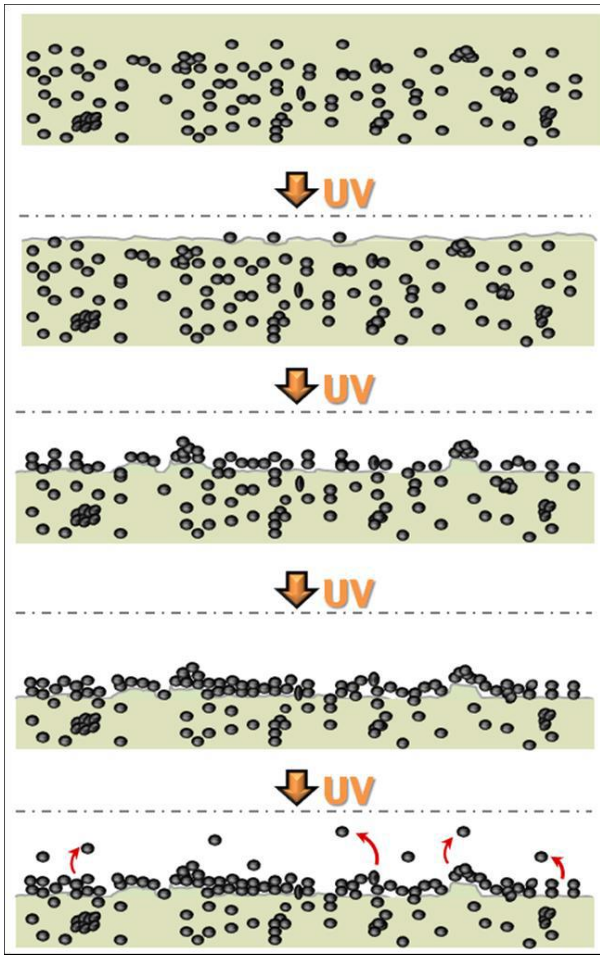


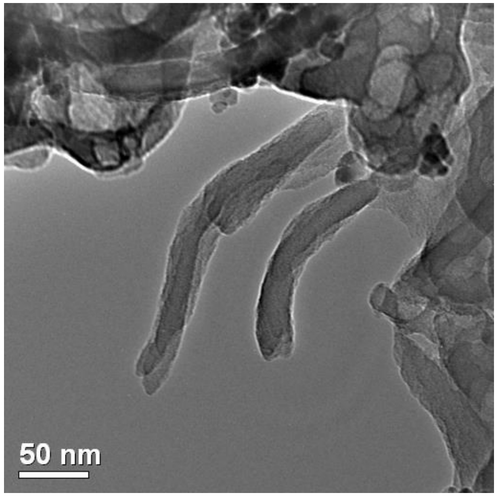


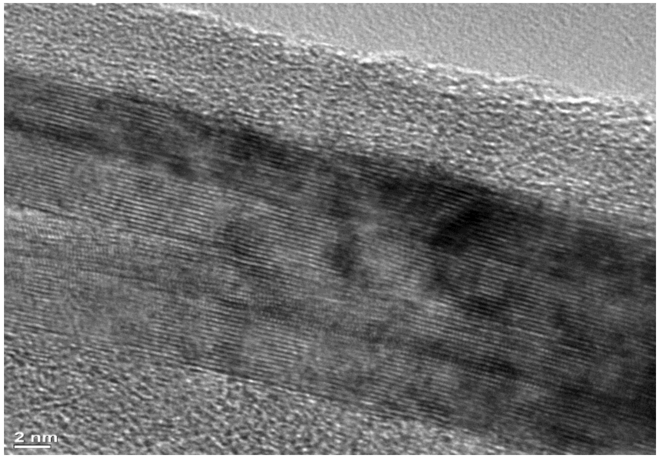
TEM image of Wash Sample of polyamide composite micro-plastic

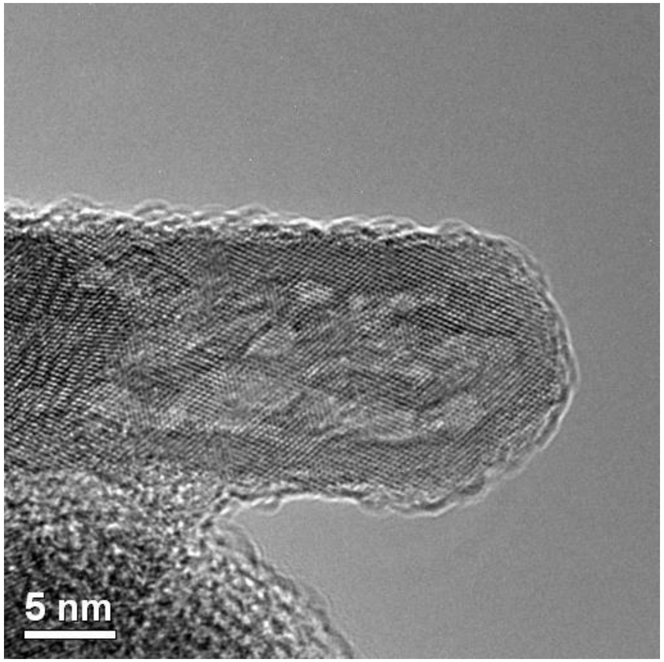


TEM image of Wash Sample of polyamide composite micro-plastic

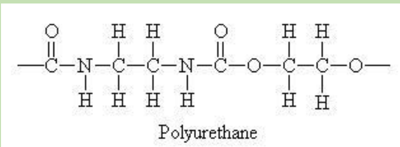
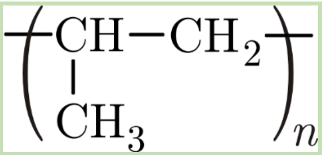
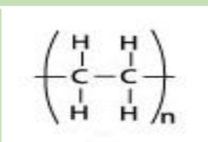
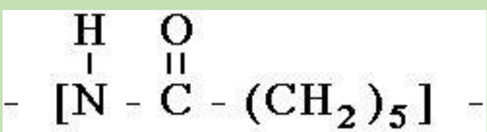
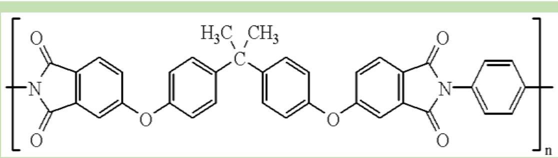






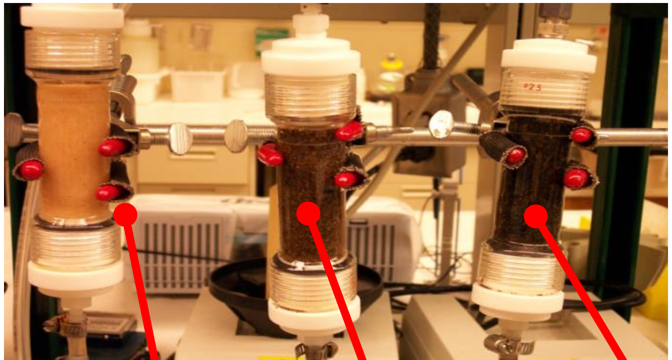


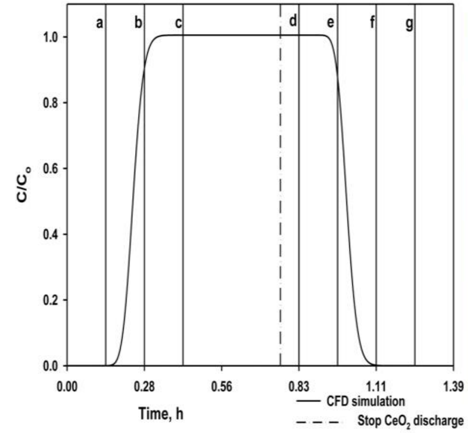
Summary of Weathering Tests

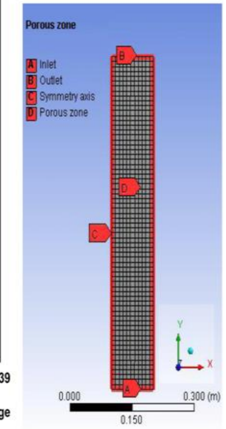
Polymer		Additive	Aging	Nanorelease
	Polyurethane	CNT/CNF		Yes
	Polypropylene	CNF / CNT	High	Yes
	Polyethylene	Nano-clay (2-6%)	medium	May be
	Nylon 6 (Polyamide)	CNT	Low	Not detected
	Ultem® 1000 Polyetherimid	CNT	Little	Not detected

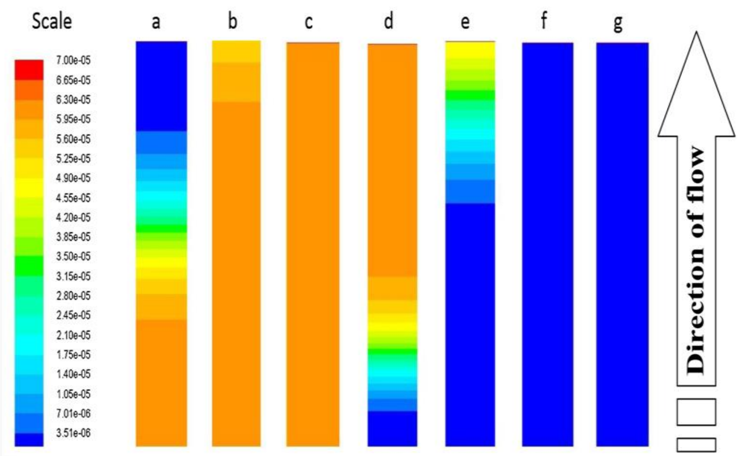
Polymer composites of different chemical structure vary remarkably in their resistance of degradation. Polyolefin and polyurethane composites not suitable for outdoor use.

