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

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NanoSafe 2016

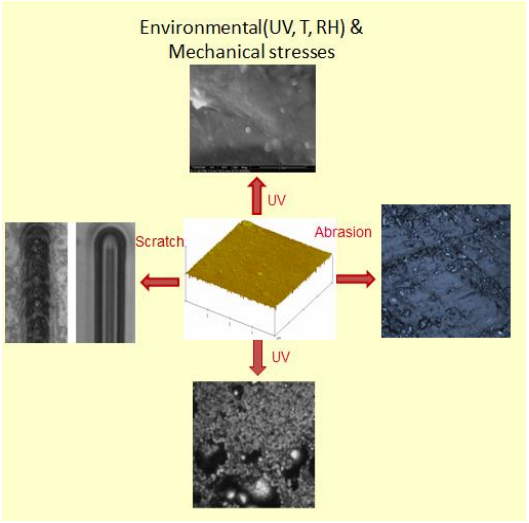
Outline

- 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.



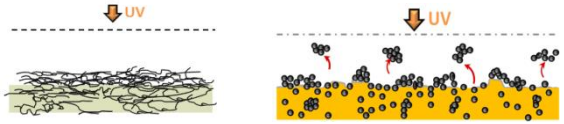
Mechanical abrasion#

Polyurethane (PU) flooring coatings on wood substrates
- SiO_2
- Al_2O_3

Latex Coatings on a dry-wall substrate
- TiO_2
- ZnO
- Ag

Matrix Degradation via UV

Model Epoxy (EP)
- MWCNT
- SiO_2



Exterior Coatings and Paints
- **SiO_2-PU**
- ZnO -Latex

***Abrasion after UV exposure**

Airborne release particles- *working with Indoor Air Quality Group/EL*

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

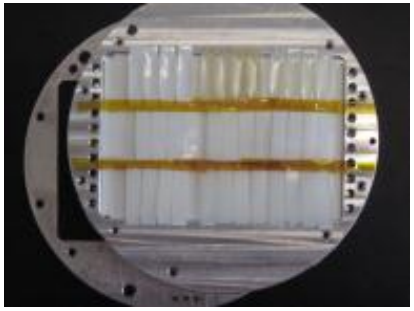
→ Providing data needed for assessing and managing potential EHS risks of NP release during nanocomposites' life cycles.

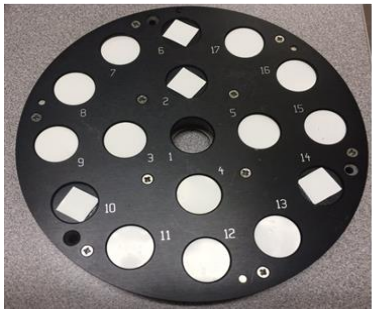
NIST SPHERE

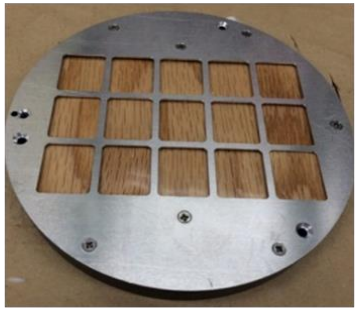
Simulated **P**hotodegradation via **H**igh **E**nergy **R**adiant **E**xposure

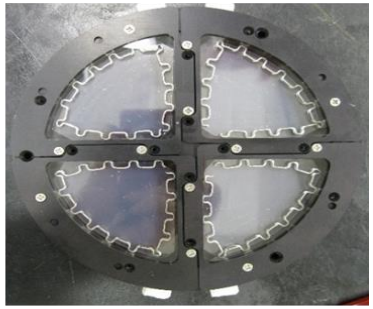
- **Provide well-controlled environmental stressors (UV, T, RH, mechanical)**

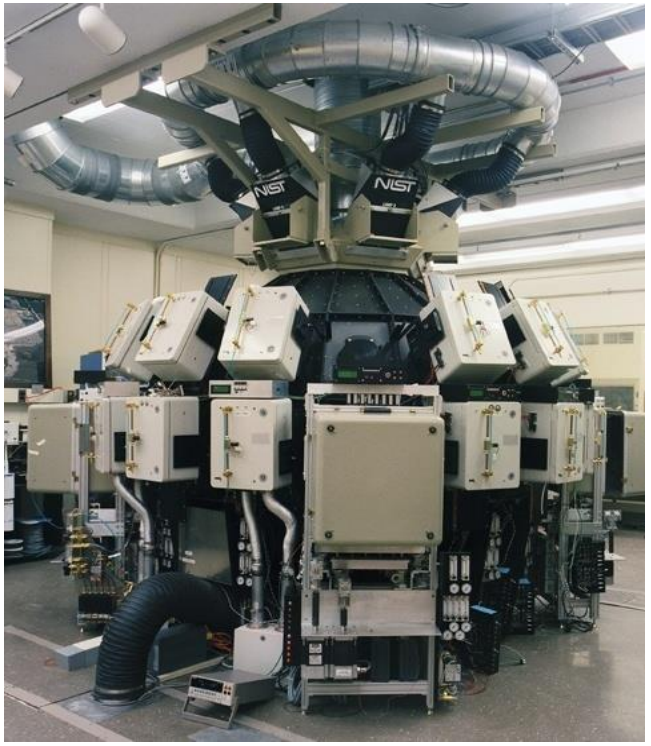
✓ UV spectra and irradiance
✓ High through-put
✓ Exposure at output: 295 nm - 450 nm
✓ Incident irradiance on sample: 140 W/m^2











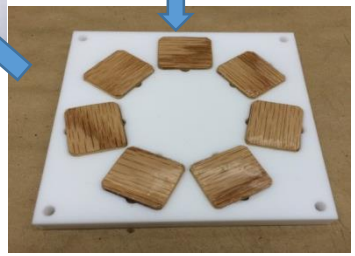
Chin et al, Review of Scientific Instruments 75(11), 4951-4959, 2004.

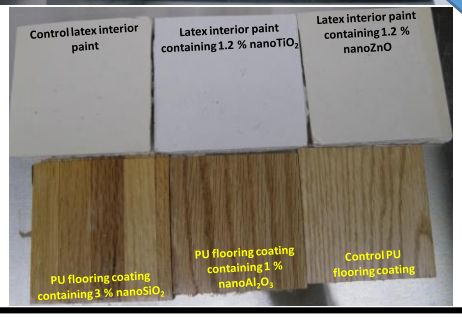
→ **Degradation rate, mechanism, kinetics, ….**

Nanoparticle Release Process and Collection

Mechanical abrasion

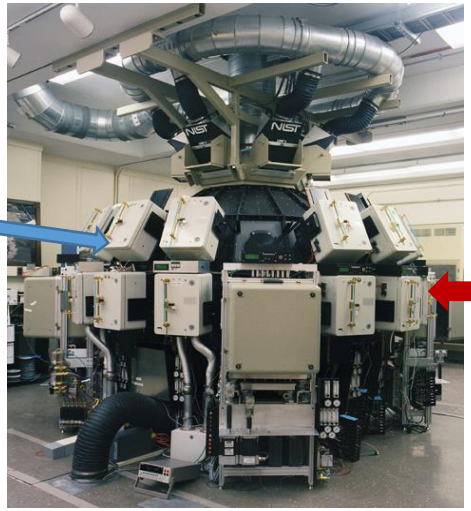
Taber rotary abraser
(ASTM D 4060-14, organic coatings)

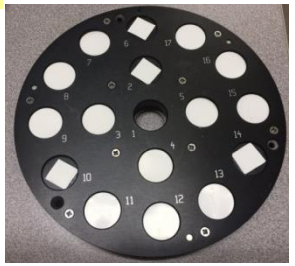


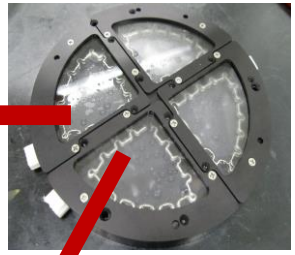


Matrix Degradation via UV

NIST SPHERE High Throughput, High Intensity UV Chamber



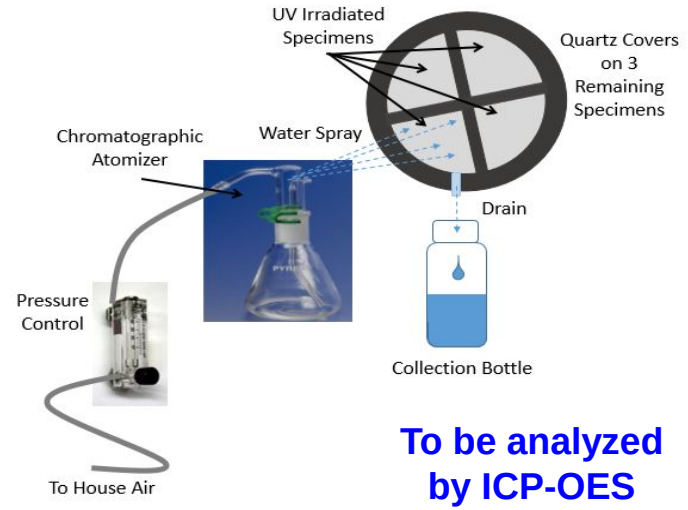




1. Characterize abraded surfaces (LSCM, SEM, EDX)
2. Remove Particles from Abraded Surface (TEM grid pressed against the surface or using an Adhesive Tape)
3. Collect residues from abrasion wheels

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

Simulated Rain Test (Water Spraying)



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: ~15 nm Diameter.

Nanocoating Preparation:

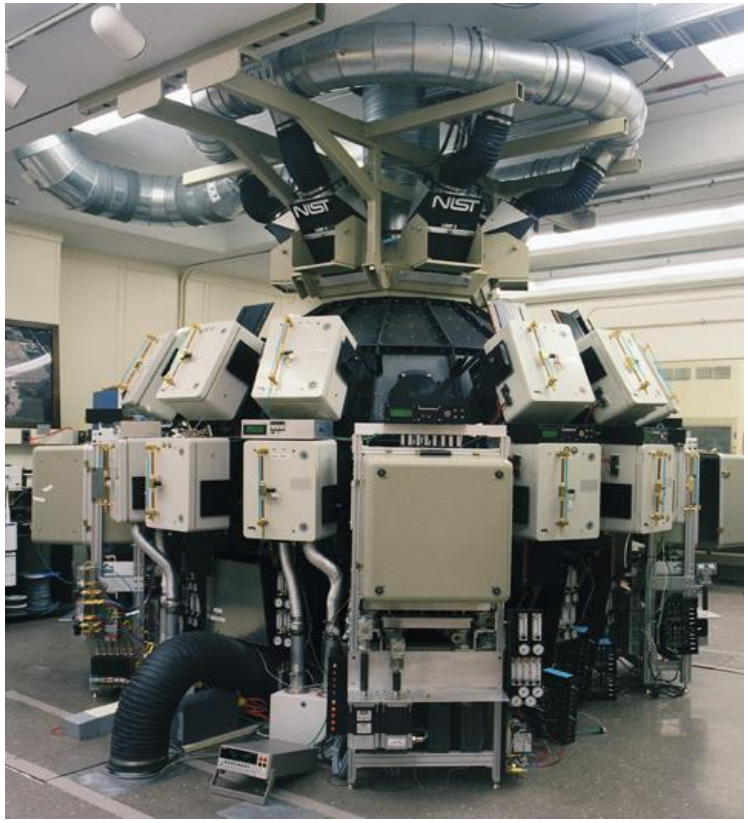
Loading: 5 % (based on polymer mass).

