Anti-corrosion Organic Coatings

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August 20, 2019

Texas A&M PTIC Consortium

Consortium Objectives:

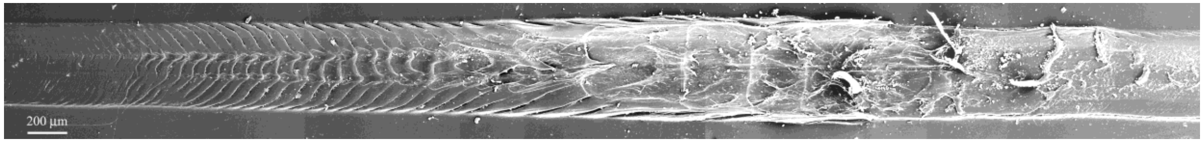
- Promote University-Industry Interaction
- Prepare Students for the Industry
- Facilitate Multi-disciplinary Research
- Attract Industrial Funding

Texas A&M Scratch Behavior Consortium

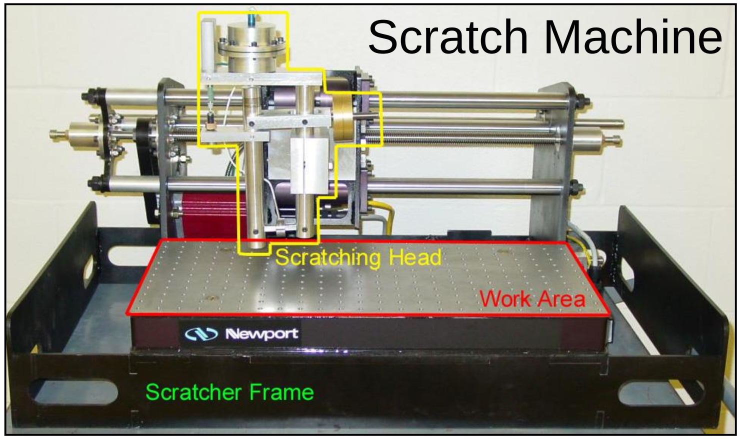
Consortium Objectives:

- Develop Test Methodology
- Understand Scratch Mechanics
- Correlate to Materials Science
- Build Physics-Based Scratch Model

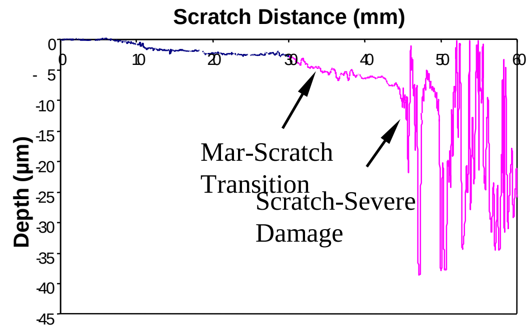
Scratch Research

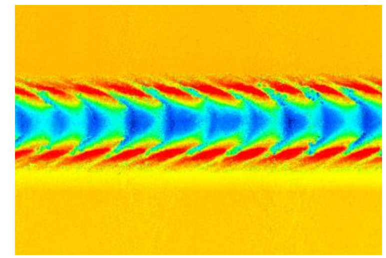


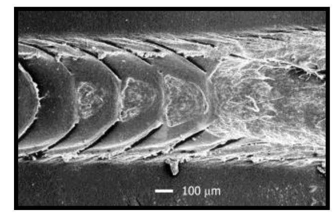
ASTM D7027-13
ISO 19252:08



Materials Science



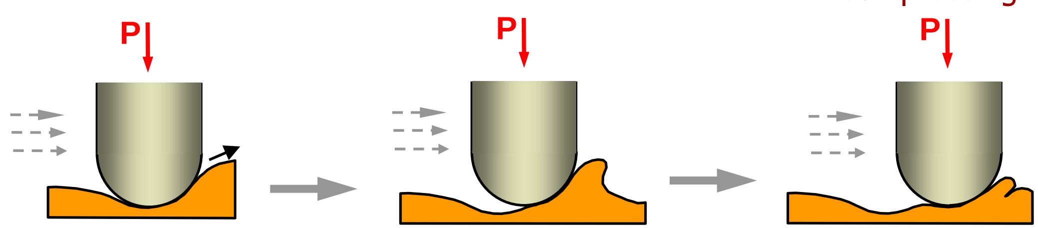




- Bulk Samples
- Packaging Films
- Coatings/Paints
- Laminates
- Textured Surfaces