Nanoparticles flow through sand filters









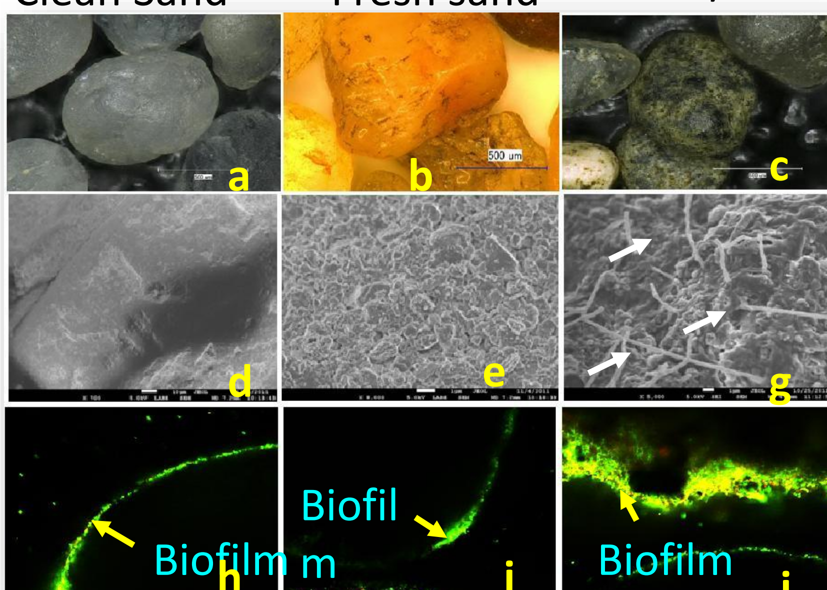
Used sand/Biofilm

Images | Clean Sand | Fresh sand

Optical Microscopic

SEM

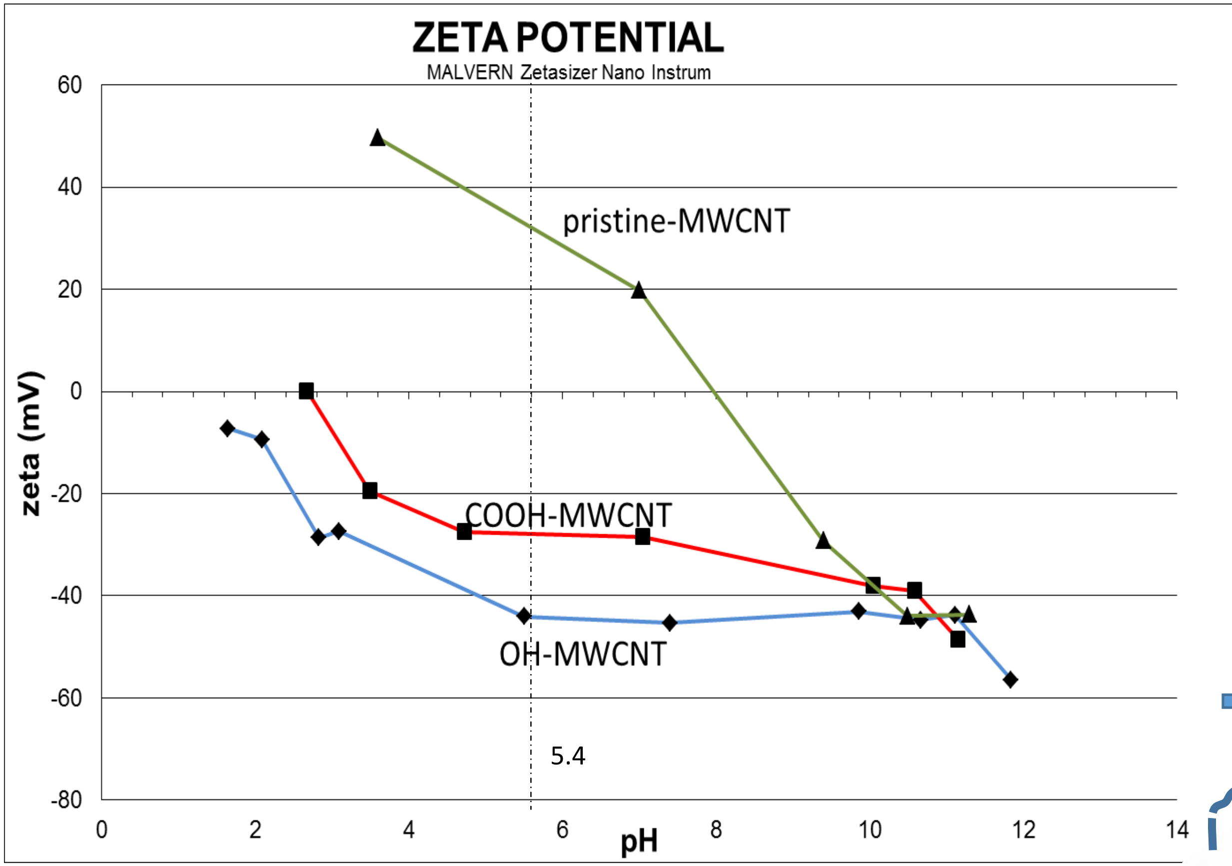
Laser Confocal Scanning Microscopy

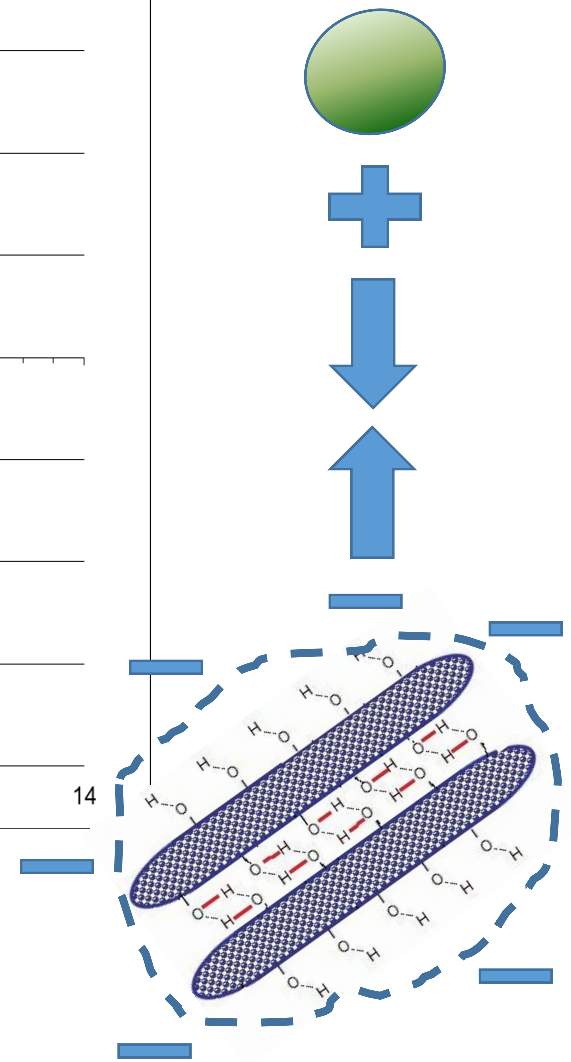


Computational Fluid Dynamics modeling of transport of nanoparticles through a porous media

A. Hassan, Sahle-Demessie, et. al, J. Hazard. Materials, *244–245*, *251-25* 2013.

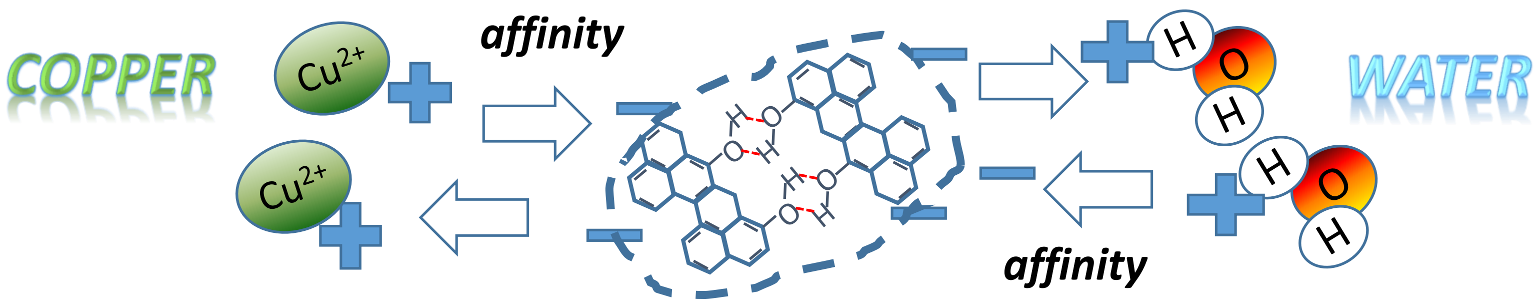
Surface charge of MWCNT

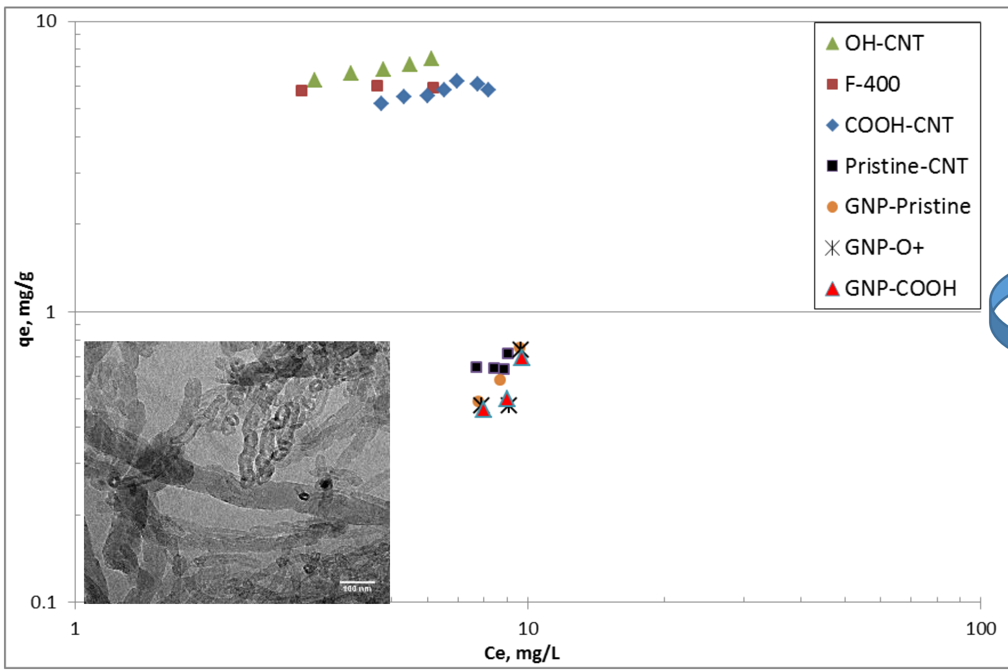




Isotherm curves for Carbonaceous Adsorbents

COPPER INITIAL CONCENTRATION 10 mg/L – 2 DAYS EXPERIMENT DI WATER pH 5.1



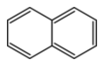
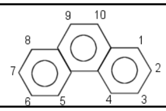
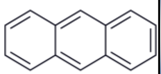
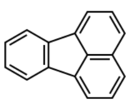
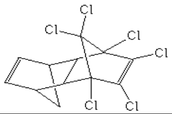
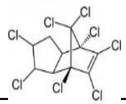
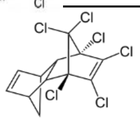


