Impact of Temperature on the Kinetics of Photodegradation and Nanoparticles Release in Nanocoatings

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Outline

• Nanoparticle release research in EL/NIST

• Case study: Accelerating weathering a nanosilica/epoxy coating
  • Kinetics of photodegradation
  • Surface accumulation of nanoparticle
  • Qualification of particle release
NIST/EL Nanoparticle Release Research

Release Pathways of Nanoparticles (NP) During the Life Cycle of Nanocomposites: Mechanical, Matrix Degradation, Chemical Dissolution, Fire/Incineration, etc.

Mechanical abrasion
- Polyurethane (PU) flooring coatings on wood substrates
  - SiO₂
  - Al₂O₃
- Latex Coatings on a dry-wall substrate
  - TiO₂
  - ZnO
  - Ag

Matrix Degradation via UV
- Model Epoxy (EP)
  - MWCNT
  - SiO₂
- Exterior Coatings and Paints
  - SiO₂-PU
  - ZnO -Latex

*Abrasion after UV exposure

Goal:
- To develop test methods and measurement protocols for determining the quantities and properties of nanoparticles released from polymer nanocomposites
- To understand the mechanism that causes nanoparticles to leave the polymer matrix during exposures to the environments
  → Providing data needed for assessing and managing potential EHS risks of NP release during nanocomposites’ life cycles.
NIST SPHERE

Simulated Photodegradation via High Energy Radiant Exposure

- Provide well-controlled environmental stressors (UV, T, RH, mechanical)

- UV spectra and irradiance
- High throughput
- Exposure at output: 295 nm - 450 nm
- Incident irradiance on sample: 140 W/m²

→ Degradation rate, mechanism, kinetics, ....

Nanoparticle Release Process and Collection

### Mechanical abrasion

Taber rotary abraser (ASTM D 4060-14, organic coatings)

### Matrix Degradation via UV

NIST SPHERE High Throughput, High Intensity UV Chamber

1. Characterize abraded surfaces (LSCM, SEM, EDX)
2. Remove Particles from Abraded Surface (TEM grid pressed against the surface or using an Adhesive Tape)
3. Collect residues from abrasion wheels

2 & 3 → Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), SEM/EDX

Simulated Rain Test (Water Spraying)

- UV Irradiated Specimens
- Chromatographic Atomizer
- Water Spray
- Quartz Covers on 3 Remaining Specimens
- Drain
- Collection Bottle
- Pressure Control
- To House Air

To be analyzed by ICP-OES
Case Study - a nanosilica/epoxy coating

Objective

- To better understand the degradation mechanism, surface accumulation, and possible release of nanoparticles in exterior nanocoatings.

- Acceleration effect of temperature on
  - Kinetics of photodegradation
  - Surface accumulation of nanoparticle
  - Particle release

Effect of Key Environmental Factors on Polymer Degradation
(Laboratory Exposure – accelerate weathering)
UV, T, RH, mechanical stress
Materials

Polymer:

Amine-cured epoxy, typically used for composites, coatings, and adhesives.

Nanoparticle:

Pure SiO$_2$ Nanoparticles (untreated)

Individual particle size: $\sim$15 nm Diameter.

Nanocoating Preparation:

Loading: 5% (based on polymer mass).

Thickness:

$\sim$ 7 µm on a CaF$_2$ substrate – for UV-vis, FTIR

$\sim$125 -150 µm free-standing films – ATR-FTIR, mass loss, XPS, AFM

$\sim$ 300 µm, free-standing films – for particle release study
UV Radiation Exposure

NIST SPHERE High-Throughput High Intensity UV Chamber


Martin and Chin, U.S. Patent 6626053

**Simulated Photodegradation via High Energy Radiant Exposure**

Exposure cell – general purpose

Exposure cell for nanosilica release
Exposure Conditions and Characterization

SPHERE

Spectral UV intensity:
Wavelength: 295 - 400 nm
Temp: 60 °C, 50 °C, 40 °C, 30 °C (± 0.1°C)
RH: 0 % ± 0.2%

Characterization

• Chemical Degradation (rates, mechanism)
  - ATR-FTIR, UV-vis, and XPS
• Surface Morphologies (AFM)
• Release rate by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), using specially-designed holder.
• The inset is a transmission FTIR spectrum of the pure, untreated silica nanoparticles.
• New FTIR band around 1074 cm⁻¹ related to Si-O band in 5 % SiO₂-epoxy system.
A substantial amount of silica nanoparticles (SiO$_2$) has accumulated on the sample surface – mainly due to photodegradation of the matrix.