Thickness:

- ~ 7 μm on a CaF_2 substrate – for UV-vis, FTIR
- ~125 -150 μm free-standing films – ATR-FTIR, mass loss, XPS, AFM
- ~ 300 μm, free-standing films – for particle release study

UV Radiation Exposure

NIST SPHERE High-Throughput High Intensity UV Chamber

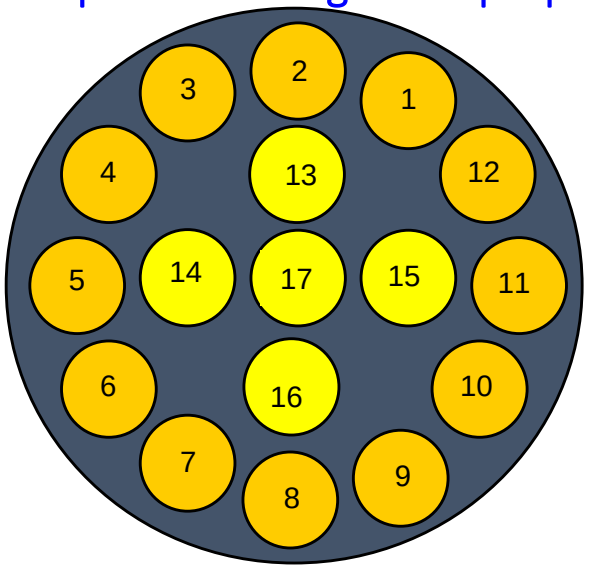


Chin et al, *Review of Scientific Instruments* (2004), 75, 4951.

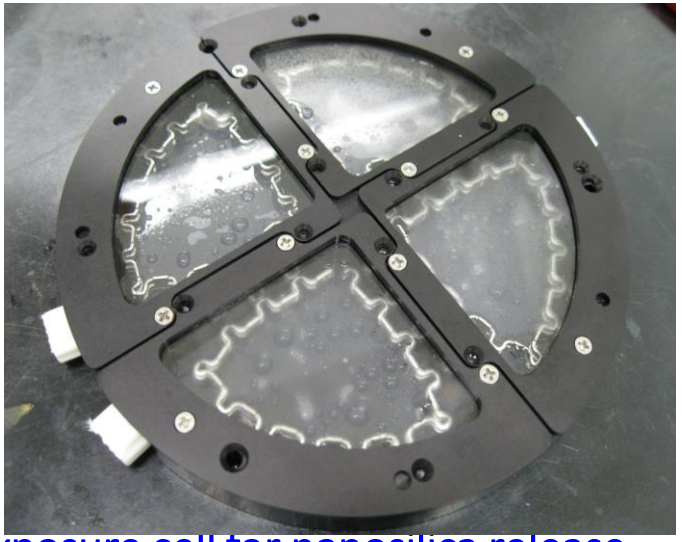
Martin and Chin, U.S. Patent 6626053

Simulated Photodegradation via High Energy Radiant Exposure

Exposure cell – general purpose



19 mm diameter specimens



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)

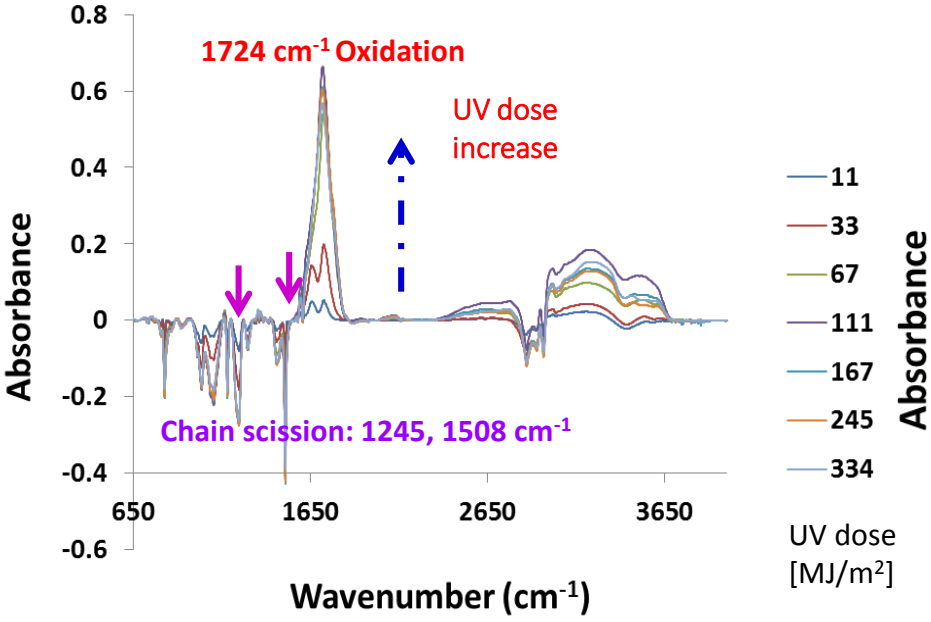
- Release rate by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), using specially-designed holder.

Photodegradation

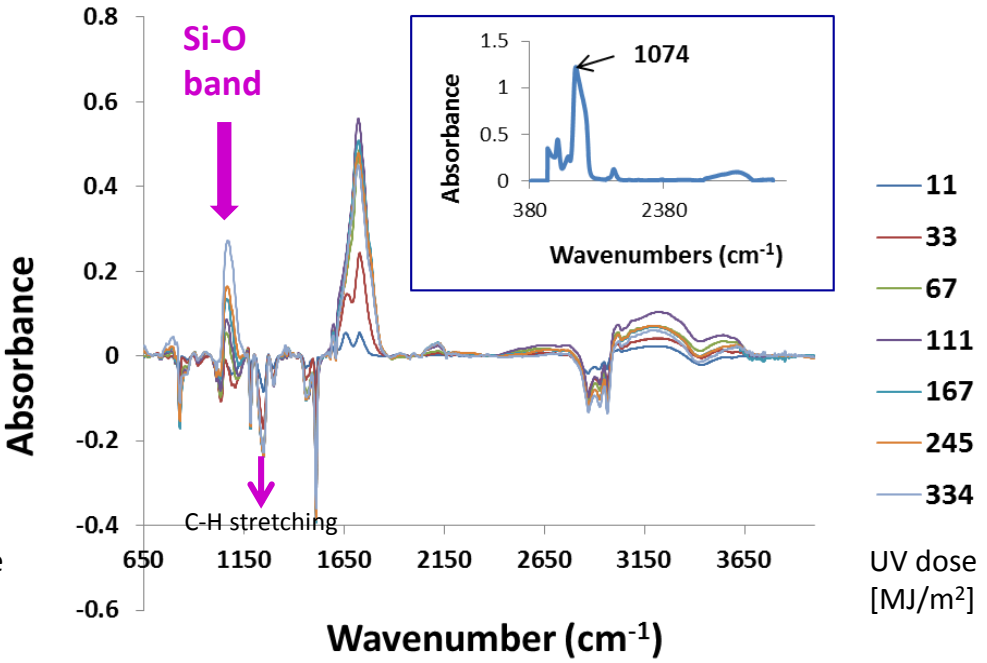
Model Epoxy-SiO_2 (60°C, Dry)

Difference ATR-FTIR Spectra

Neat Epoxy



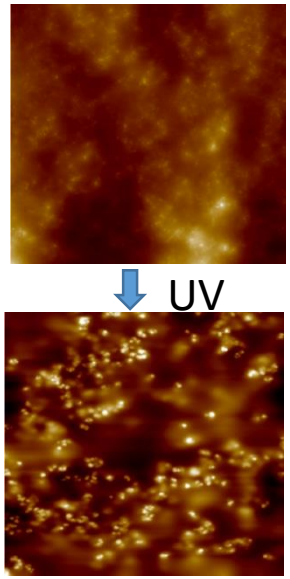
5 % SiO_2-Epoxy

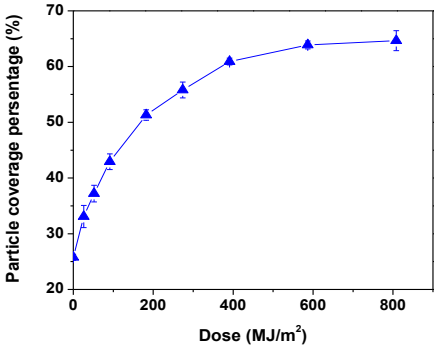


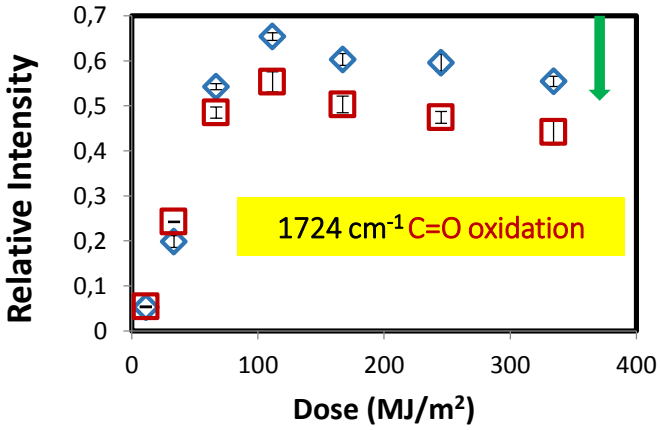
- **The inset is a transmission FTIR spectrum of the pure, untreated silica nanoparticles**
- **New FTIR band around 1074 cm^{-1} related to Si-O band in 5 % SiO_2-epoxy system**

