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

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Life Cycle Specific Exposure of Nanomaterials

End of Life
Recycling
Land fills
Incineration

Nanocomposite
Machining
Sanding, Drilling
Polishing, cutting

Manufacturing

Occupational release risks

Consumer use
Weathering(photoxidation)
Wear, and tear, wash out

Environmental release
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!
Hazard Assessment of NM
Consumer nanomaterial research

Polymer (type)

Nanomaterial (CNT, GO, wt. %)

Characterization
Physical
Chemical
Structural

Transformation Interaction with:
• Pollutants
• NOM
• Biofilm

Weathering
Temp, UV dose, time

Composite Changes

nanorelease

Size, composition

Predictive model

Develop a predictive model

Effect studies

Fate

Transport

Toxicity

Water filtration
Porous media channels

ROX,
Cell viability
In vitro

Aging & Release Studies

Nanocomposite (Thickness, wt. % NM)
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 $\sim 10^3$ years
- Release persistent organic pollutants (POP)
- Accumulate POP such as PAHs, PCBs, DDT
- Release chemical additives -
## Factors influencing Nanorelease from composites

<table>
<thead>
<tr>
<th>C-C Backbone</th>
<th>Heteroatoms in Backbone</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>PET</td>
</tr>
<tr>
<td>PP</td>
<td>PU</td>
</tr>
<tr>
<td>PS</td>
<td>Cl</td>
</tr>
<tr>
<td>PVC</td>
<td></td>
</tr>
</tbody>
</table>

### Stress Conditions
- Physical Stress
- Environmental Stress → Weathering

### NanoFillers
- Metals
- Metal oxides, $\text{SiO}_2$, $\text{Fe}_2\text{O}_3$, clay
- Carbon based:
  - CNT, CF, graphene
  - Functionalized CNT
Diffusion of NP in Polymer and Mass transfer for Surface Release

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

Diffusion of Nanoparticles in Polymers

Athermal NP-NP Interaction
Attractive NP-Polymer Interaction for Miscibility

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

For semi-crystalline polymers below the glass transition temperatures

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

$t_D \sim 1.7 \times 10^5 h$
Mechanism of Nanorelease matrix degradation

- UV exposure
- Reactive species
- Cracking and de-bonding
- Surface Weathering
- Defect evolution in polymer layers
- Polymer nanocomposite

Main mechanism for nanorelease

- Polymer structural degradation
- Surface erosion
- Microplastics release
- Nanoparticle release
Conceptual model illustrating degradation pathways for polymer

- Polymer material
- Change in chemical functionality
  - Degradation
    - Macro (> 5 mm), Meso (≤ 5 mm > 1 mm), Micro (1 mm to 0.1 μm), Nano (≤ 0.1 μm)
  - Leaching of additives
  - Transformation / Degradation
- Nanorelease
  - Binding to NOM
  - Natural colloids
  - Aggregation
  - Sedimentation
- Dissolution
  - Transformation: Biological degradation, photolysis, hydrolysis
# Materials Tests

<table>
<thead>
<tr>
<th>Polypropylene (PP) (Pristine)</th>
<th>PP-MWCNT 4 Wt.%</th>
<th>Epoxy</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP01, ( L = 0.25 \pm 0.01 \text{ mm} )</td>
<td>( L = 0.35 \pm 0.03 \text{ mm} )</td>
<td>Neat</td>
</tr>
<tr>
<td>PP02, ( L = 0.39 \pm 0.02 \text{ mm} )</td>
<td>( L = 0.50 \pm 0.01 \text{ mm} )</td>
<td>Epoxy-CNT</td>
</tr>
<tr>
<td>PP03, ( L = 0.69 \pm 0.04 \text{ mm} )</td>
<td>( L = 2.07 \pm 0.06 \text{ mm} )</td>
<td>Epoxy-CNT-COOH</td>
</tr>
<tr>
<td>( T_g = -13 \degree \text{C} )</td>
<td></td>
<td>Epoxy-CNT-NH2</td>
</tr>
<tr>
<td>Tg = 60 - 110 \degree \text{C}</td>
<td></td>
<td>Epoxy-Graphene</td>
</tr>
</tbody>
</table>
Preparation of polypropylene (PP) and PP-MWCNT film