Carbonaceous Adsorbent	Freundlich parameters		
	K_F	1/n	R^2
F-400	5.557	0.037	0.548
OH-CNT	4.628	0.251	0.997
COOH-CNT	3.245	0.306	0.972
Pristine-CNT	0.175	0.636	0.997
GNP-pristine	0.006	2.107	0.978
GNP-O+	0.005	2.206	0.567
GNP-COOH	0.004	2.226	0.834

higher uptake of copper by OH-CNT in a shorter time than for activated carbon

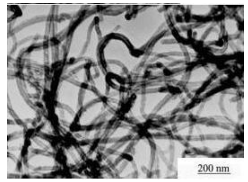
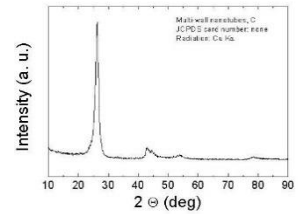
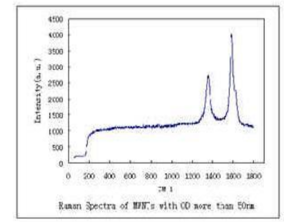
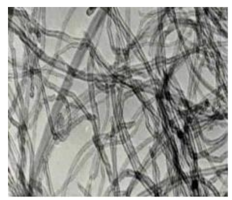
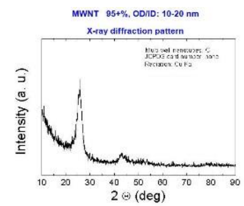
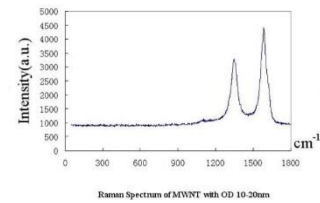
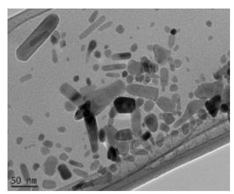
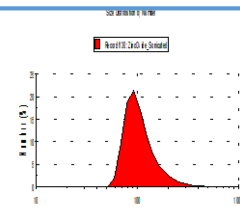
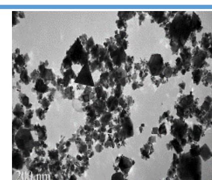
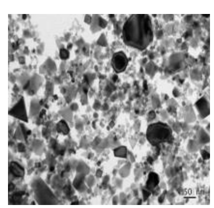
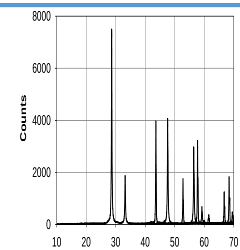
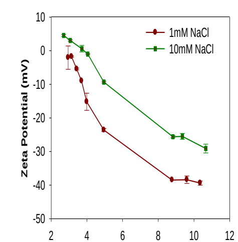
*Rozenzwig, Sahle Demessie Water Air Soil Pollution (**2014**) 225:1913,*
*J. Hazardous Materials, **2014**, Volume 279, 30 August 2014, Pages 410–417.*
*Chemosphere, Volume 90, Issue 2, January **2013**, Pages 395-402.*

Properties of selected pollutants

Compound	Mole weight g mole^{-1}	Boiling point °C	Water solubility mg l^{-1}	Log K_{ow}	Toxicity	LC_{50} [1)]
Naphthalene 	128	218	31.7	3.5	Human toxic	3.8
Phenanthrene 	178	339	1.29	4.45	PBT	0.6
Anthracene 	178	340	0.075	4.46	Ecotoxic	4.46
Flouranthene 	202	375	0.26	4.90	carcinogen	0.5
Heptachlor 	178	340	0.075	4.46	Ecotoxic	4.46
Chlordane 				6.32		
Aldrin 	364		0.003%	6.5		

[1)] *Neanthes arenaceodentata* expressed as $LC_{50\ 96h}$ I mg l^{-1} (Cerniglia, 1992; Rossi and Neff, 1978)

NPs Tested for Adsorption study

MWCNT ID = 5-15 nm, ρ = 0.18 g/ml OD>50 nm, L= 30 nm				
MWCNT-COOH ID = 5-15 nm, ρ = 0.22 g/ml OD= 20-30 nm, L = 30				
ZnO, Mean = 50 nm, Mode = 91 nm		 – Dynamic Light Scattering		
TiO_2				
CeO_2				

Simulated NP-Dissolved partition of hydrophobic pollutants

$$Pollu_{Free} + NP \leftrightarrow Pollu_{NP} \ldots\ldots\ldots (1)$$

Partition Coefficient of pollutant between NP and dissolved phase

$$K_{NP} = \frac{[POllu]_{NP}}{[POllut]_{Free}\ [NP]}, \quad \text{(ml/g)}\ldots\ldots(2)$$

Mass balance of pollutant:

$$[Pollu]_{tot} = [Pollu]_{Free} + [Pollu]_{NP}$$

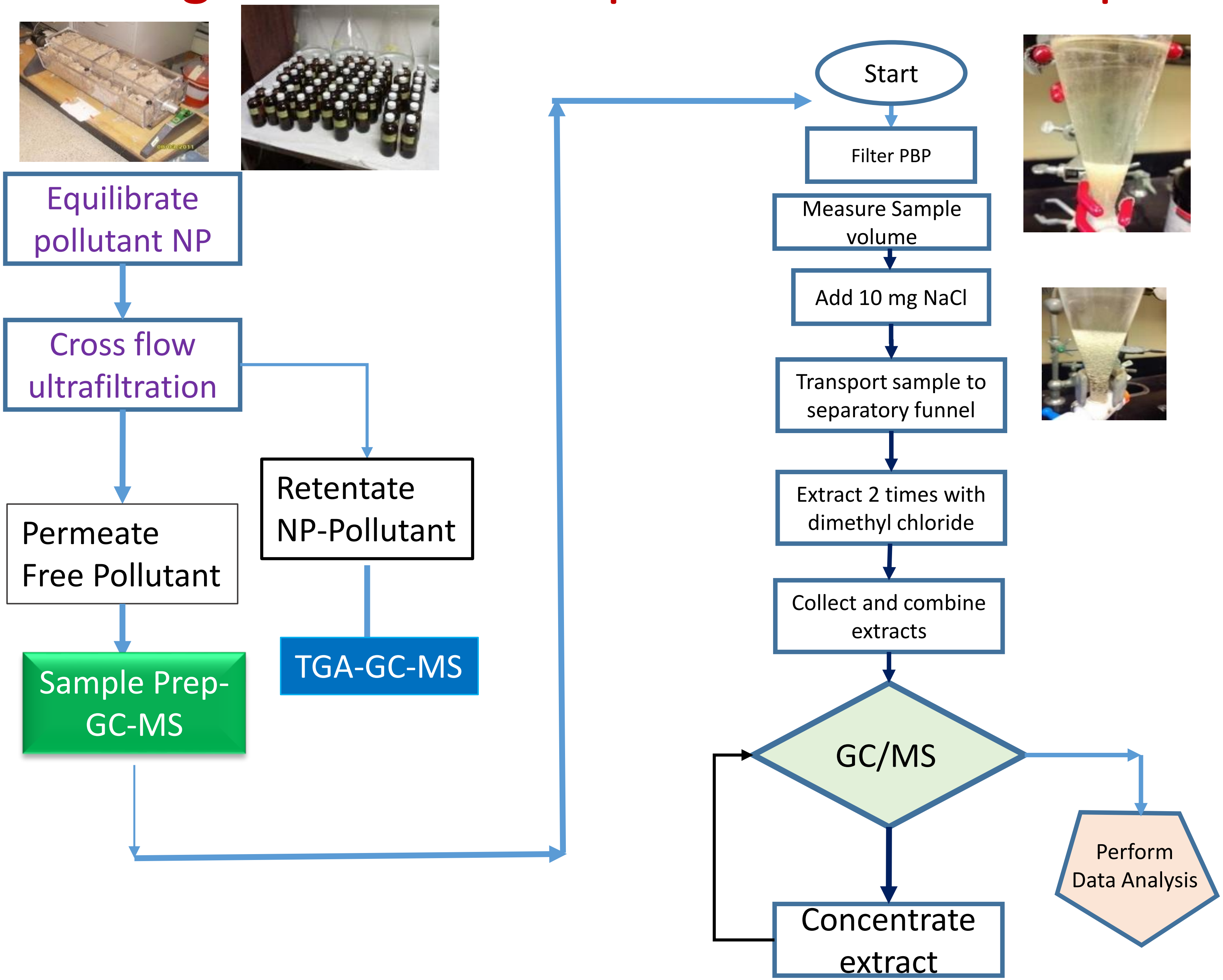
$$[pollu]_{total} / [Pollu]_{Free} = 1 + K_{Np}\,[NP] \ \ldots\ldots(3)$$

$$[Pollu]_{total} = Retentate\ concentration$$

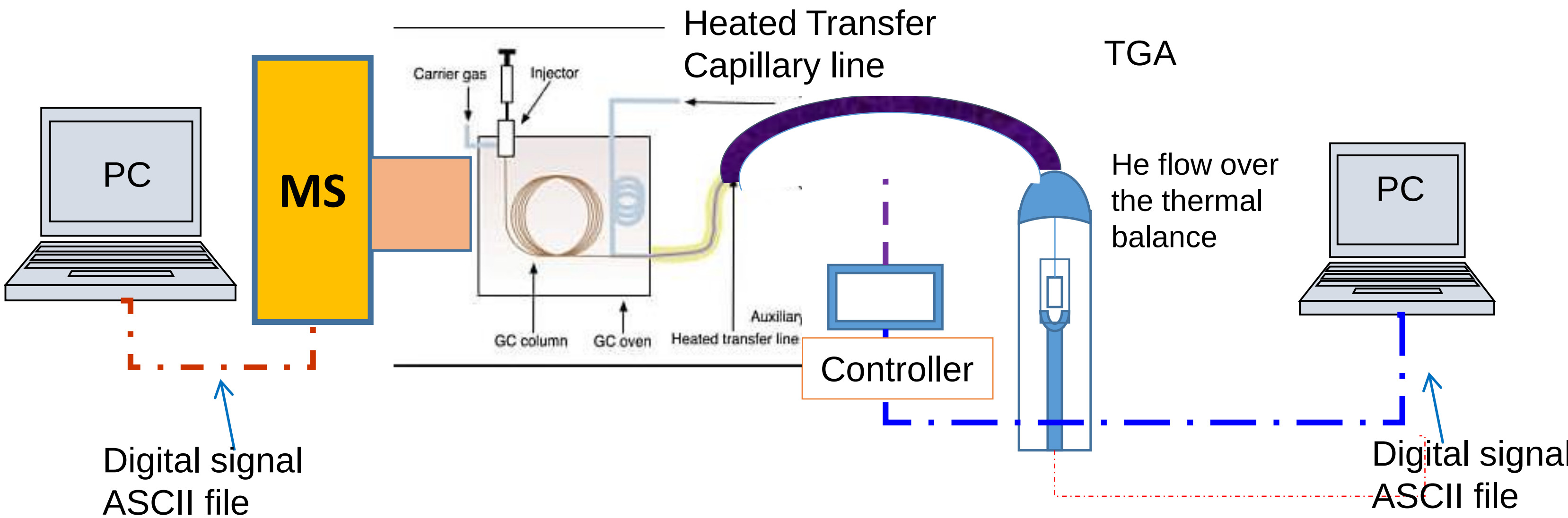
$[Pollu]_{Free}$ = permeate concentration