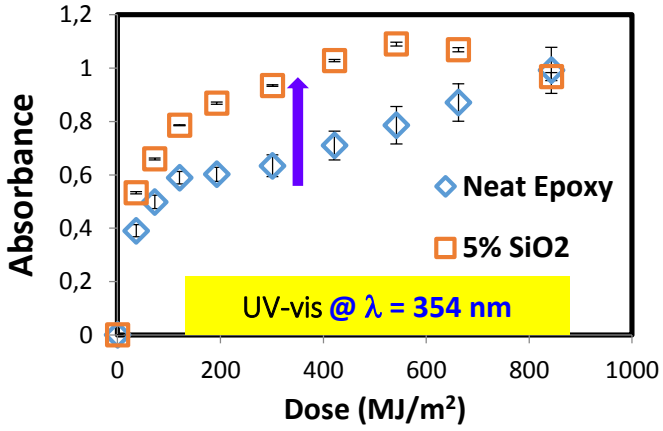
Surface accumulation of nanoparticle (60°C, Dry)

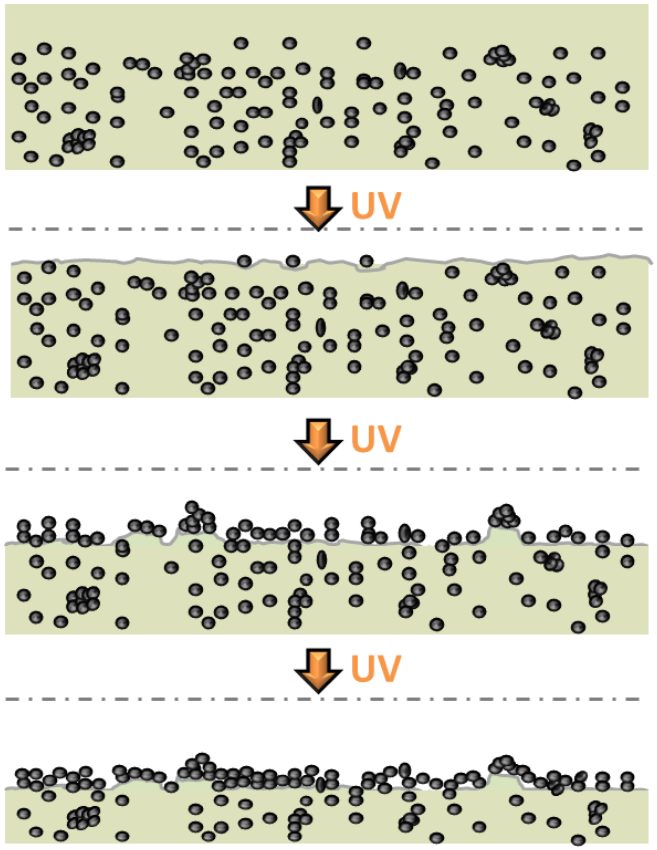
- A substantial amount of silica nanoparticles (SiO_2) has accumulated on the sample surface – mainly due to photodegradation of the matrix.
- Direct evidence of SiO_2 particles release was observed during exposure of epoxy/nanosilica coatings to UV radiation.











Temperature Effects

Kinetics?

Arrhenius-like kinetics?

$$k = Ae^{-E_a/(RT)} \Rightarrow \ln(k) = \frac{-E_a}{R}\left(\frac{1}{T}\right) + \ln(A)$$

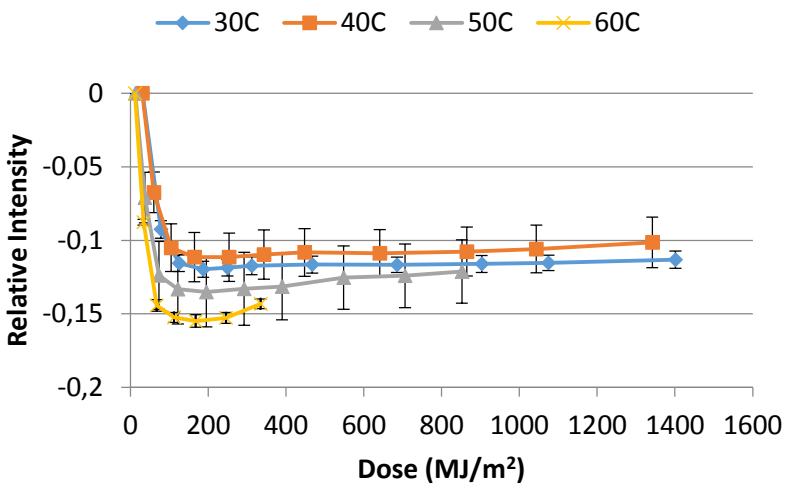
E_a is the activation energy

K: rate, T in °K

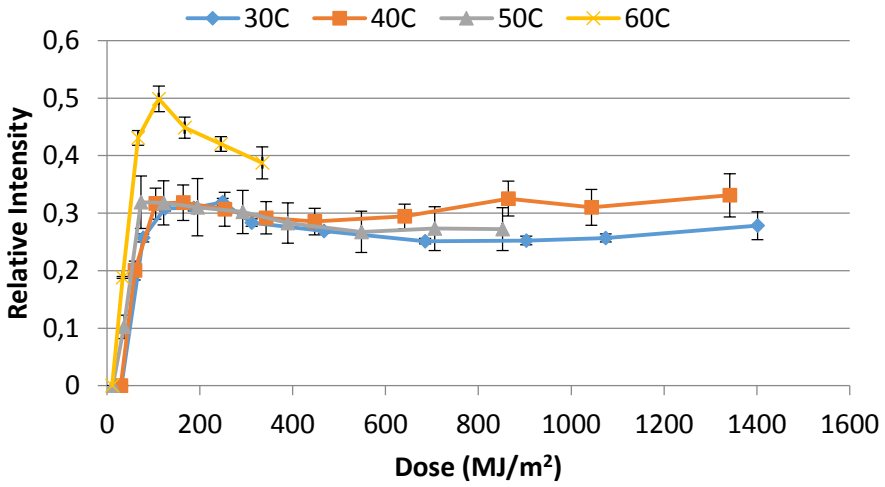
Kinetics data of polymer coatings containing nanoparticles under different UV environments is essential for better understanding the degradation mechanism and predicting the release of nanopartices from exterior nanocoatings.

Temperature Effects: Chemical Changes (ATR-ATIR)

1245 cm^{-1}: chain scission

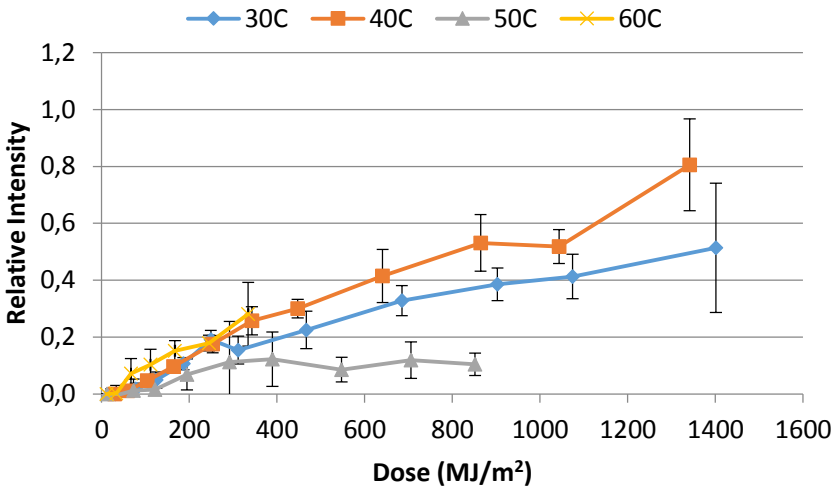


1724 cm^{-1} C=O oxidation



All intensities were Normalized at dose = 0

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}**

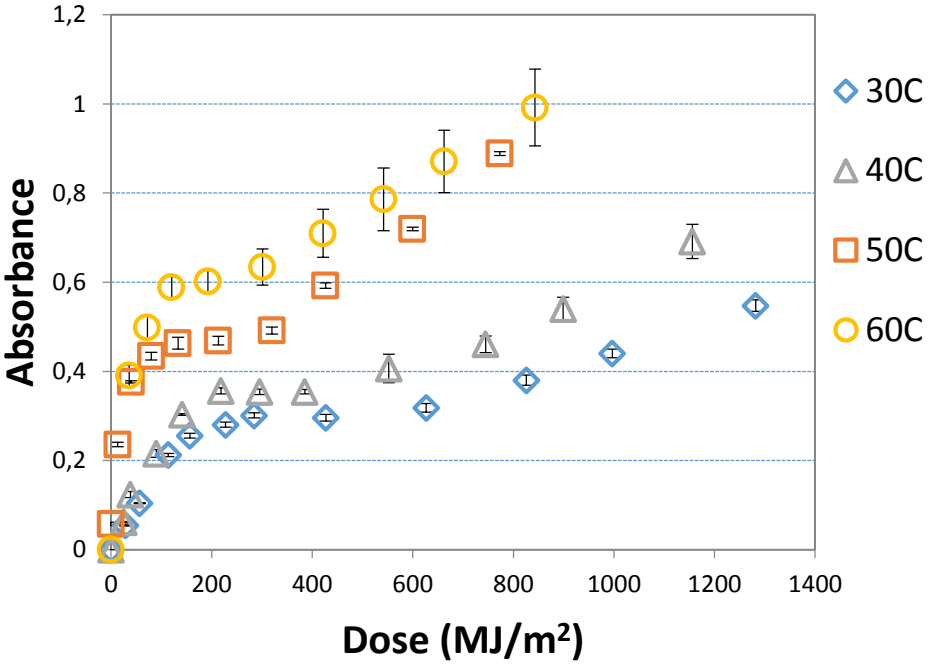
→ increases as UV dose increases

→ no clear trends in temperature effects

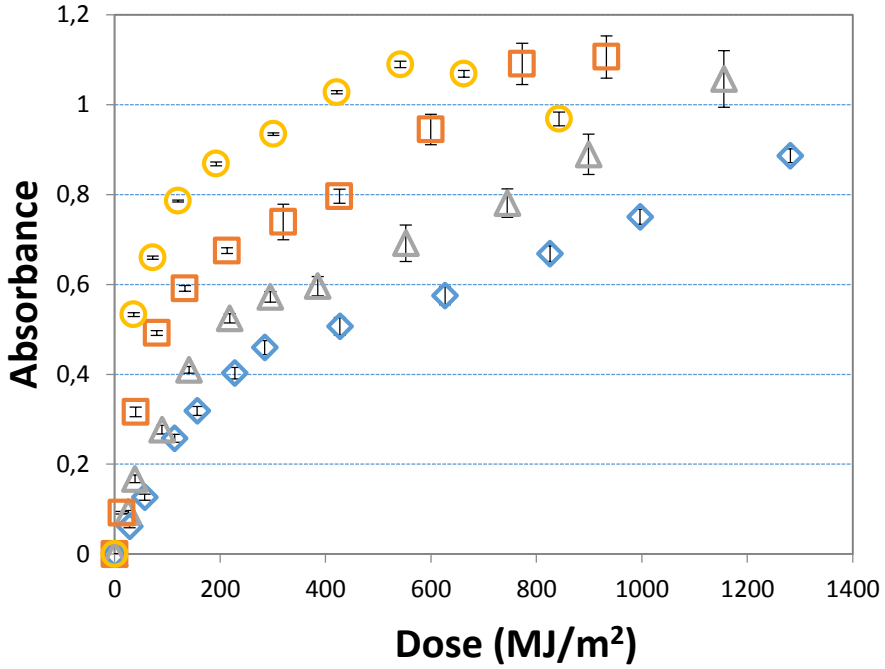
Two oppositely competing processes : loss of epoxy material (C-O loss) & increase of silica nanoparticles on the surface (Si-O increase).