Melting and mixing of PP and MWCNTs

1. Heating chamber
2. Mechanical mixing rods

Melt PP + CNT mix

T > 150 °C

Extruded Air cooled

Melt mix with screw extruder

PP

PP01 PP02 PP03

PP-MWCNT

PP41 PP42 PP43
Operating conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A cycle of weathering</td>
<td>120 min (sunshine: 108 min and rain: 12 min)</td>
</tr>
<tr>
<td>Humidity</td>
<td>8-20% for Sunshine and over 60% for Rain</td>
</tr>
<tr>
<td>Solar light irradiation</td>
<td>700 W/m²</td>
</tr>
<tr>
<td>Wavelength of solar light</td>
<td>300-800 nm</td>
</tr>
<tr>
<td>Chamber Temperature</td>
<td>33-37 °C</td>
</tr>
<tr>
<td>Black Substance Temperature</td>
<td>65 °C</td>
</tr>
</tbody>
</table>

June 21, clear day

<table>
<thead>
<tr>
<th>Wavelength range</th>
<th>Arizona</th>
<th>Florida</th>
<th>Frankfurt</th>
<th>Barcelona</th>
<th>CIE No. 85 (Tab. 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>nm</td>
<td>E (W/m²)</td>
<td>E (W/m²)</td>
<td>E (W/m²)</td>
<td>E (W/m²)</td>
<td>E (W/m²)</td>
</tr>
<tr>
<td>280-300</td>
<td>0.016</td>
<td>0.017</td>
<td>0.008</td>
<td>0.018</td>
<td>0.010</td>
</tr>
<tr>
<td>300-400</td>
<td>60</td>
<td>62</td>
<td>48</td>
<td>61</td>
<td>66</td>
</tr>
<tr>
<td>400-800</td>
<td>566</td>
<td>584</td>
<td>469</td>
<td>542</td>
<td>617</td>
</tr>
<tr>
<td>800-4000</td>
<td>420</td>
<td>387</td>
<td>350</td>
<td>373</td>
<td>434</td>
</tr>
<tr>
<td>280-4000</td>
<td>1046</td>
<td>1033</td>
<td>867</td>
<td>976</td>
<td>1117</td>
</tr>
</tbody>
</table>
Aging and thermal stability of Composites

TGA Data for Raw PE and PE-nanoclay

Polyimide with 2% CNT wafer
Epoxy with 4% CNT
Polyimide with 4% CNT wafer
Polyimide wafer

TGA Data for aged PE and PE-nanoclay

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

- Xenon Arc Weathering – simulates terrestrial solar irradiation
- Irradiation: 700 W/m² and Wavelength: 300-800 nm
- Chamber Temp: 33-37 °C, Black Substance Temp.: 65 °C, air cooled
The primary weathering factors

- **Solar Radiation**
  - Radiation
  - Irradiance
  - Spectral power distribution

- **Temperature**
  - Min/Max
  - Dwell times
  - Cycles

- **Water**
  - Quantity
  - Duration
  - Phase
  - Cycles

+ secondary factors (urban pollutants, acid rain, etc. ...)

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Polymer Composite

1. Chemical microscopic damage
2. Visual macroscopic damage
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$_2$SO$_4$ was added in 100 mL of the bubbled water.
   b. 0.1 M Na$_2$S$_2$O$_3$ solution was added to the acidified water (#2).
   c. Observe color changes of the solution from transparent to pale yellow.

**Results**

- Due to dissolved O$_3$, color became **pale yellow**.