Direct evidence of SiO$_2$ particles release was observed during exposure of epoxy/nanosilica coatings to UV radiation.
Temperature Effects

Kinetics?

Arrhenius-like kinetics?

\[ k = A e^{-\frac{E_a}{RT}} \]

\[ \ln(k) = \frac{-E_a}{R} \left( \frac{1}{T} \right) + \ln(A) \]

\( E_a \) is the activation energy  \( k: \text{rate}, T \text{ in } ^\circ K \)

Kinetics data of polymer coatings containing nanoparticles under different UV environments is essential for better understanding the degradation mechanism and predicting the release of nanoparticles from exterior nanocoatings.
Temperature Effects:

Chemical Changes (ATR-ATIR)

1245 cm\(^{-1}\): chain scission

1060 cm\(^{-1}\): C-O and Si-O

- IR bands 1245 cm\(^{-1}\) & 1724 cm\(^{-1}\)
  → change rapidly at earlier exposure time/dose (< 200 MJ/m\(^2\)), reach a plateau value for dose > 400 MJ/m\(^2\)
  → 60 °C – highest degrade rate
- IR bands 1060 cm\(^{-1}\)
  → increases as UV dose increases
  → no clear trends in temperature effects

Two oppositely competing processes: loss of epoxy material (C-O loss) & increase of silica nanoparticles on the surface (Si-O increase).

All intensities were Normalized at dose = 0
• Absorbance increased as UV dose increased
• Higher temperature had a higher rate of increase
**Temperature Effects:** Chemical Changes (UV-Vis)- data fitting

### Neat Epoxy

<table>
<thead>
<tr>
<th></th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>$y_0$</td>
<td>0.316±0.015</td>
<td>0.389±0.022</td>
<td>0.462±0.007</td>
<td>0.603±0.015</td>
</tr>
<tr>
<td>$A$</td>
<td>-0.239±0.017</td>
<td>-0.399±0.022</td>
<td>-0.400±0.011</td>
<td>-0.600±0.023</td>
</tr>
<tr>
<td>$R_0$</td>
<td>-0.0094±0.001</td>
<td>-0.0098±0.0016</td>
<td>-0.0399±0.003</td>
<td>-0.027±0.003</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.983</td>
<td>0.987</td>
<td>0.996</td>
<td>0.995</td>
</tr>
</tbody>
</table>

### 5 % SiO$_2$-Epoxy

<table>
<thead>
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<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>$y_0$</td>
<td>0.596±0.015</td>
<td>0.652±0.025</td>
<td>0.765±0.021</td>
<td>0.895±0.038</td>
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<tr>
<td>$A$</td>
<td>-0.607±0.015</td>
<td>-0.656±0.024</td>
<td>-0.766±0.028</td>
<td>-0.879±0.059</td>
</tr>
<tr>
<td>$R_0$</td>
<td>-0.0049±0.0003</td>
<td>-0.0069±0.0007</td>
<td>-0.012±0.0012</td>
<td>-0.020±0.003</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.996</td>
<td>0.9954</td>
<td>0.991</td>
<td>0.978</td>
</tr>
</tbody>
</table>

**Graph:**
- Exponential Fit of Sheet1 C
- Model:
  

\[
y = y_0 + A\exp(R_0 \cdot x)
\]

**Model Summary:***
- **Equation:** $y = y_0 + A\exp(R_0 \cdot x)$
- **Reduced Chi-Sqr:** 1.38283E-4
- **Adj. R-Square:** 0.99668

<table>
<thead>
<tr>
<th>Model</th>
<th>Value</th>
<th>Standard Err</th>
</tr>
</thead>
<tbody>
<tr>
<td>$y_0$</td>
<td>0.59627</td>
<td>0.01462</td>
</tr>
<tr>
<td>$A$</td>
<td>-0.6069</td>
<td>0.01452</td>
</tr>
<tr>
<td>$R_0$</td>
<td>-0.0049</td>
<td>3.13289E-4</td>
</tr>
</tbody>
</table>

**Chemical Changes (UV-Vis):**

- **$y_0$ values higher with SiO$_2$**

**Dose Response:**

- **30°C Exponential Fit of Sheet1 C**

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**Temperature Effects:**

- Neat Epoxy
- 5 % SiO$_2$-Epoxy

**Data Fitting:**

- **Equation:** $y = y_0 + A\exp(R_0 \cdot x)$
- **Reduced Chi-Sqr:** 1.38283E-4
- **Adj. R-Square:** 0.99668