Temperature Effects: Chemical Changes (UV-Vis) @ λ = 354 nm

Neat Epoxy



5 % SiO_2-Epoxy



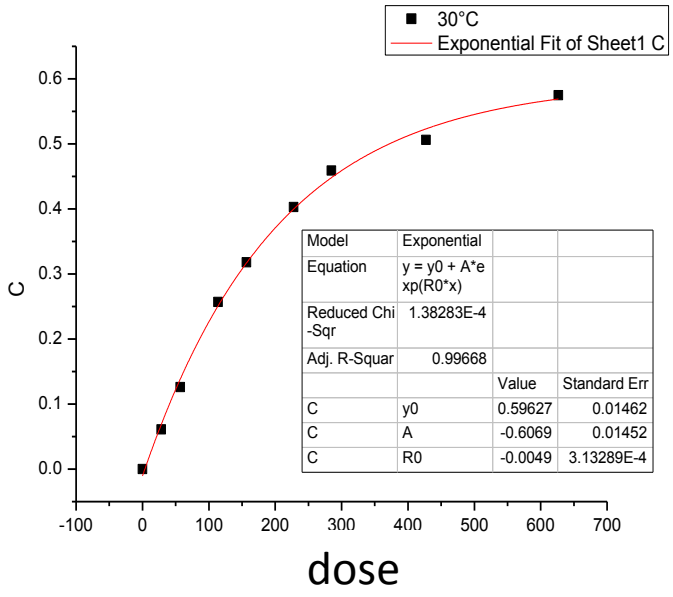
- Absorbance increased as UV dose increased
- Higher temperature had a higher rate of increase

Temperature Effects: Chemical Changes (UV-Vis)- data fitting

Neat Epoxy

	30	40	50	60
y_0	0.316±0.015	0.389±0.022	0.462±0.007	0.603±0.015
A	-0.239±0.017	-0.399±0.022	-0.400±0.011	-0.600±0.023
R_0	-0.0094±0.001	-0.0098±0.0016	-0.0399±0.003	-0.027±0.003
R^2	0.983	0.987	0.996	0.995

$$y = y_0 + A*\exp(R_0*x)$$



5 % SiO_2-Epoxy

	30	40	50	60
y_0	0.596±0.015	0.652±0.025	0.765±0.021	0.895±0.038
A	-0.607±0.015	-0.656±0.024	-0.766±0.028	-0.879±0.059
R_0	-0.0049±0.0003	-0.0069±0.0007	-0.012±0.0012	-0.020±0.003
R^2	0.996	0.9954	0.991	0.978

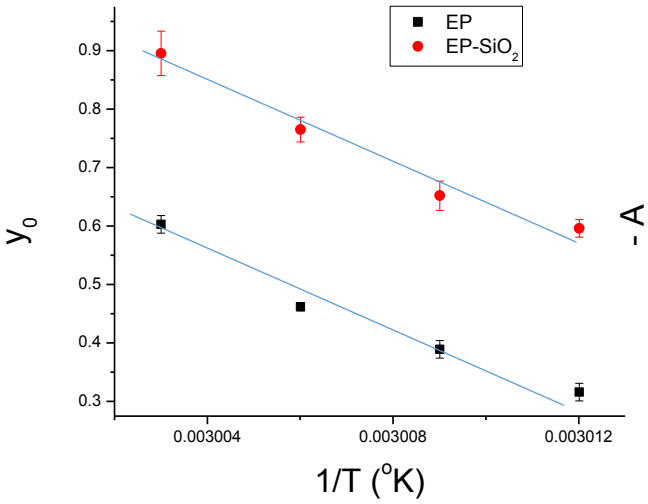
Y_0 values higher with **SiO_2**

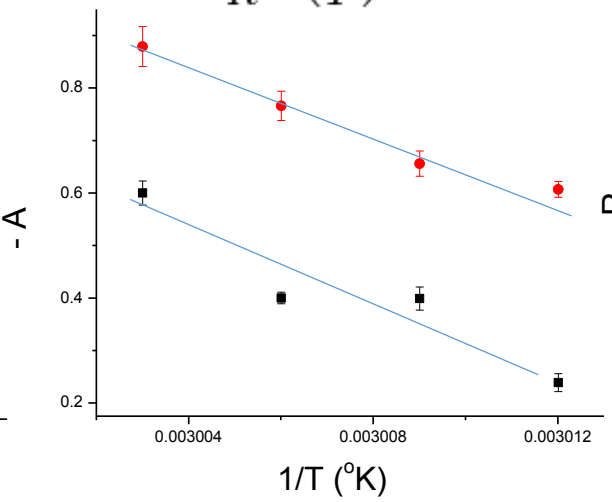
Temperature Effects – with and without SiO_2 (UV-Vis Data)

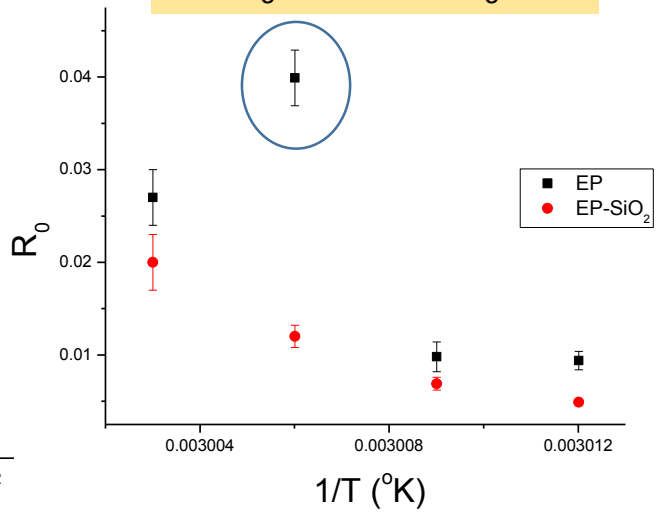
$$k = Ae^{-E_a/(RT)}$$

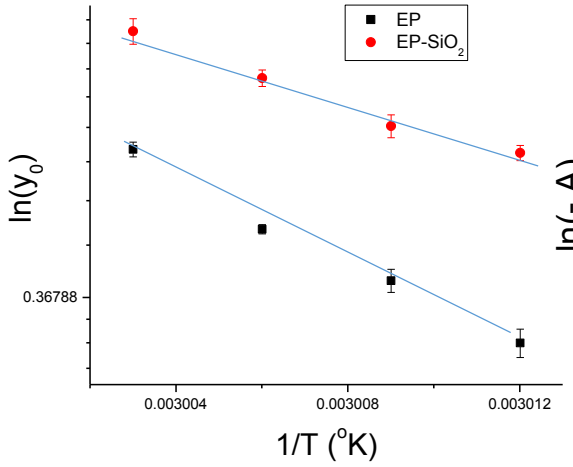
$$\ln(k) = \frac{-E_a}{R}\left(\frac{1}{T}\right) + \ln(A)$$