Mechanics & Modeling

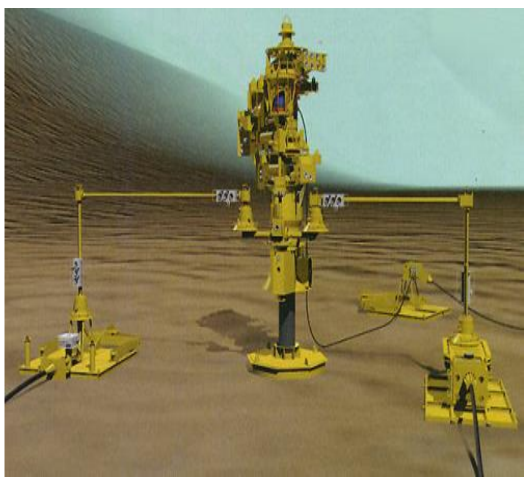
Deformation & Stretching   Pushing over   Compressing the pile-up

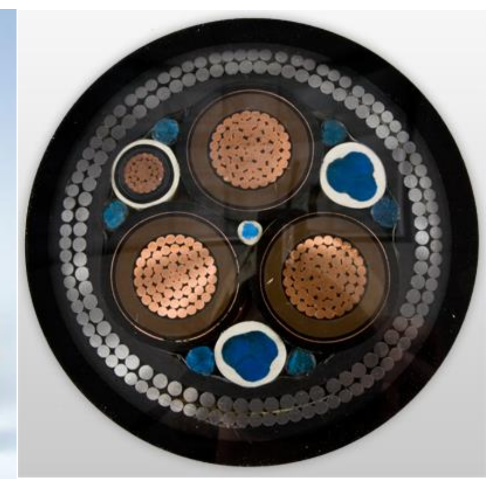


Consortium for
Advancing
Performance
Polymers in
Energy
AppLications
(http://ptc.tamu.edu/appeal.html)

APPEAL

Co-director: Tim Bremner



Texas A&M APPEAL Consortium

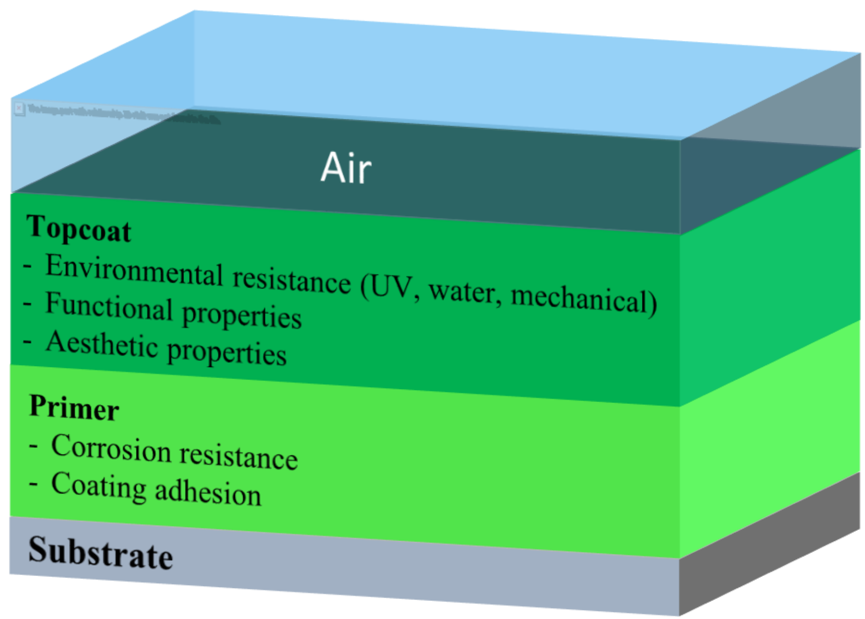
(Advancing Performance Polymers in Energy AppLications)