**Values:**

- **$y_0$**
  - Neat Epoxy: 0.316±0.015
  - 5 % SiO$_2$-Epoxy: 0.596±0.015

- **$A$**
  - Neat Epoxy: -0.239±0.017
  - 5 % SiO$_2$-Epoxy: -0.607±0.015

- **$R_0$**
  - Neat Epoxy: -0.0094±0.001
  - 5 % SiO$_2$-Epoxy: -0.0049±0.0003

**$R^2$ Values:**

- Neat Epoxy: 0.983, 0.987, 0.996, 0.995
- 5 % SiO$_2$-Epoxy: 0.996, 0.9954, 0.991, 0.978
Temperature Effects – with and without SiO₂ (UV-Vis Data)

\[ k = A e^{-E_a/(RT)} \]

\[ \ln(k) = \frac{-E_a}{R} \left( \frac{1}{T} \right) + \ln(A) \]

\[ y = y_0 + A \exp(R_0 x) \]

\( Y_0 \) values higher with SiO₂
Temperature Effects:

Mass Loss

Temperature Effects:

5% SiO₂-Epoxy

Neat Epoxy

Mass Loss (%)

Dose (MJ/m²)

Linear fit

Arrhenius-like kinetics
Results: XPS
Surface enhancement C, O, N vs. UV dose at different T

Dose < 500 MJ * m⁻²

No temperature dependence for C(1s), O(1s) and N(1s)

Dose > 500 MJ * m⁻²

- C(1s): the overall loss at 50 °C and 60 °C > that at 30 °C and 40 °C
- O(1s): no significant difference for all temperatures
- N(1s): %N₃₀ °C < %N₄₀ °C < %N₅₀ °C ≈ %N₆₀ °C.
Surface enhancement Si vs. UV dose at different T

Elemental Percentage vs. Dose (MJ/m²)

Arrhenius-like kinetics

Linear fit

Si(2p) elemental % vs. Dose (MJ/m²)
Temperature effects:

Surface Morphology - AFM

<table>
<thead>
<tr>
<th>Temperature</th>
<th>30°C</th>
<th>40°C</th>
<th>50°C</th>
<th>60°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>MJ/m²</td>
<td>31</td>
<td>30</td>
<td>12</td>
<td>52</td>
</tr>
<tr>
<td>78</td>
<td>104</td>
<td>73</td>
<td>91</td>
<td></td>
</tr>
<tr>
<td>187</td>
<td>253</td>
<td>195</td>
<td>182</td>
<td></td>
</tr>
</tbody>
</table>

Images show surface morphology at different temperatures.
Temperature effects:

Surface Morphology - AFM - data fitting

Particle Surface Coverage (%)

Dose (MJ/m²)

30°C
40°C
50°C
60°C

Remove first two points

Shift factor

Equation: y = a +

Adj. R-S: 0.981

Value Standard

C Interce: 11.417 ± 0.85071

C Slope: -3458.4 ± 270.0223

ln R₀

1/T(°K)

ln (α)

1/T(°K)
Measurement and Modeling of Nanosilica Release from Epoxy Nanocomposite Exposed to UV at 4 Temperatures using new sample holder (below) and surface treated SiO$_2$.

Quartz cover
With surface treated SiO$_2$ → improve dispersion

Large uncertainties @ high Temp!
Dispersion issue?
Non-uniform degradation
With Surface Treated SiO$_2$ $\rightarrow$ Better Dispersion

Epoxy+SiO$_2$ (untreated) – 14 d –

Epoxy+SiO$_2$ (treated)

Scan size: 20 $\mu$m X 20 $\mu$m
Non-Uniform Degradation Process

surface treated SiO$_2$

**40 °C**

**50 °C**

**60 °C**

Except 60 °C,
Release rate: no strong Temperature dependence

Linear slope: 0.126 ± 0.004

less release

more release
Summary: The effects of temperature

- The higher temperature, the higher photodegradation and surface nanosilica accumulation rate.
- The chemical degradation rate of the matrix (FTIR data UV-Vis data)
- Accumulation rate for Si on the surface (AFM and XPS data) followed the right temperature order, i.e., 60 °C > 50 °C > 40 °C > 30 °C.
- Release rate: no strong temperature dependence, except 60 °C

Acceleration effect of temperature

-Arrhenius relationship
Summary: Temp Dependence

Slopes (k) Vs T

Linearly increasing trends: \( y=kt+y_0 \)
- mass lose
- XPS Si

Exponential Decay: \( y=a*e^{-kt} +y_0 \)
- XPS C
- FTIR-ATR 1245 and 1508

Exponential Rise: \( y=a*(1-e^{-kt})+y_0 \)
- AFM
- XPS O
- UV-vis

→ Arrhenius-like kinetics