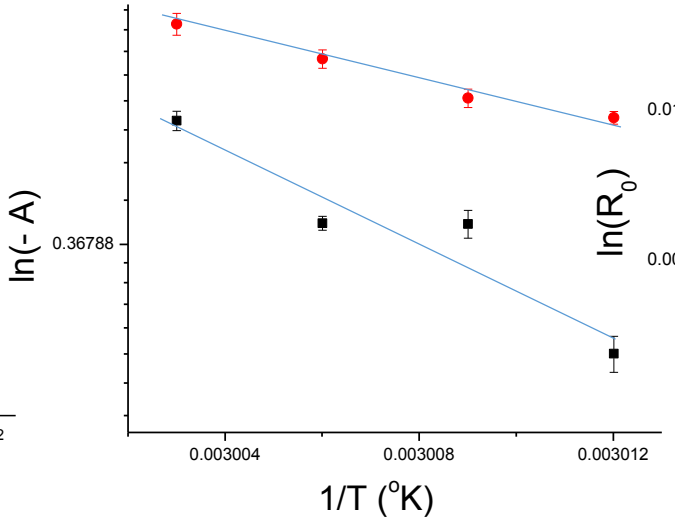
$y = y_0 + A*\exp(R_0*x)$

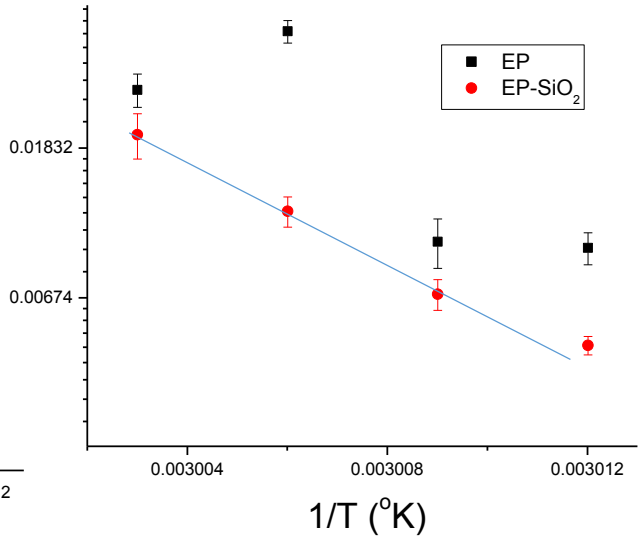






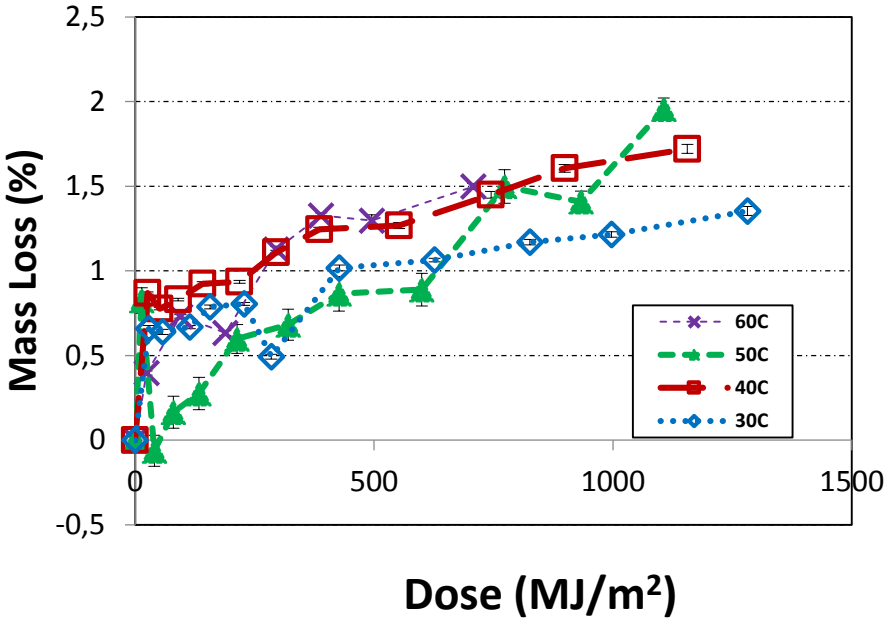


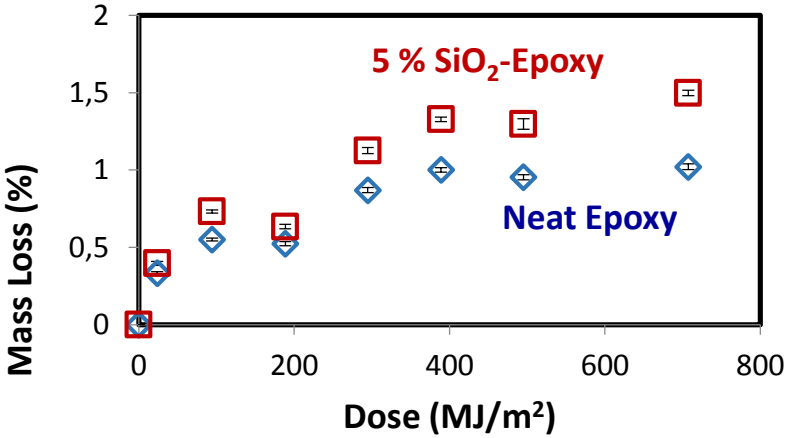




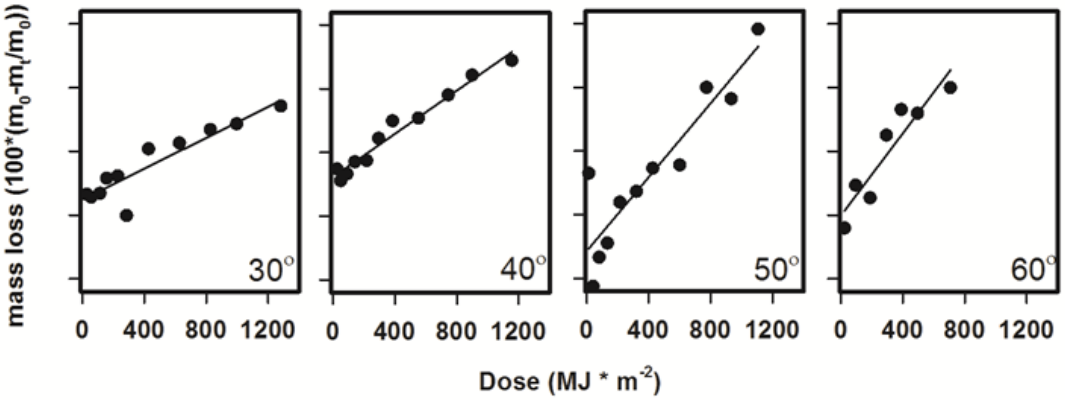
Y_0 values higher with **SiO_2**

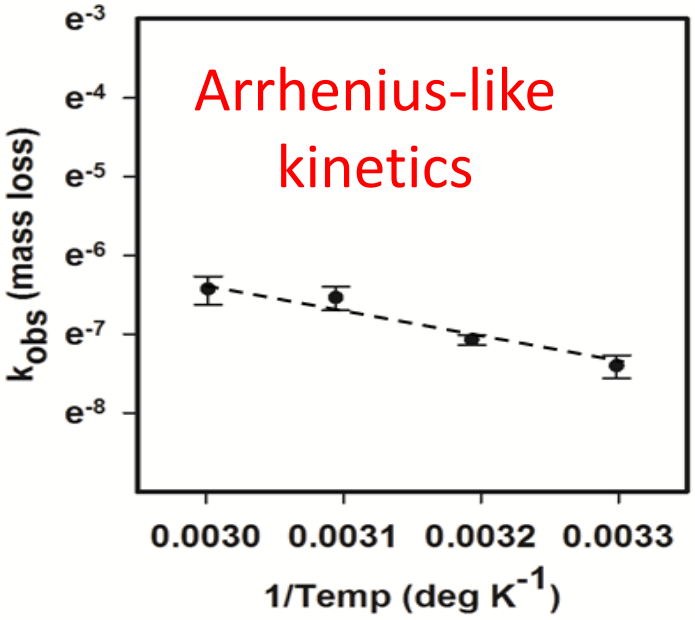
Temperature Effects: Mass Loss



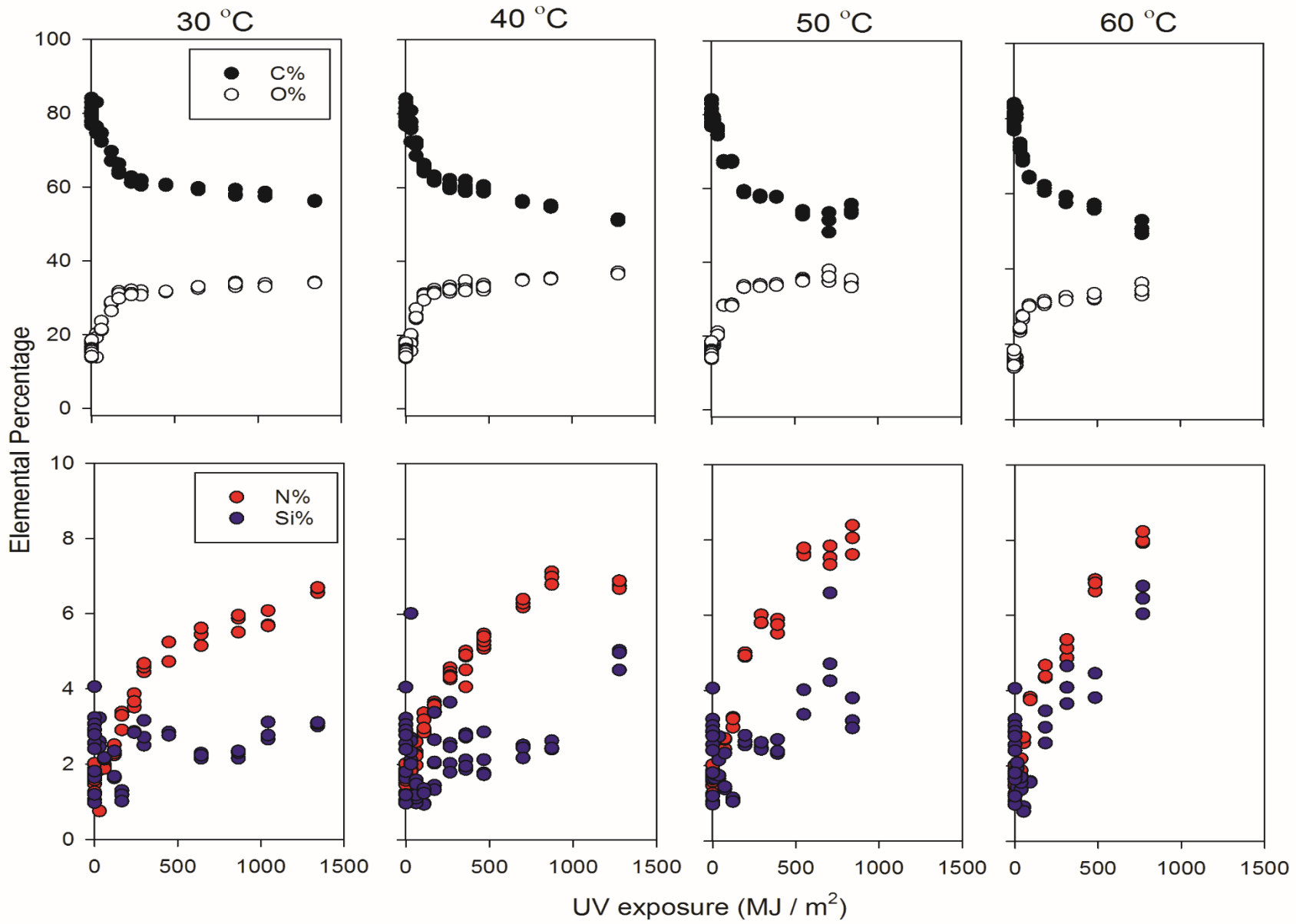


Linear fit



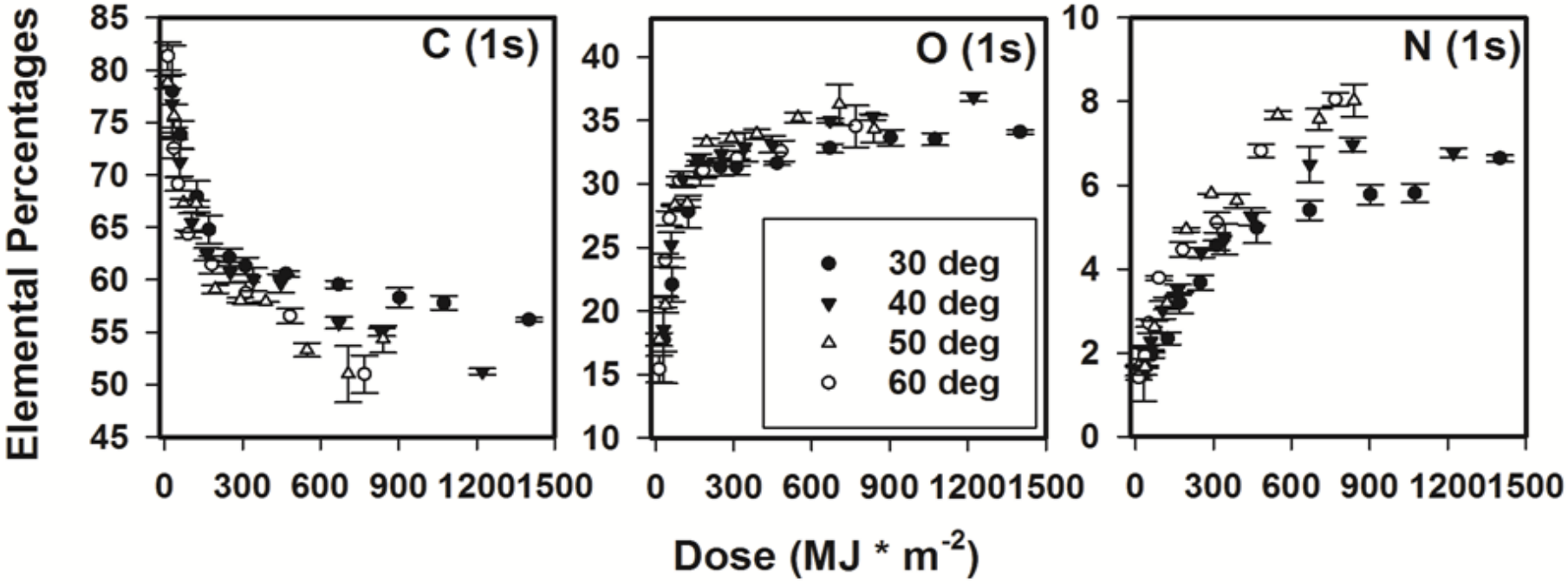


Results: XPS


30 °C
40 °C
50 °C
60 °C
C%
O%
N%
Si%
Elemental Percentage
UV exposure (MJ / m²)
0
20
40
60
80
100
0
2
4
6
8
10
0
500
1000
1500