Consortium Objectives:

- Establish fundamental structure / property relationships and models
- Determine polymer reinforcement mechanisms towards property balance manipulation and intelligent material design
- Establish consistent and appropriate methodologies for characterization of physical and mechanical properties under usage conditions (high temperature, high pressure, and highly corrosive environments)
- Provide confidence and scientific basis to end users for material design and application

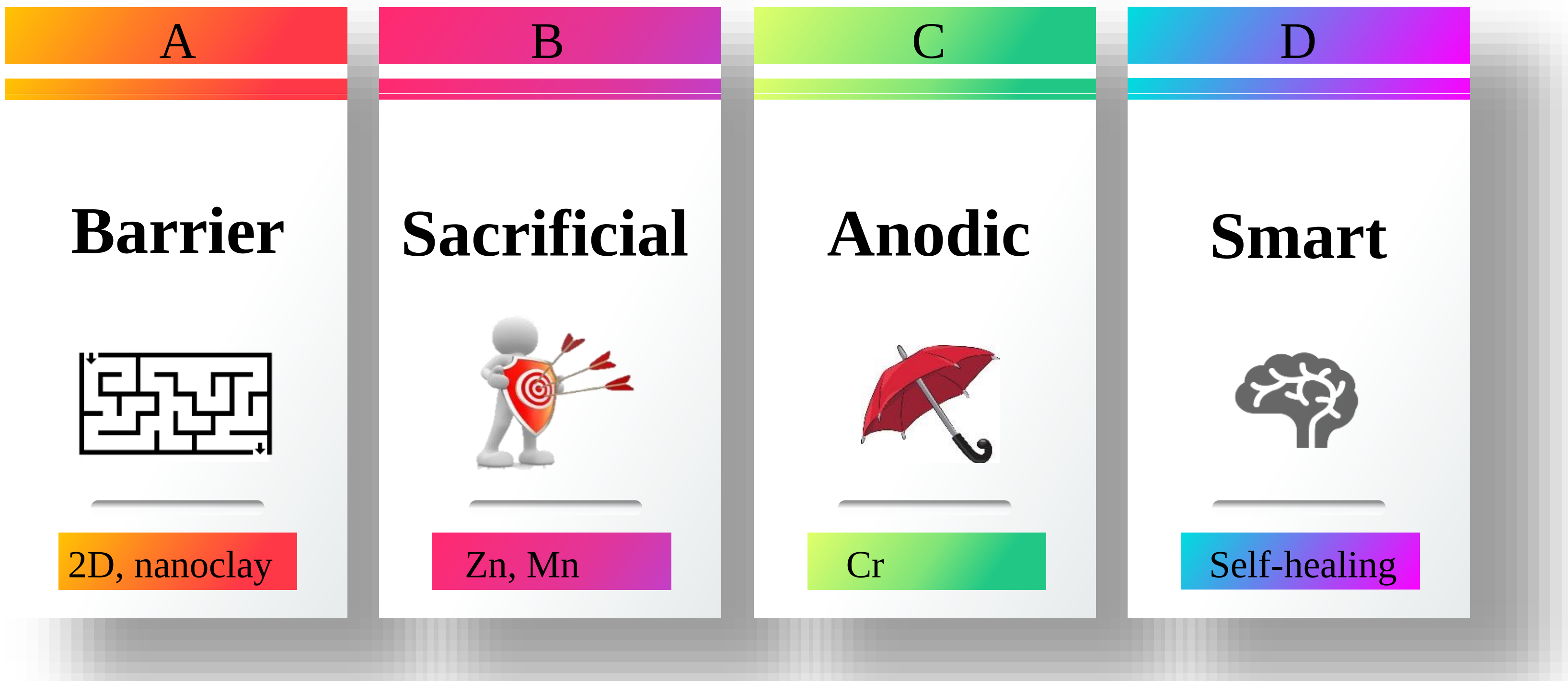
Anti-corrosion Organic Coatings

- A typical function of polymeric coatings is to serve as a physical barrier layer for a metallic substrate and block/limit the access of active corrosion enabling species, thus decreasing the corrosion rate of the metal substrate.
- Most common choices: epoxy, polyurethane, alkyds and acrylics.