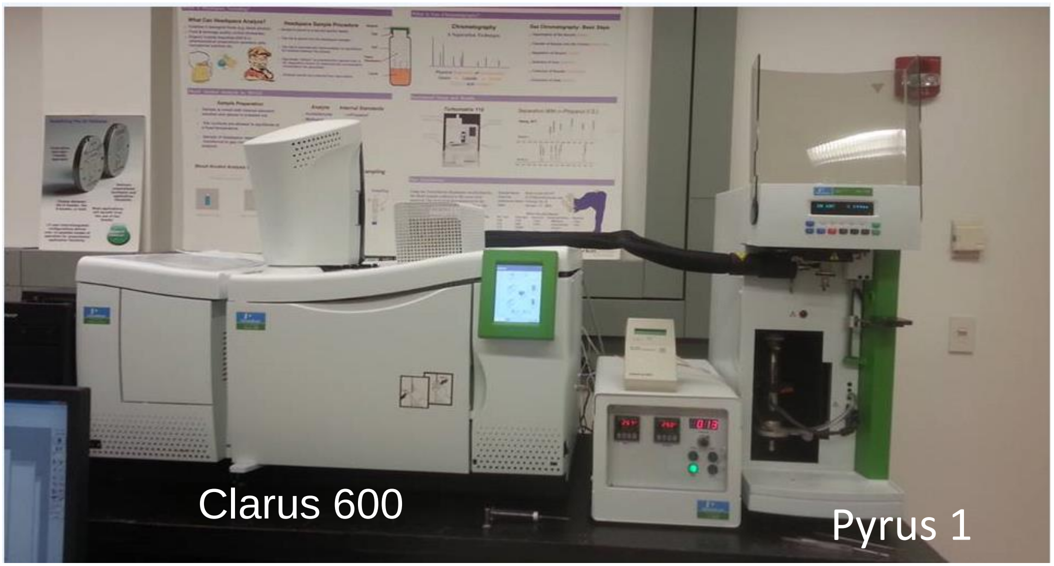
Equation (3) similar to Stern–Volmer relationship

NP-Organic Pollutant Equilibration and Sample Prep

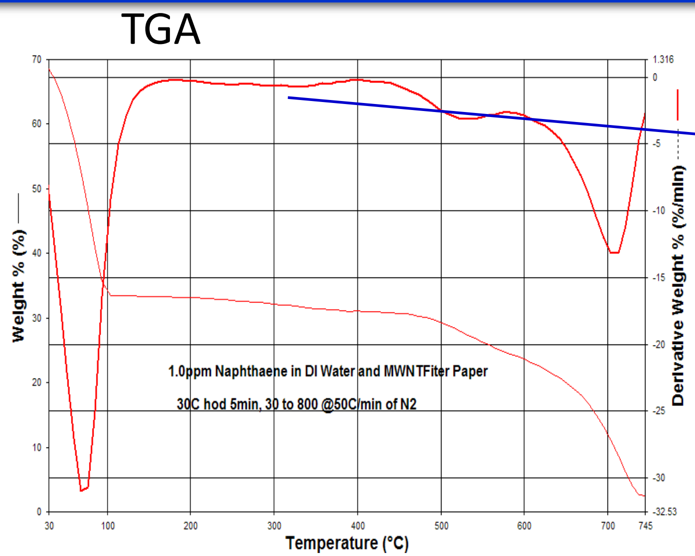


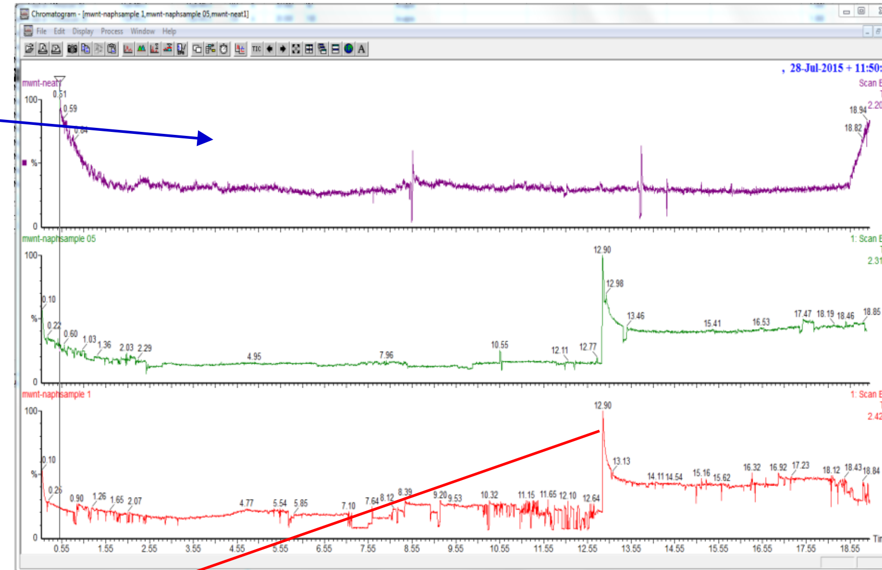
TGA-GC-MS for detecting Hydrophobic pollutants adsorbed to Nanoparticle