XPS

Surface enhancement C, O, N vs. UV dose at different T



Dose < 500 MJ * m^{-2}

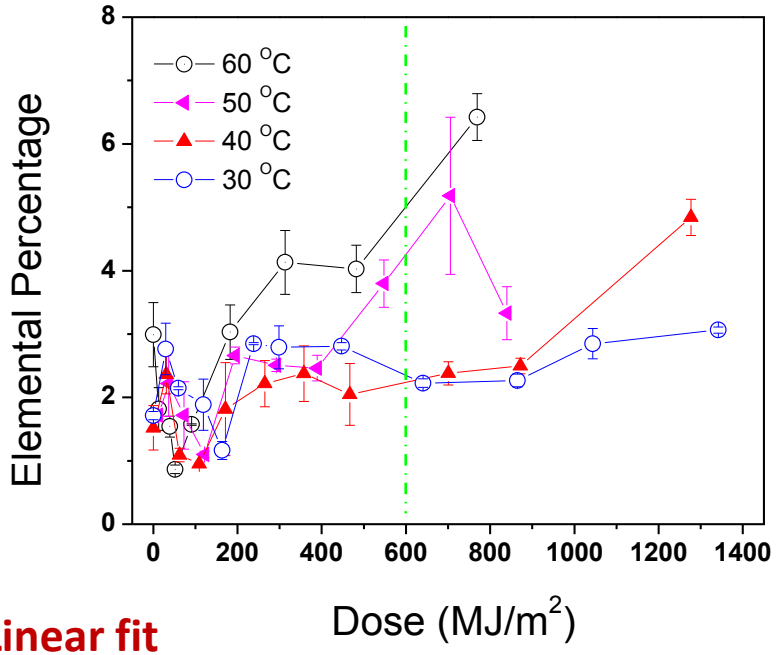
No temperature dependence for C(1s), O(1s) and N(1s)

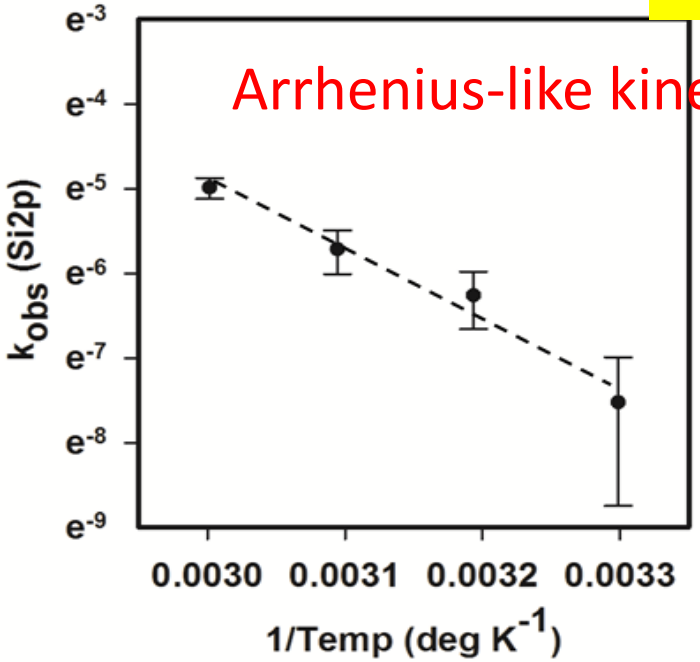
Dose > 500 MJ * m^{-2}

- 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): $\%N_{30\ °C} < \%N_{40\ °C} < \%N_{50\ °C} \approx \%N_{60\ °C}$.

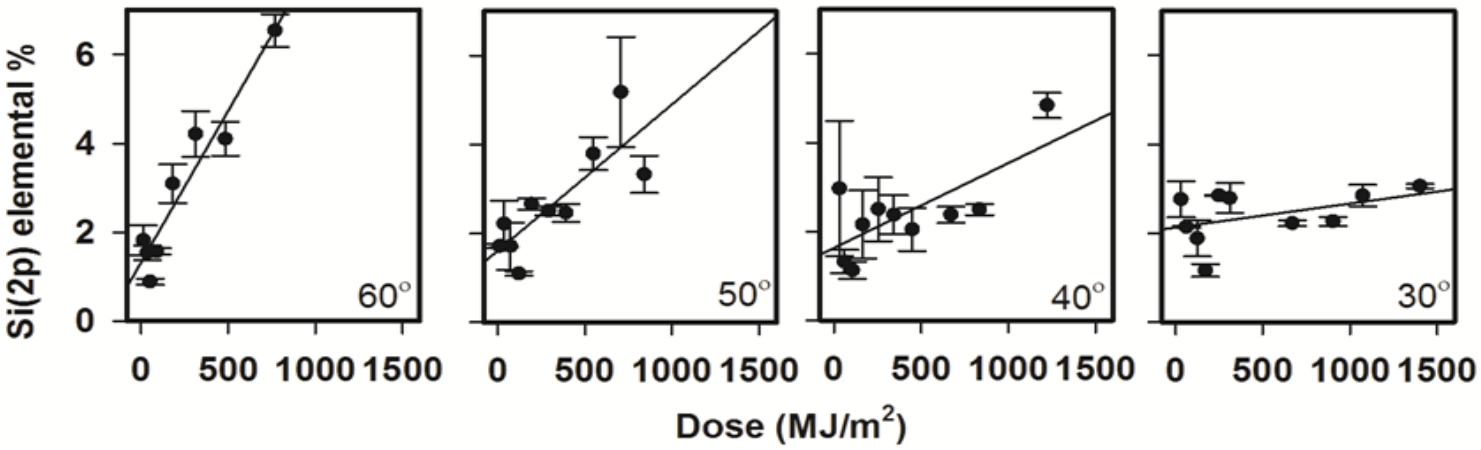
Surface enhancement Si vs. UV dose at different T

XPS

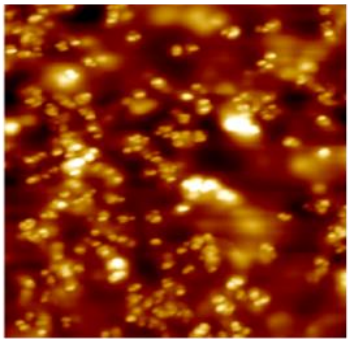
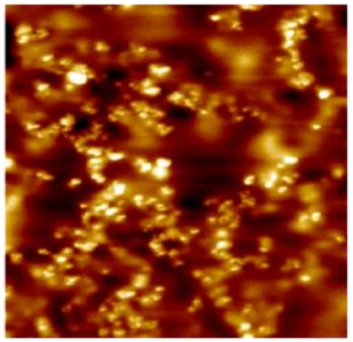
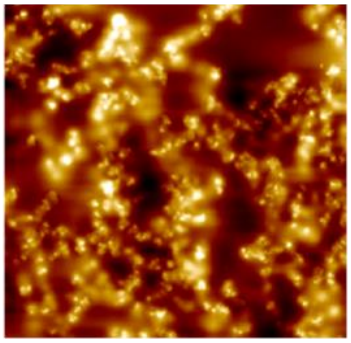
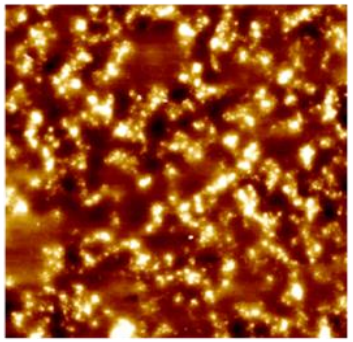
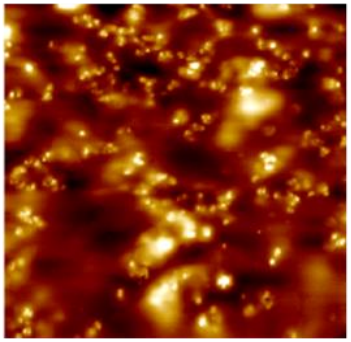
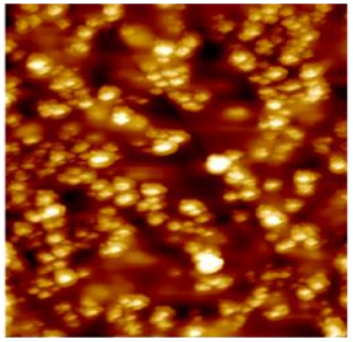
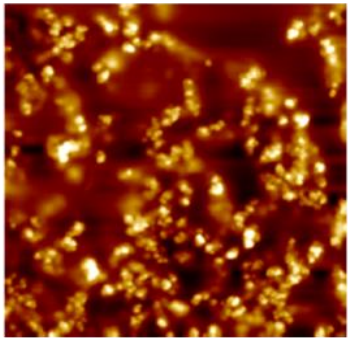
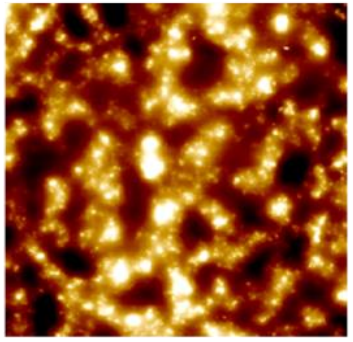
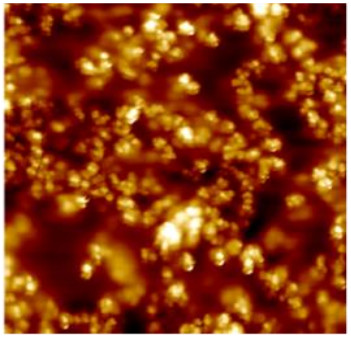
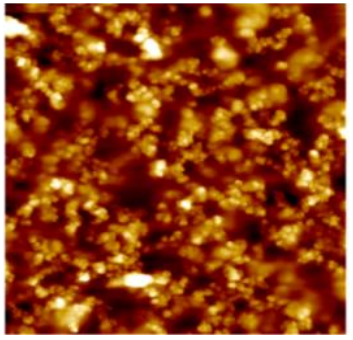
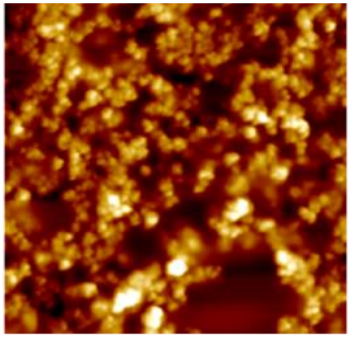
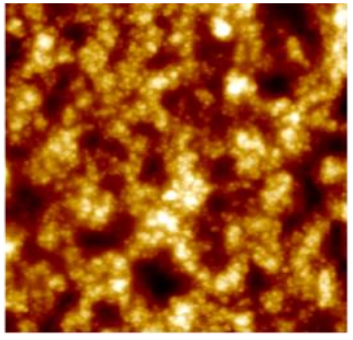