Anti-corrosion Organic Coatings

- Categories of anti-corrosion fillers based on protection mechanism:



- In addition they can provide other benefits including anti-fouling properties, hydrophobicity, & promoting uniform corrosion by increasing the conductivity.

Why Nano-materials?

- The increases in specific surface area and interfacial region lead to enhanced molecular-level interactions at the phase interfaces. The synergistic effects of these phenomena may be employed to induce significant improvements in physical and mechanical properties of nanocomposite materials, even if the nanoparticles are added at a very low volume fraction.

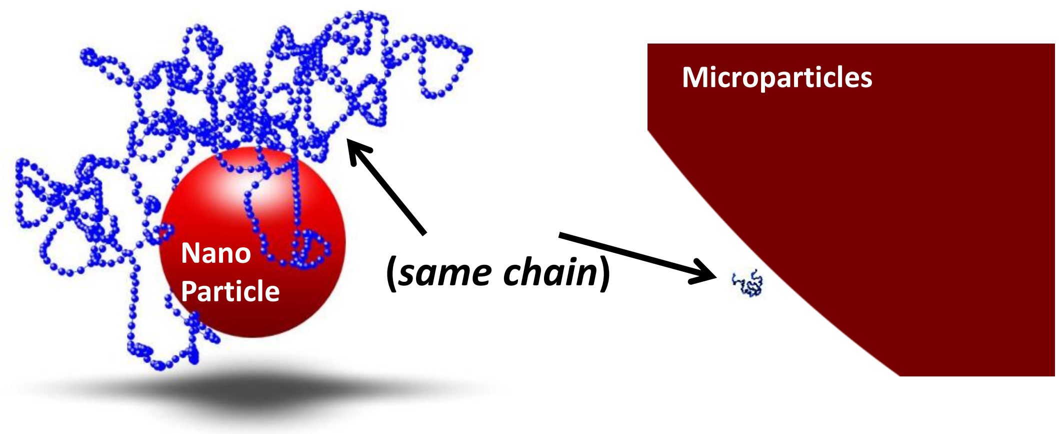
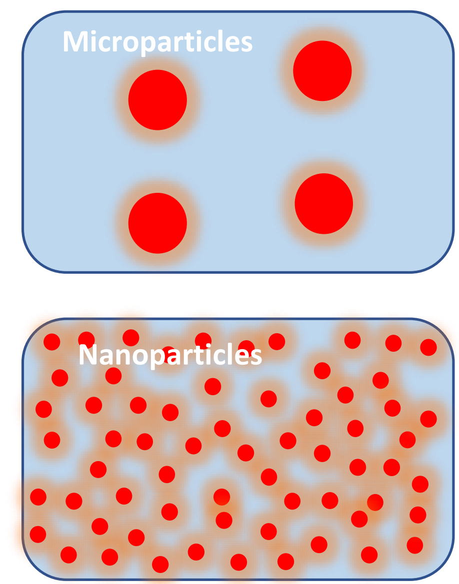


Illustration of 10-nm nanoparticle interacting with polymer chain with $R_g \sim 20$ nm.

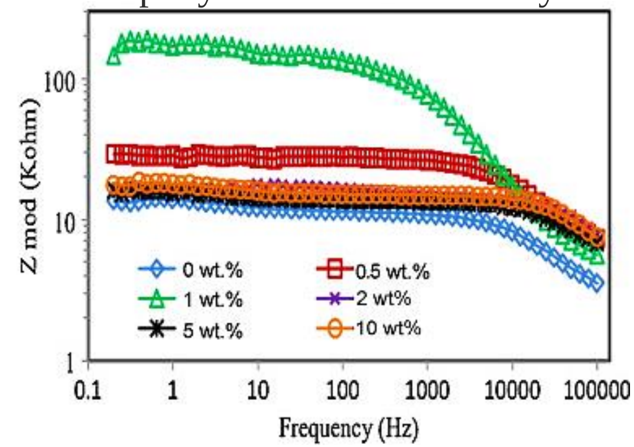
Zoom out image of the same polymer chain adjacent to 10-μm particle.