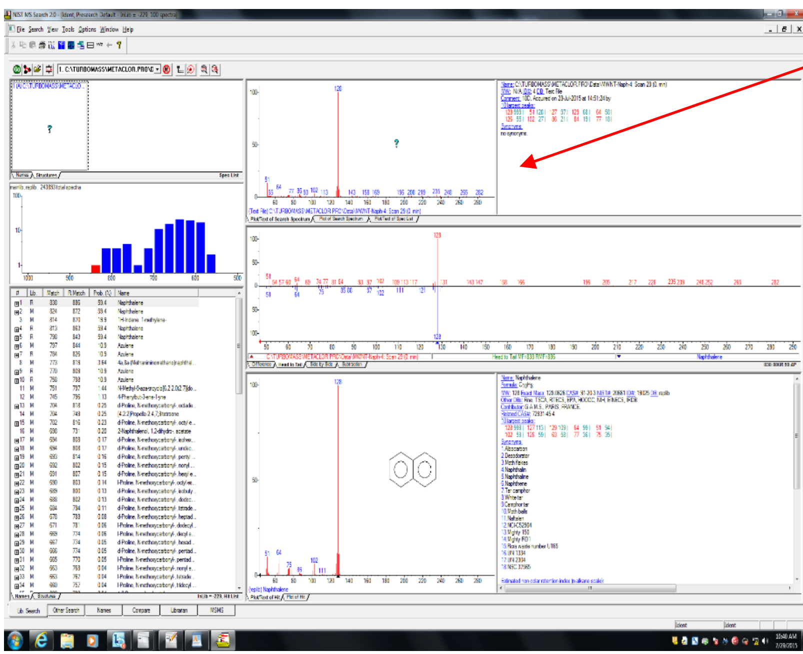




TGA–GC-MS for analysis of Naphthalene adsorbed on CNT

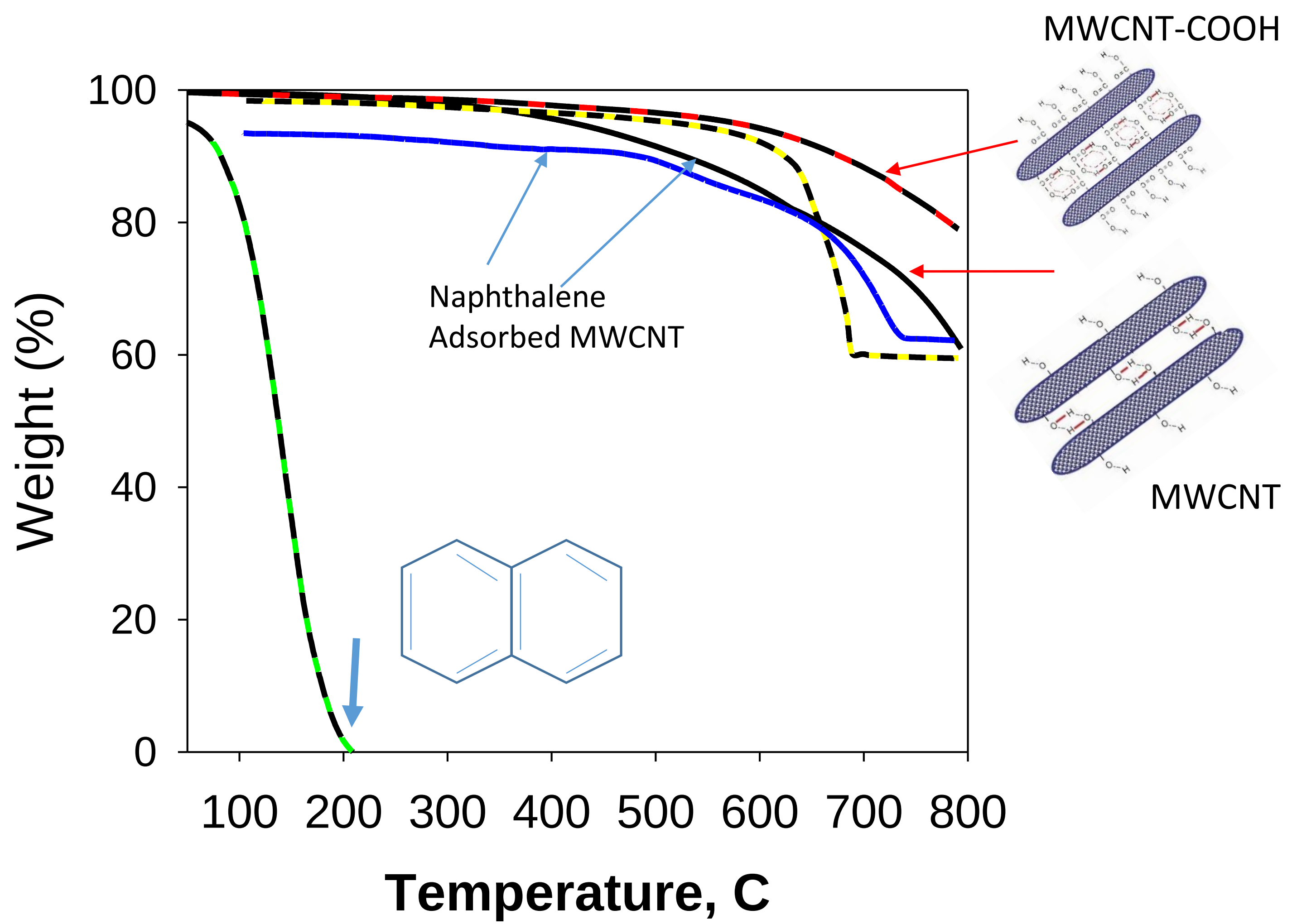






Collaboration with Bill Han, PerkinElmer

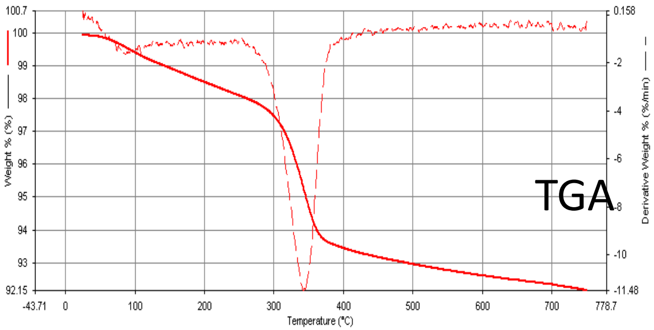
TGA for Naphthalene Adsorbed on MWCNT



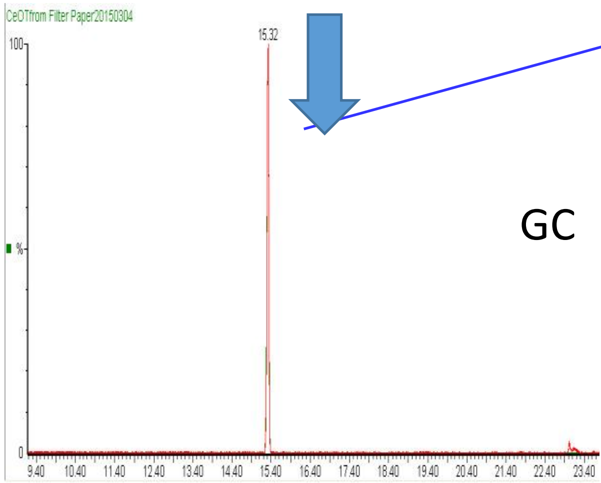
BP of Naphthalene = 137 °C, Released from MWCNT at 380 °C
Delayed release of naphthalene shows strong adsorption to CNT