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<table>
<thead>
<tr>
<th>Air bubbled Water</th>
<th>Water</th>
<th>Vent</th>
</tr>
</thead>
</table>

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**Weathering Chamber**
Weathering of Polymer Nanocomposite

Surface Degradation by Weathering

Decreasing Recrystallization Temperature by Weathering

Changing Activation Energy by Weathering

Effects of Weathering on CNT-Polypropylene

\[ \Delta \frac{dH}{dt} = \left( \frac{dH}{dt} \right)_{\text{sample}} + \left( \frac{dH}{dt} \right)_{\text{Reference}} \]

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: \( Polymer \xrightarrow{k_1} P^* \)  \hspace{1cm} (1)

Propagation: \( P^* + O_2 \xrightarrow{k_2} PO_2^* \)  \hspace{1cm} (2)

\[ PO_2^* + PH \xrightarrow{k_3} PO_2H + P^* \]  \hspace{1cm} (3)

\[ P^* + P^* \xrightarrow{k_4} \]

\[ P^* + PO_2^* \xrightarrow{k_5} \text{Inactive species} \]  \hspace{1cm} (4)

\[ PO_2^* + PO_2^* \xrightarrow{k_6} \]

\[ - \frac{d [O_2]}{dt} \approx k_2 \left( \frac{r_i}{k_4} \right)^2 [O_2] \]

\( r_i = a l^{2\gamma} \) where \( a \) and \( \gamma = \) constants depending on the mechanism, and \( \gamma \) 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)

\[ TOC \approx \Phi^{-1} = \left( \frac{D}{k} \right)^{1/2} \]

Audoulin et al., J. Material Science, 29 (1994) 560-583
Audoulin et al., Die angewandte Makromelekulare 1998, 25-34
Intensity of the light source: \( 10.06 \pm 0.1 \text{ mW/cm}^2 \)

Light intensity of Lamp: \( 10.06 \pm 0.1 \text{ mW/cm}^2 \)

<table>
<thead>
<tr>
<th>Aging Time (h)</th>
<th>PP01</th>
<th>PP02</th>
<th>PP03</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.65 ± 0.02</td>
<td>8.30 ± 0.01</td>
<td>7.75 ± 0.03</td>
</tr>
<tr>
<td>756</td>
<td>6.52 ± 0.03</td>
<td>5.24 ± 0.03</td>
<td>4.33 ± 0.02</td>
</tr>
<tr>
<td>1512</td>
<td>3.02 ± 0.03</td>
<td>4.45 ± 0.02</td>
<td>2.08 ± 0.01</td>
</tr>
<tr>
<td>2268</td>
<td>2.10 ± 0.01</td>
<td>0.95 ± 0.01</td>
<td>1.12 ± 0.02</td>
</tr>
<tr>
<td>3024</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

All PP01 samples were broken at 1512 h.
All PP02 samples were broken at 2268 h.

→ UV transmittance decreased as PP aged showing thermo-oxidative degradation.
NanoRelease: Particle size distribution

PP41 = 0.25 mm

PP42 = 0.50 mm

PP43 = 2.07 mm

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

10^{-12} s

1 s - 1h
**Experimental setup**

- Total Irradiance (MJ/m²): 6588
- Solar Irradiance (W/m²): 700
- Black Substrate Temperature (°C): 65
- Weather: 111 min of daylight and 9 min of raining

**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 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 °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

Epoxy

Wavelength (nm)

Absorbance (a.u.)

Epoxy-CNT

Wavelength (nm)

Absorbance (a.u.)

Epoxy-CNT-COOH

Wavelength (nm)

Absorbance (a.u.)

Epoxy-CNT-NH₂

Wavelength (nm)

Absorbance (a.u.)
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

<table>
<thead>
<tr>
<th></th>
<th>3 Months</th>
<th>6 Months</th>
<th>12 Months</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure CNT</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CNT COOH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CNT NH(_2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G peak Wavenumber (cm(^{-1}))</td>
<td>1580.46</td>
<td>1586.44</td>
<td>1590.91</td>
</tr>
<tr>
<td>D peak Wavenumber (cm(^{-1}))</td>
<td>1351.74</td>
<td>1359.42</td>
<td>1359.42</td>
</tr>
</tbody>
</table>

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 is 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

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