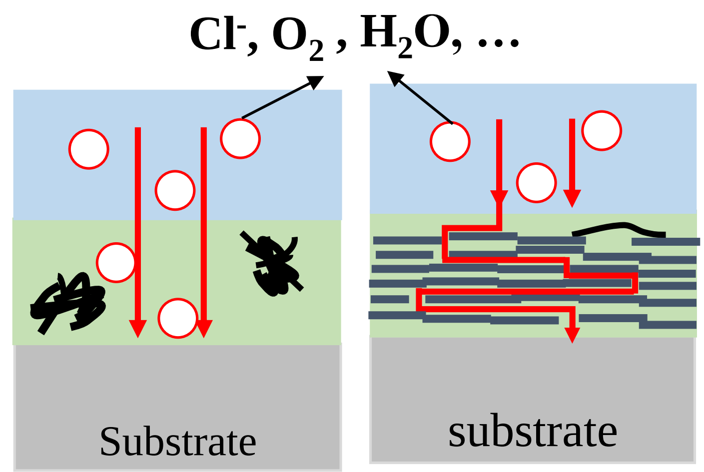
Effect of Dispersion

- Data form literature shows almost always after adding a certain amount of nanofillers, the anti-corrosive properties reduces. This is due to aggregation.
- In the literature the nanofillers content is usually very low, due to difficulties in exfoliating and uniformly dispersing the nanofillers. In clays it is usually below 5 wt%.

Epoxy/montmorillonite clay



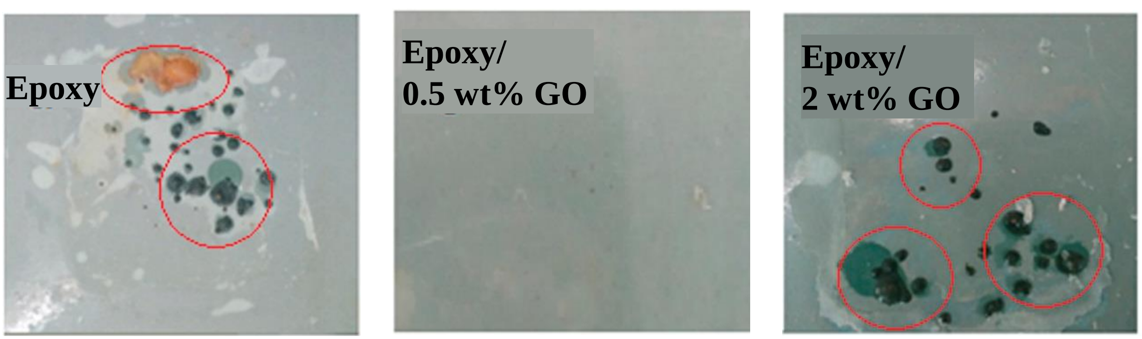
Progress in Organic Coatings 76.11 (2013): 1576-1580