TGA –MS for analysis of Polyaromatic hydrocarbons adsorbed on nano-TiO_2

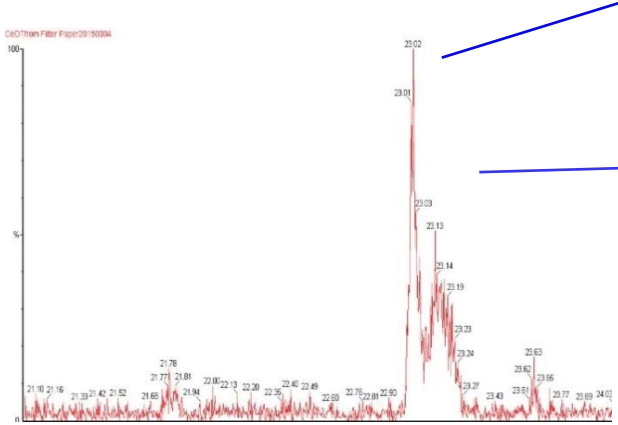
MS

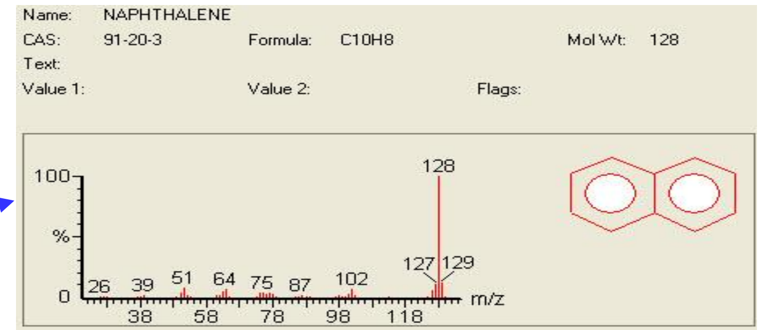


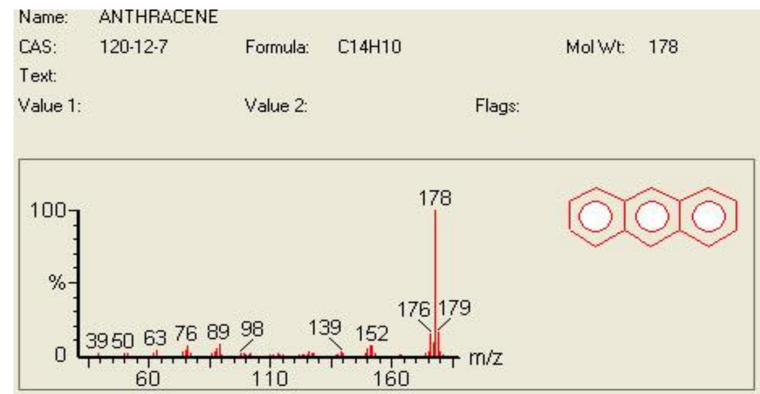
TGA

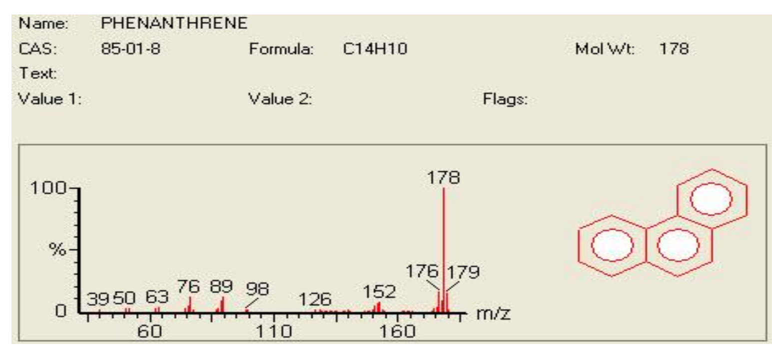


GC

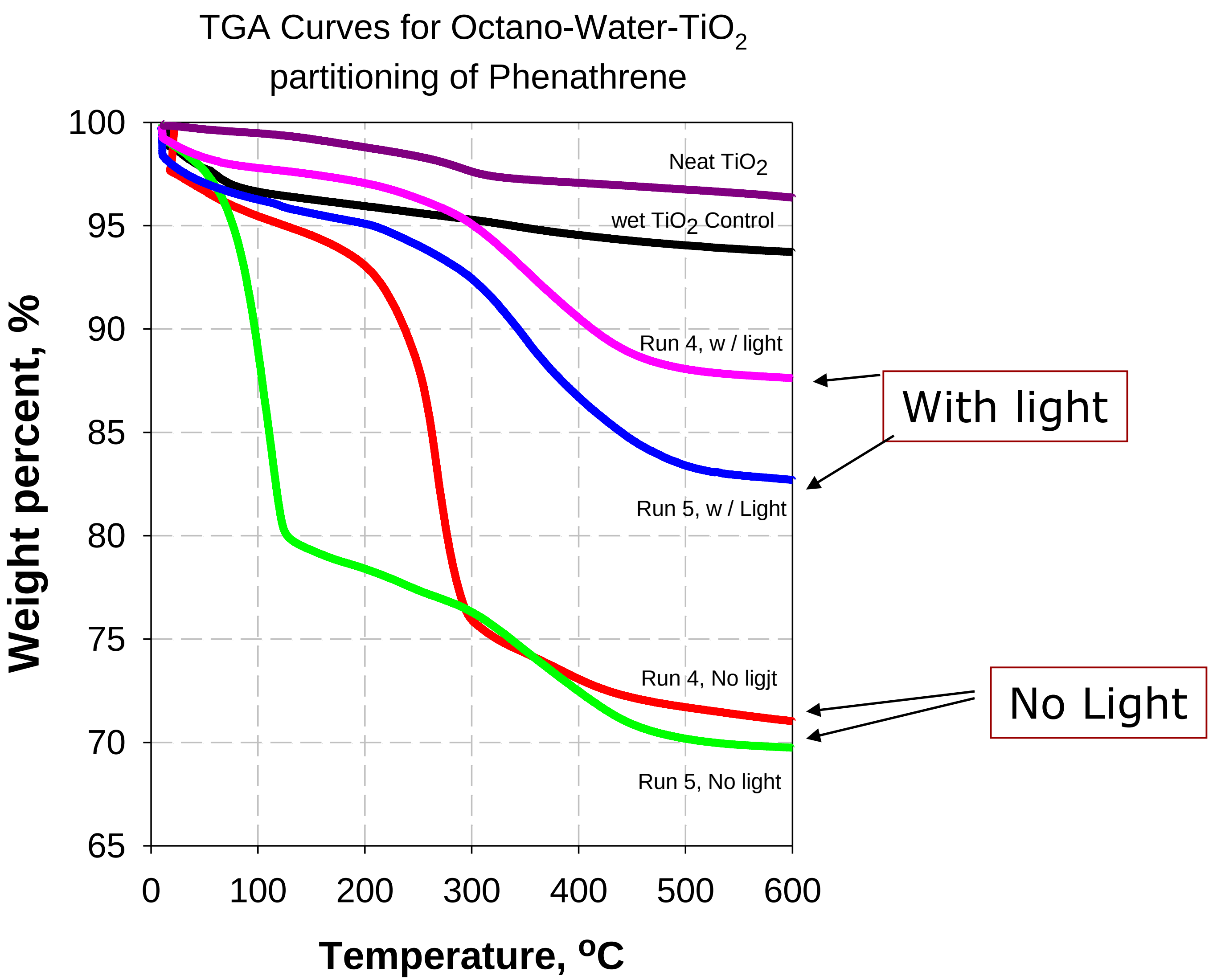






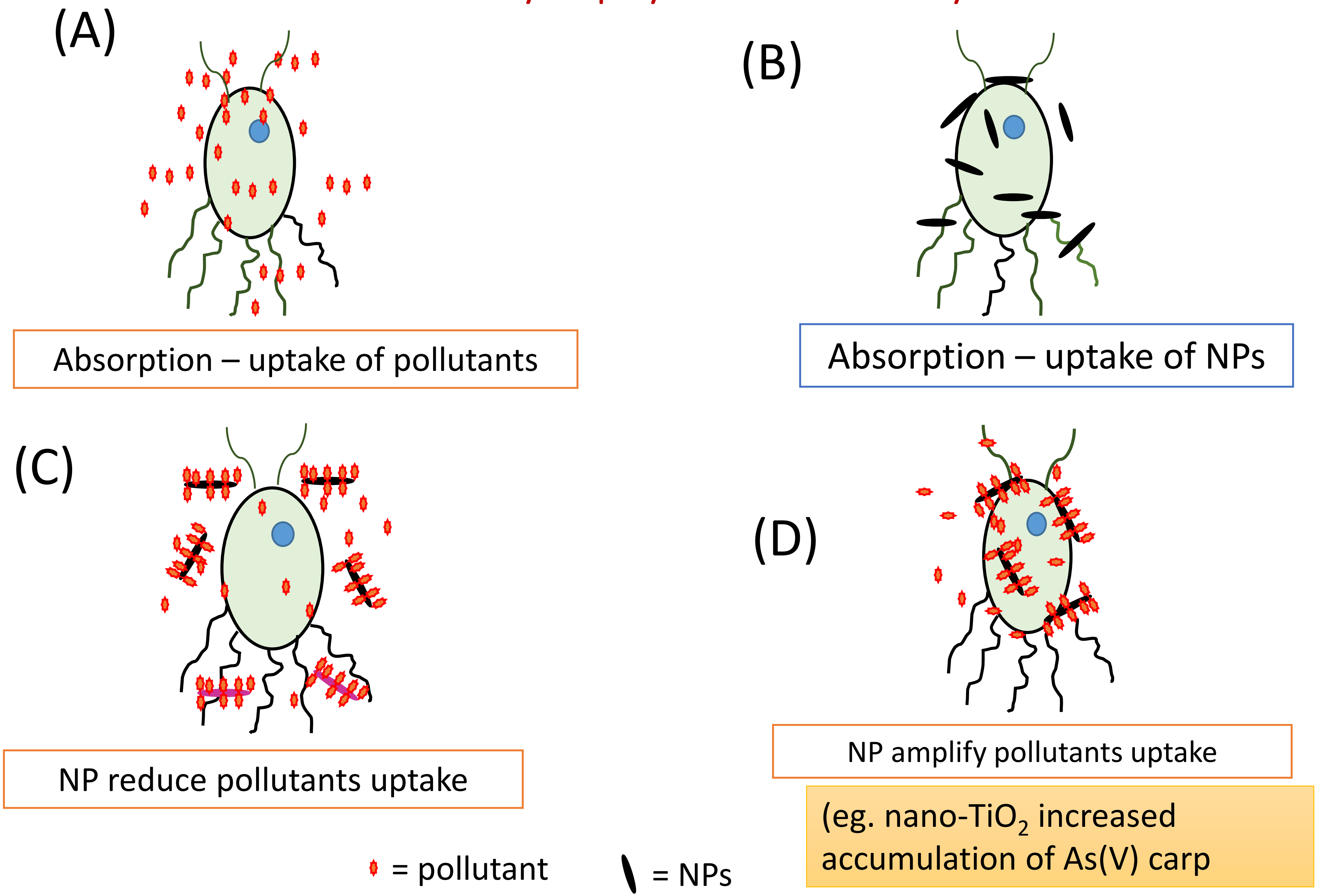


Increased partitioning of phenanthrene adsorbed on nano-TiO_2 – effect of light illumination

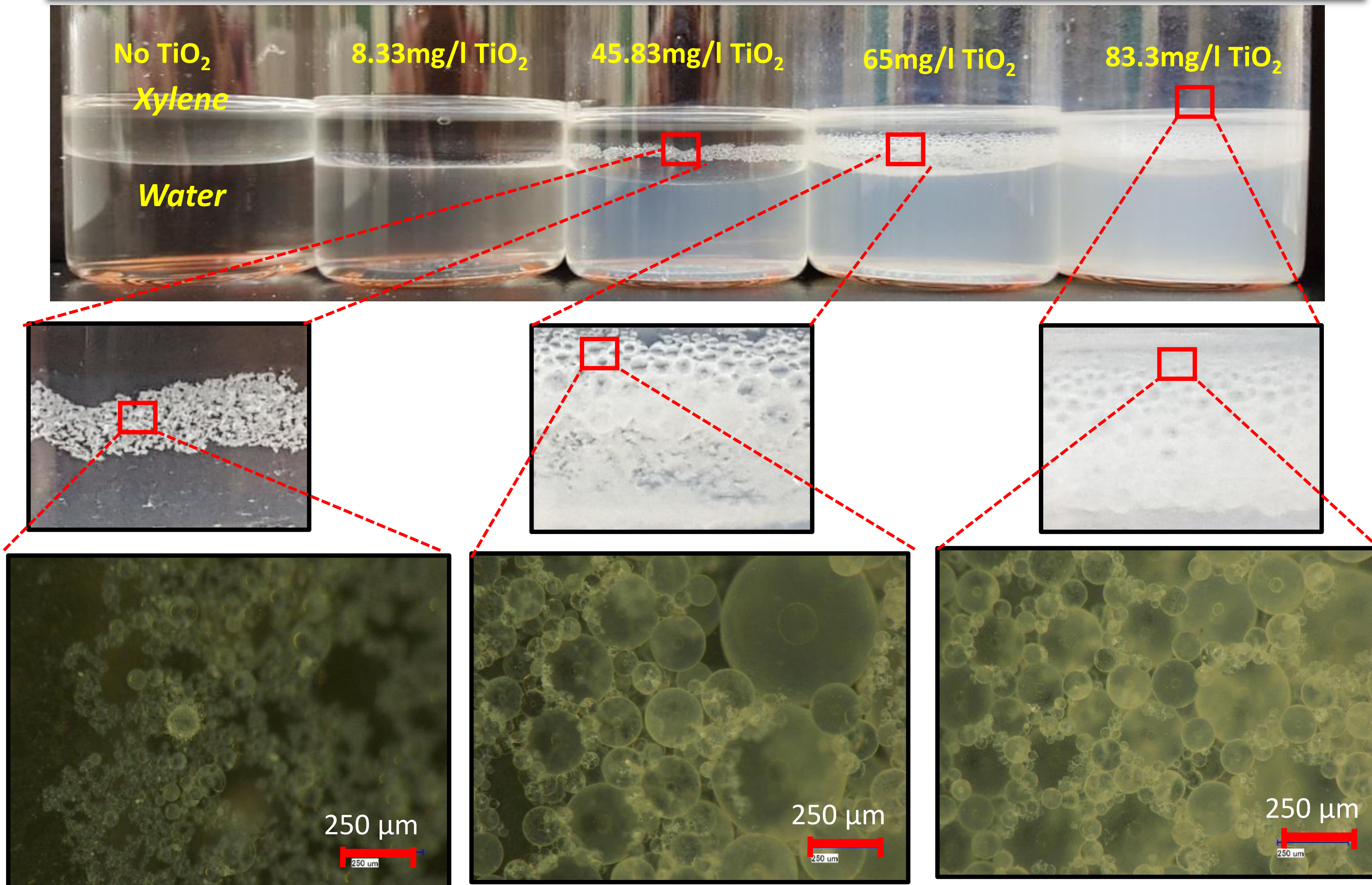


Aquatic organisms and the Interaction of Pollutants and NPs

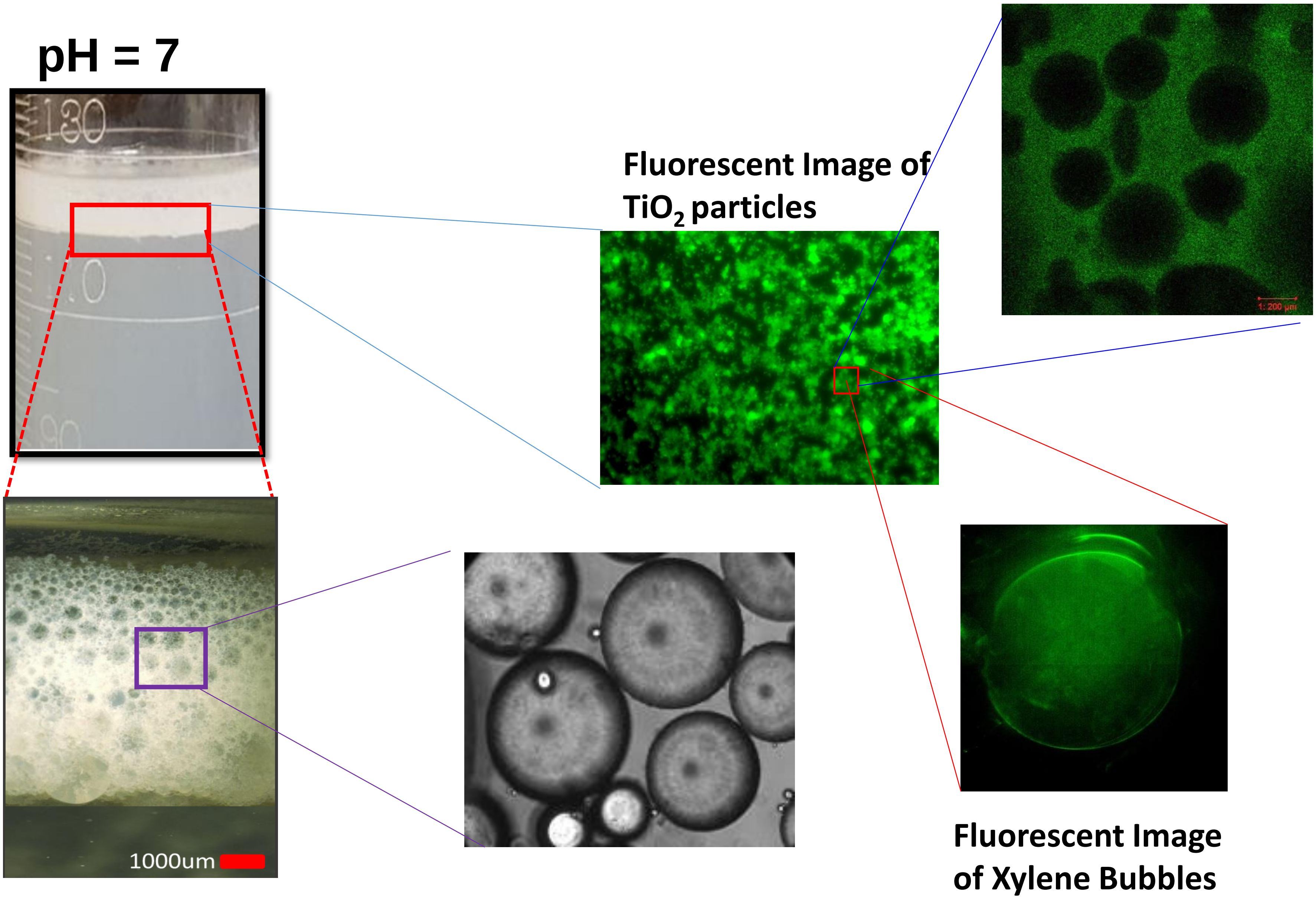
Do they amplify or alleviate toxicity?