Linear fit

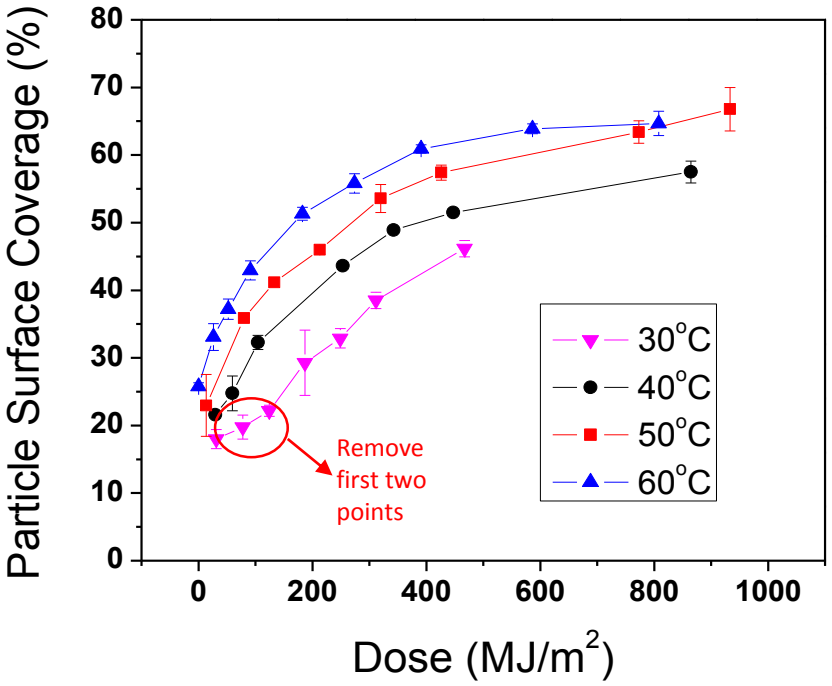


Temperature effects: Surface Morphology - AFM

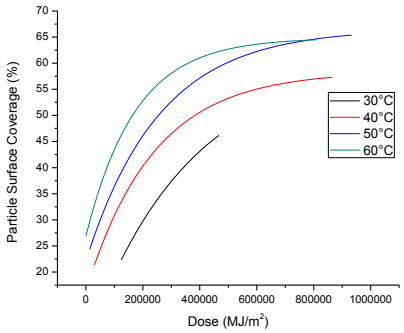
30°C	40°C	50°C	60°C
31 MJ/m^2	30 MJ/m^2	12 MJ/m^2	52 MJ/m^2
			
78 MJ/m^2	104 MJ/m^2	73 MJ/m^2	91 MJ/m^2
			
187 MJ/m^2	253 MJ/m^2	195 MJ/m^2	182 MJ/m^2
			

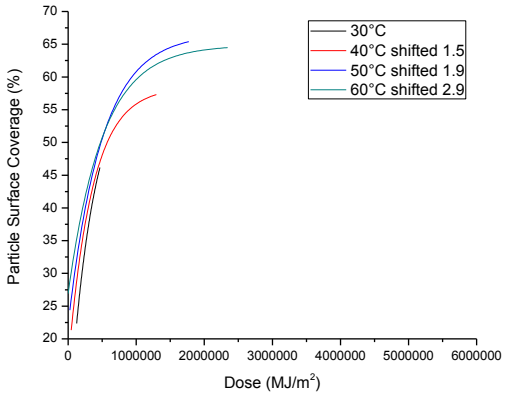
Temperature effects:

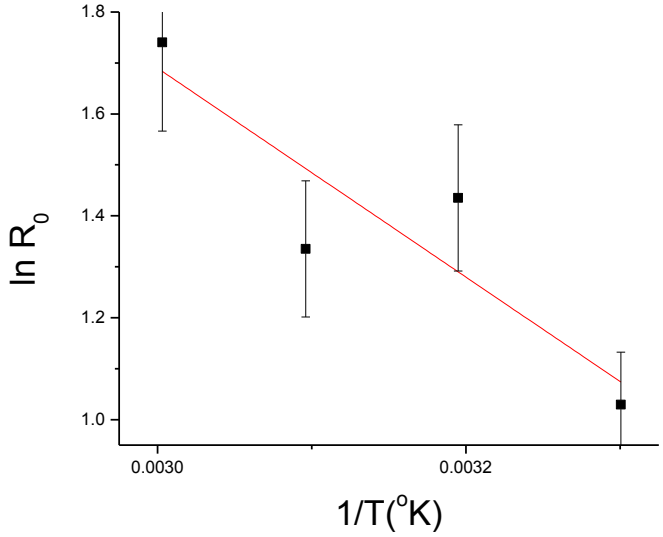
Surface Morphology - AFM - data fitting

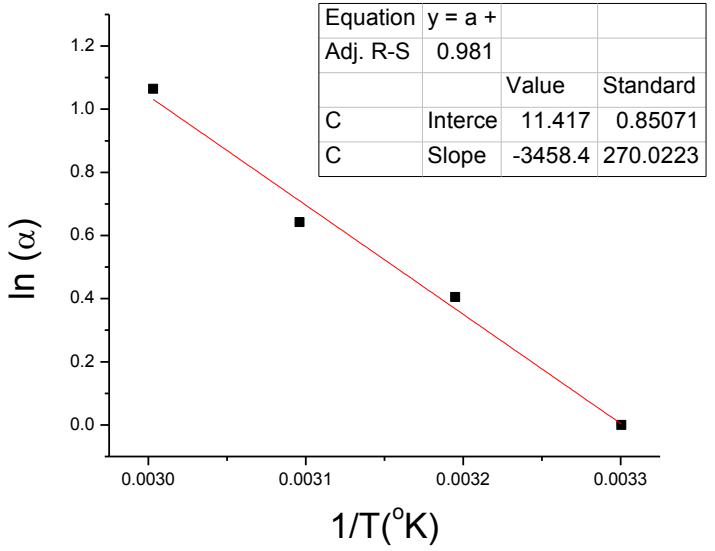


Shift factor





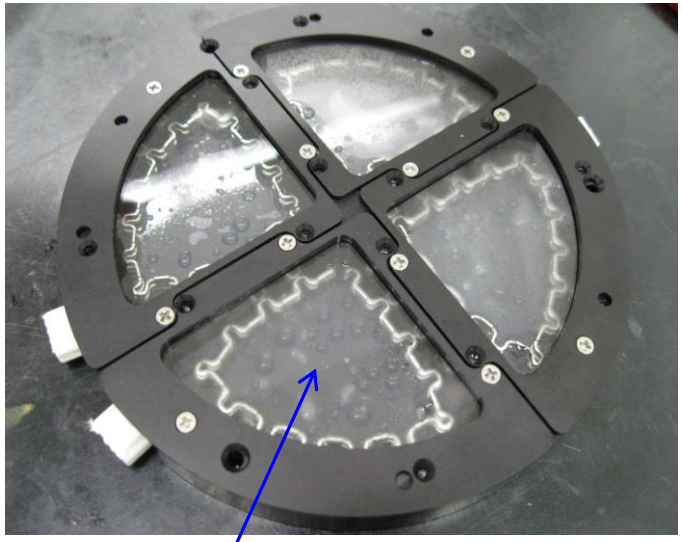




Equation	y = a +		
Adj. R-S	0.981		
		Value	Standard
C	Interce	11.417	0.85071
C	Slope	-3458.4	270.0223

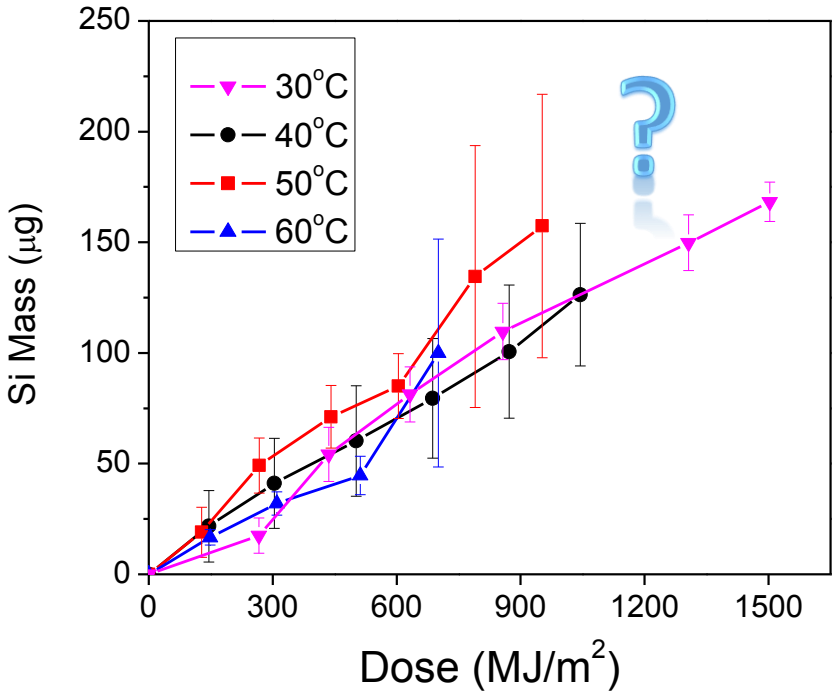
Collecting Released Nanoparticles – Using ICP-OES

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

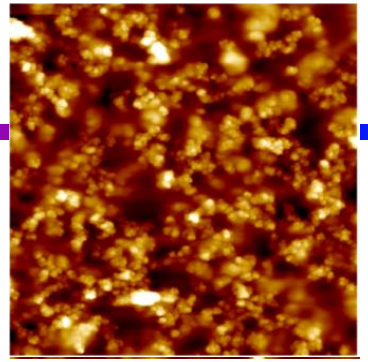
With surface treated SiO_2
→ improve dispersion



Large uncertainties @ high Temp !