Poor dispersion of nanoplatelets

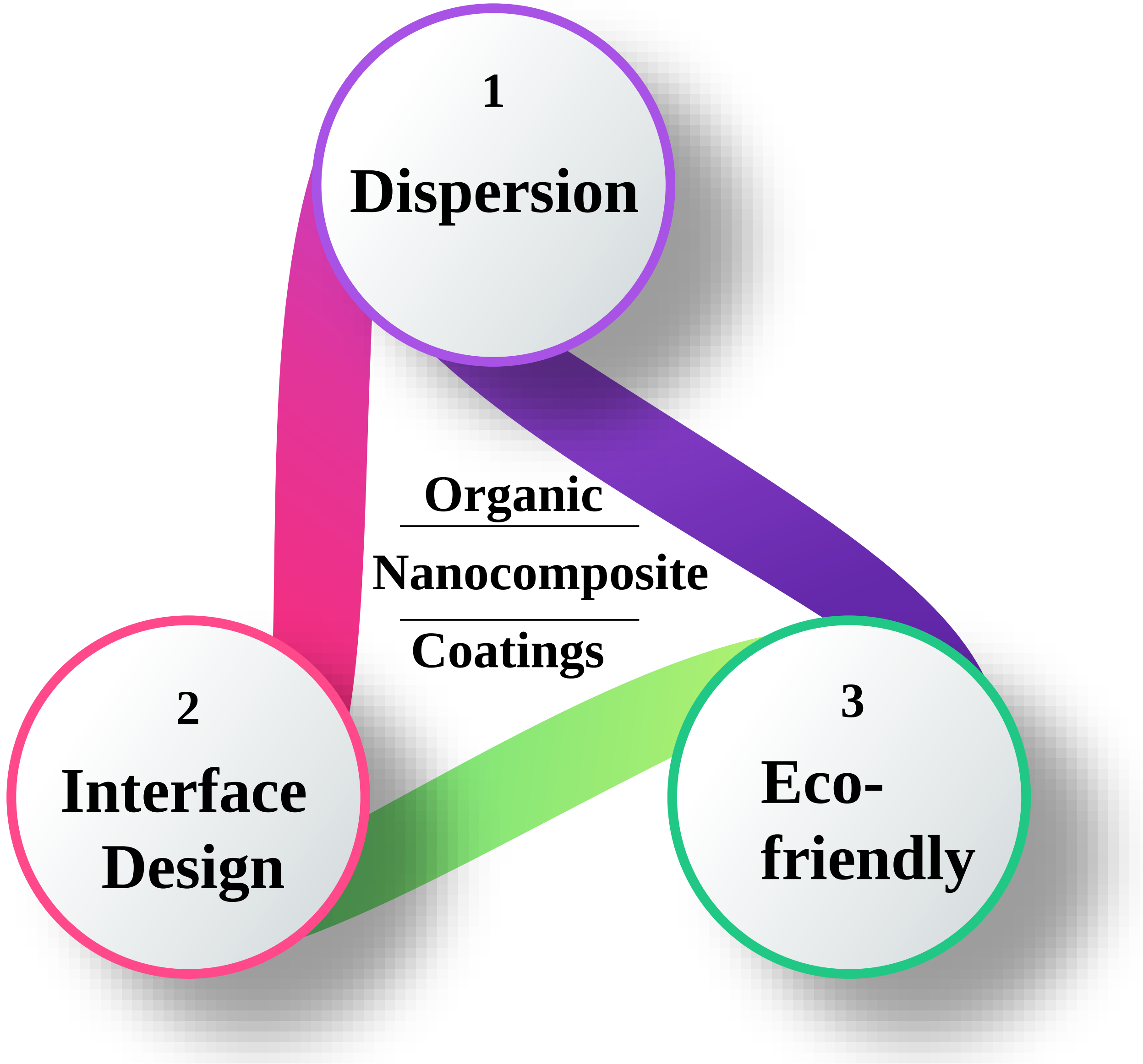
Fully exfoliated

After exposure in salt spray for 500 h