Effect TiO_2 concentration on Xylene-Water-TiO_2 dispersion in the presence of light

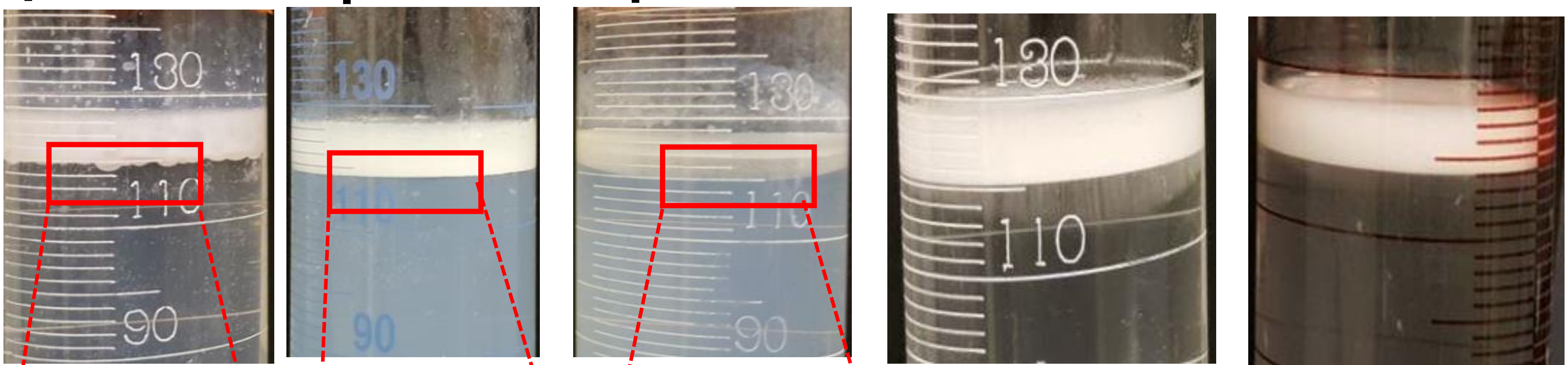


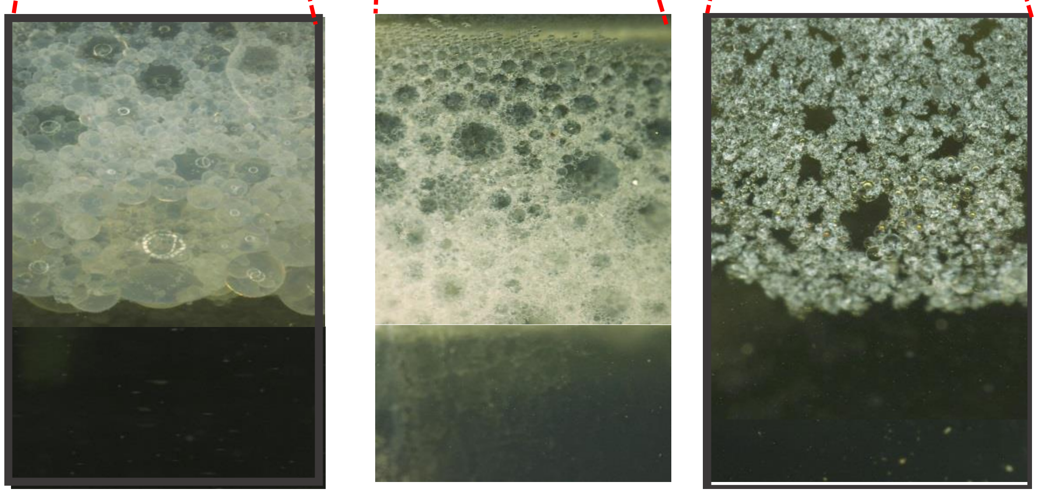
Organics-NP-Aggregated Dispersion



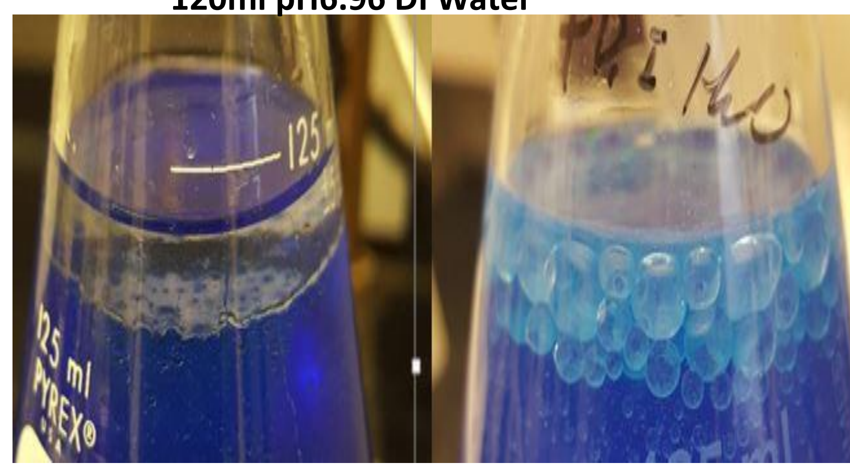
Effect pH on Xylene-Water-TiO_2 dispersion in the presence of light