Dispersion issue?
Non-uniform degradation

With Surface Treated SiO_2 → Better Dispersion

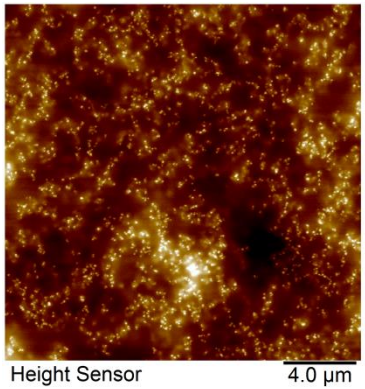


Epoxy+SiO_2 (untreated)
– 14 d –

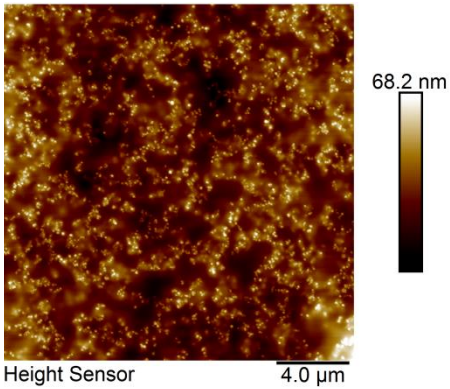
Epoxy+SiO_2 (treated)

Height

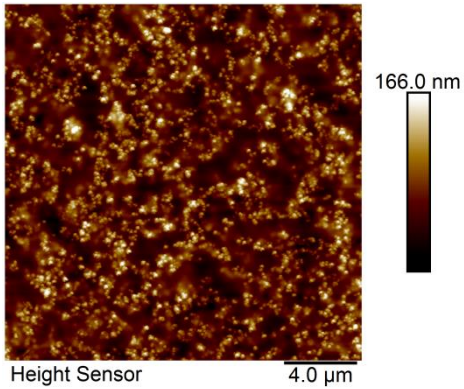
1 d



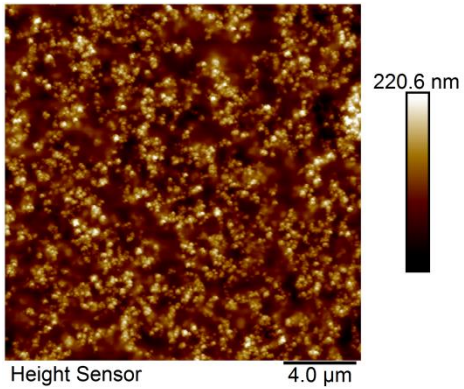
3 d



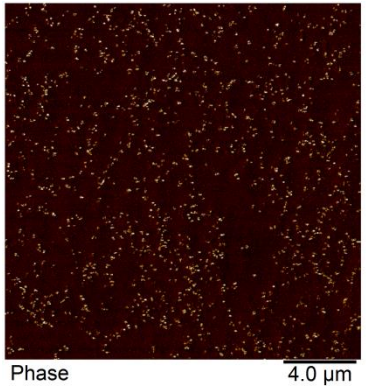
7 d

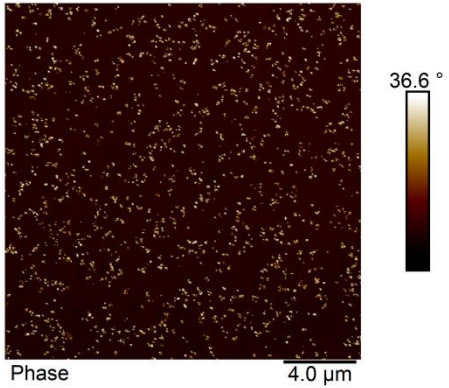


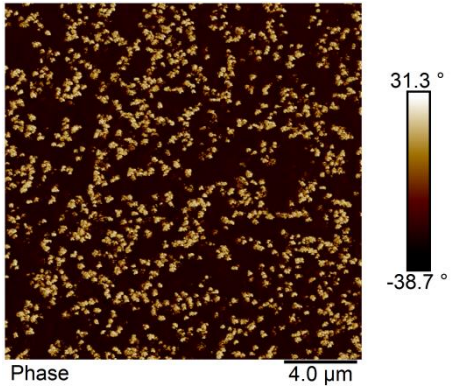
10 d

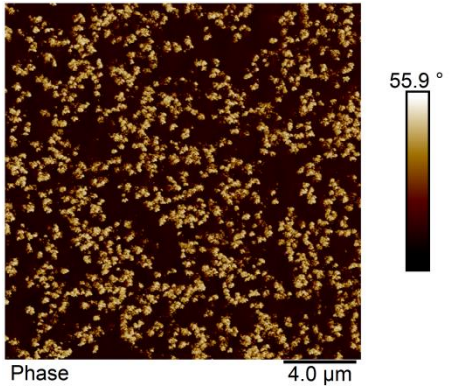


Phase



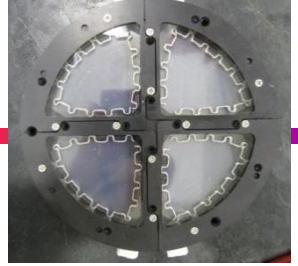




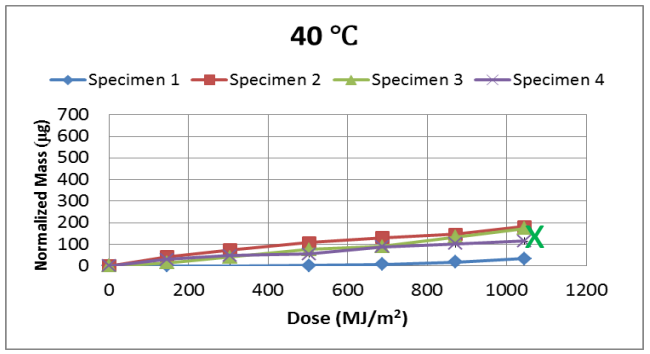


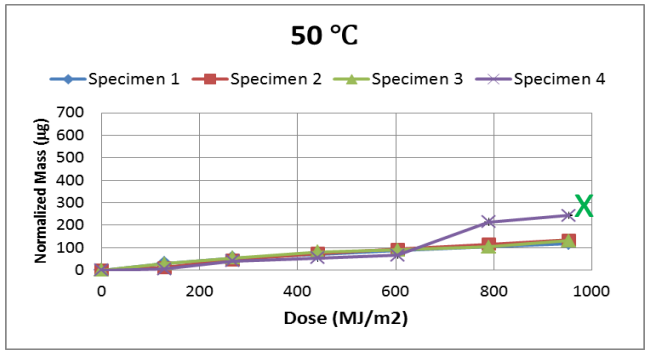
Scan size : 20 µm X 20 µm

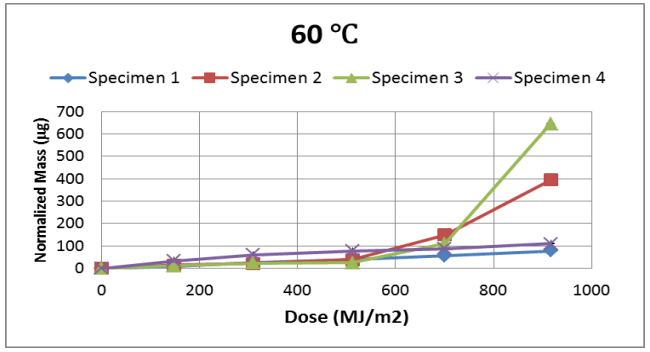
Non-Uniform Degradation Process

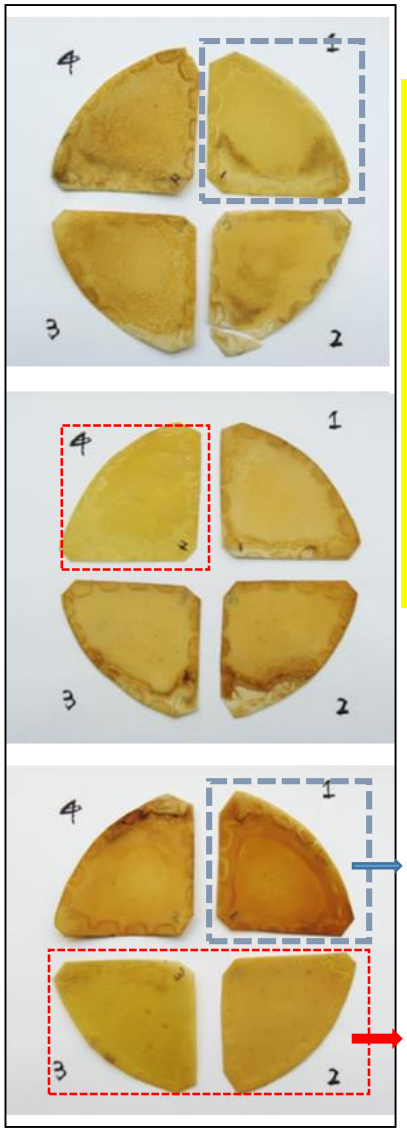


surface treated SiO_2



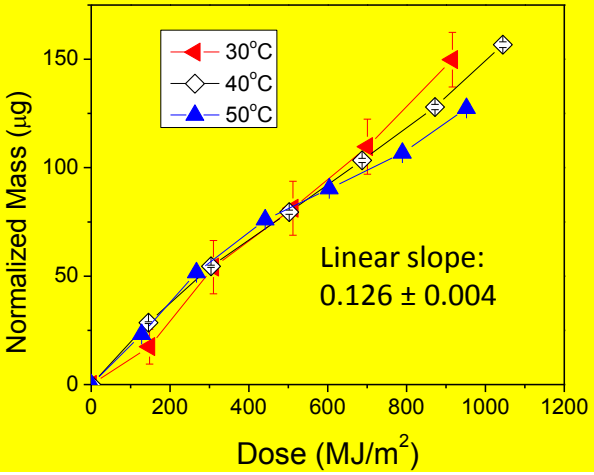






less release

more release



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

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 ^{o}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