pH = 3 | **pH = 7** | **pH = 10** | **Tomadol** at CMC | 5*CMC

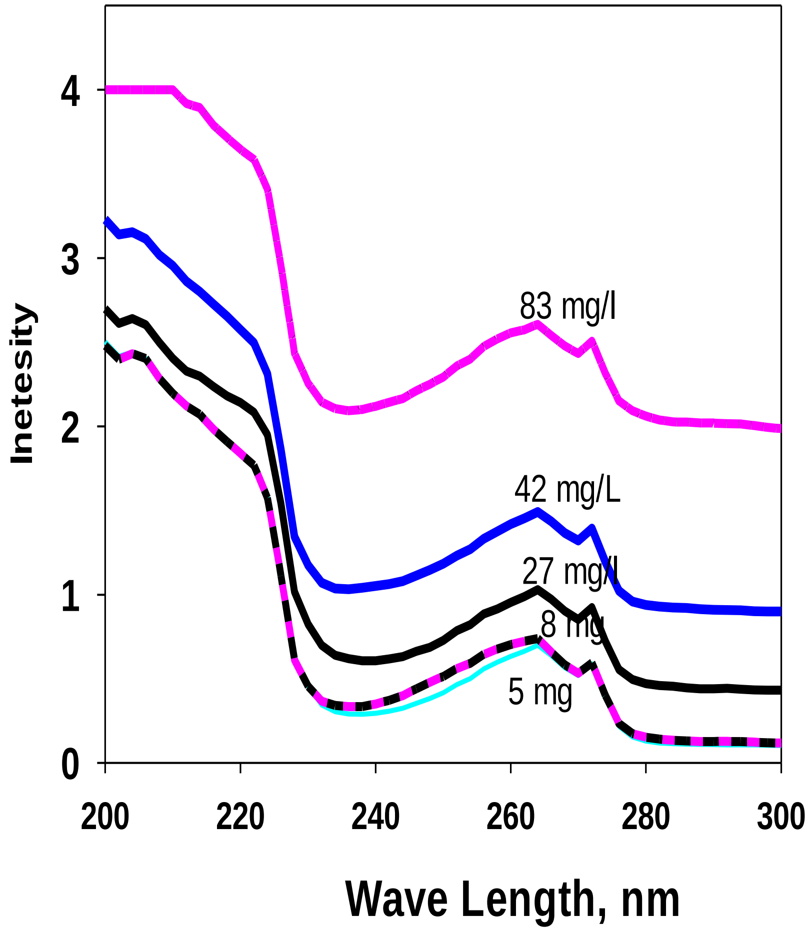


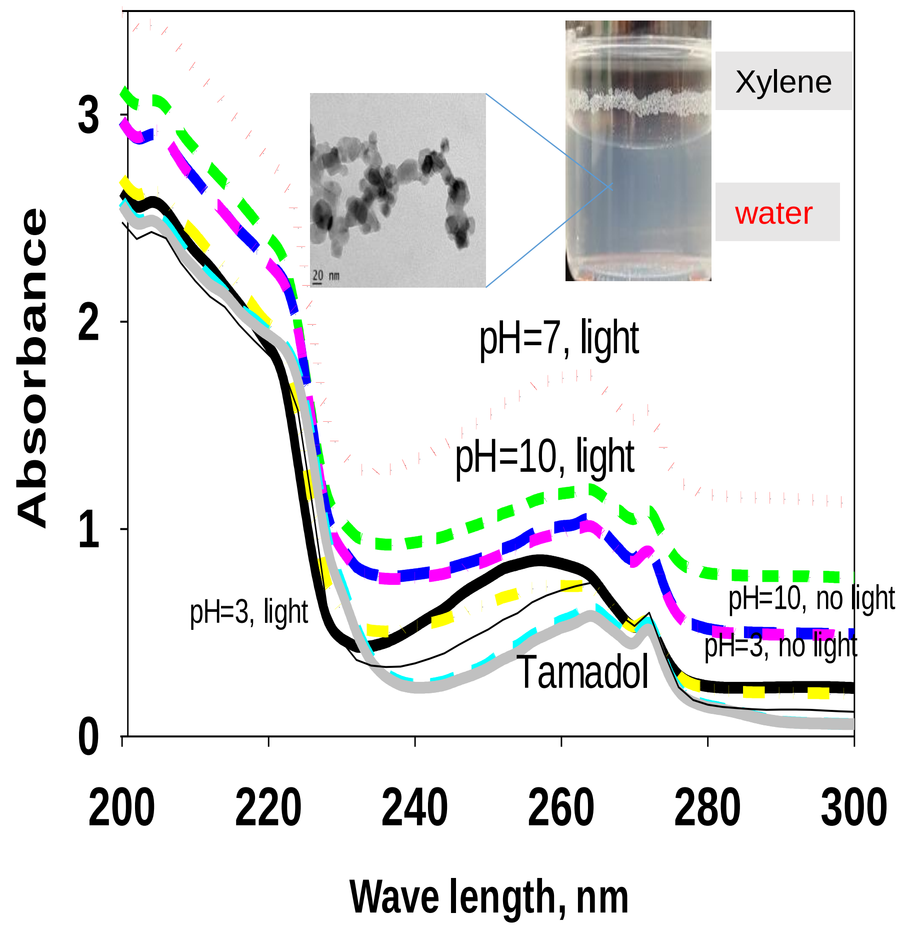


0.0033g Methylene Blue
5ml m-xylene,0.0077g TiO_2
120ml pH6.96 DI Water

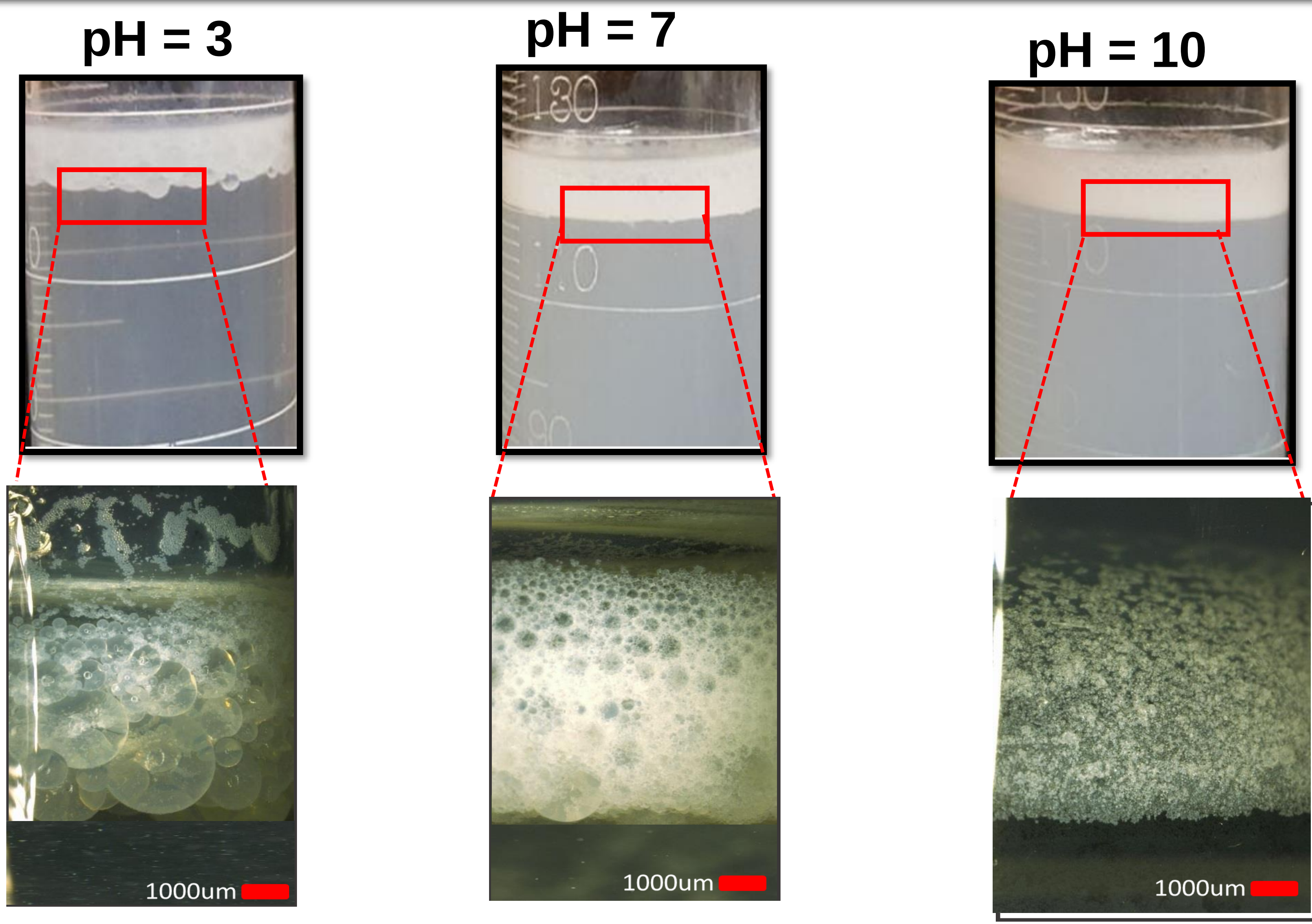


UV-Vis spectroscopic measure of the Effect of TiO_2 in dispersing Xylene in Water the absence of light

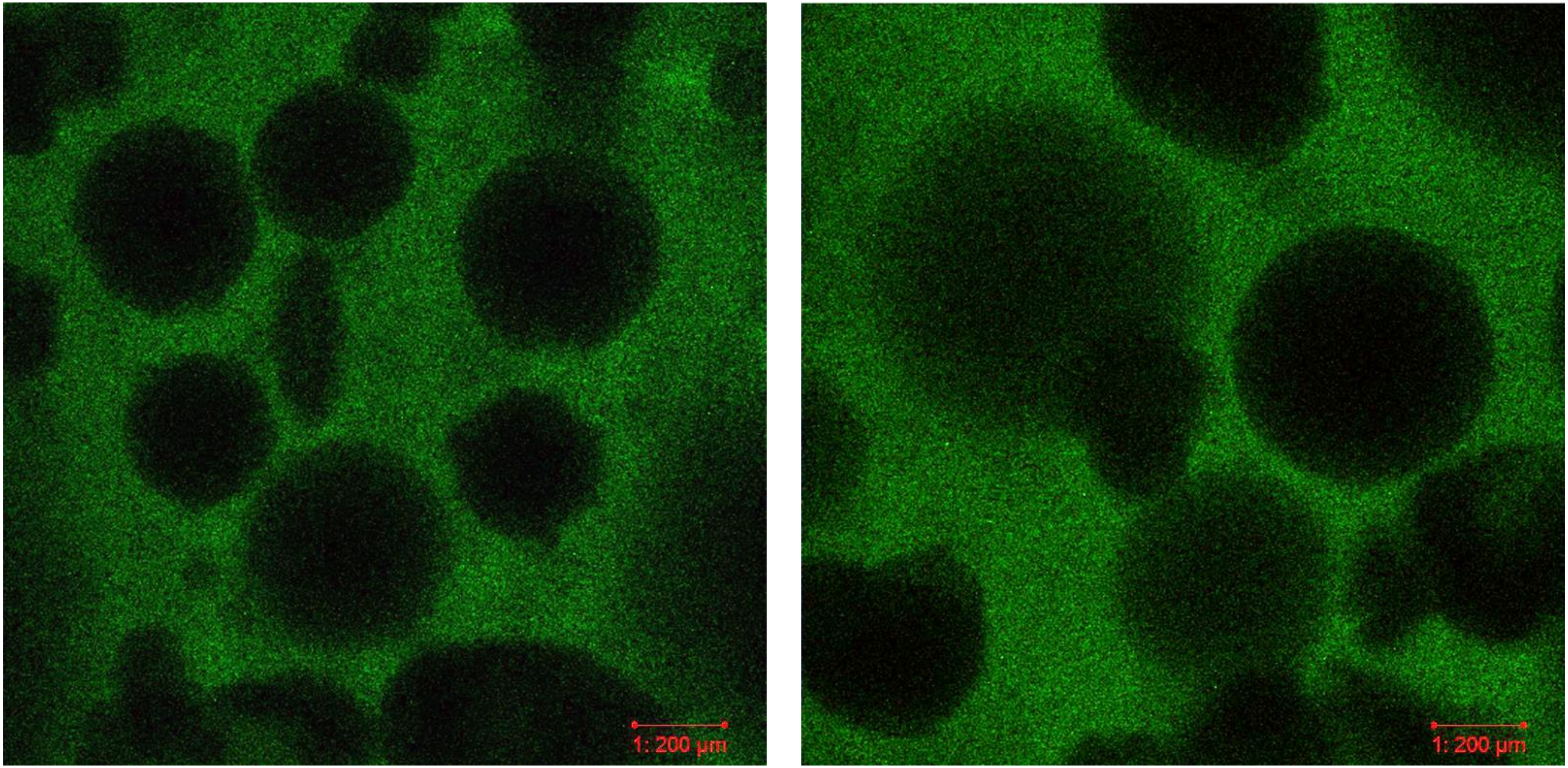




Effect of TiO_2 in dispersing Xylene in Water the absence of light



Confocal microscope images of TiO_2 particles and Xylene bubbles



Procedure for dyeing TiO_2 nanoparticles with a fluorescent green dye

1) Disperse 50 mg TiO_2 (P25, Degussa) particles in 3 mL methanol (MeOH)

2) Add 20 mg Fluorescein O-methacrylate (Sigma-Aldrich) in the prepared TiO_2 solution

3) Place the solution under vigorous stirring for 30 min

4) Centrifuge to collect dyed TiO_2 particles

5) Wash TiO_2 particles with methanol and centrifuge it.

6) Repeat the washing process three times to remove unabsorbed dyes on TiO_2 particles

7) Dry TiO_2 particles at 60 ^{o}C for 3 hr in a conventional lab oven to remove MeOH

8) Record images of TiO_2 particles with a Nikon Eclipse TE2000-S microscope

Summary

- **UV light and ozone exposure degrade nanocomposites and nanoparticles could be released to the environment,.**
- **Degradation of nanocomposite modulated by polymer matrix, environmental conditions, type of nano-reinforcement,**
- **Fate and transport of nanoparticles influenced by their characteristics and environmental chemistry.**
- **Nano-particles can influence adsorption and dispersion of hydrophobic/low water soluble contaminants by an order of magnitude.**
- **Many analytical techniques are available to analyze the fate, transport and transformation of nanoparticles in the environment**
- **Analytical tools/approaches are needed to better understand the degradation of nanocomposites, release of NPs, and detection in the environmental matrices.**

Acknowledgement

- Dr. Zhen Li
- Dr. Ashraf Aly Hassan
- Dr. Haregewine Tadesse
- Dr. Shirley Rosenweig
- Beniyam Mezgebe
- Hengye Jing
- Tom Deinlein
- Albert Foster
- Stephen Harmon
- Hafiz Salih
- Christina Benett-Stamper
- Jun Wang, Bill Han, Chady , PerkinElmer