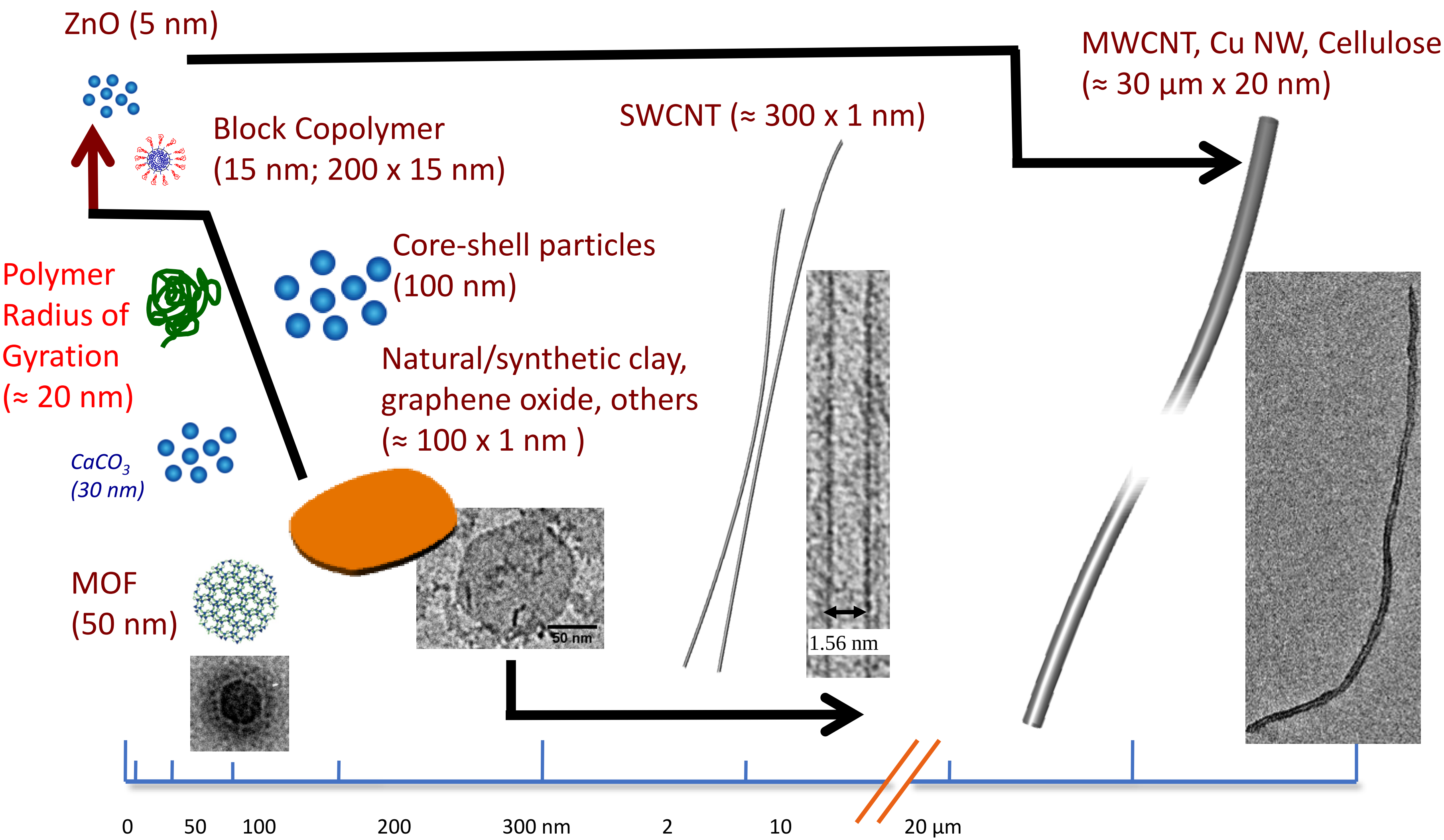


Progress in Organic Coatings, *109* (2017): 126-134.

Research Focuses

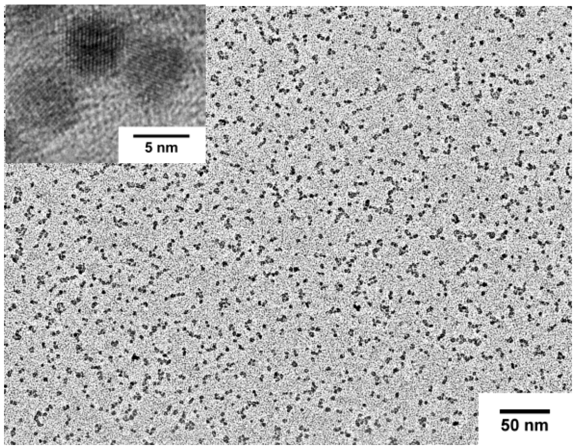


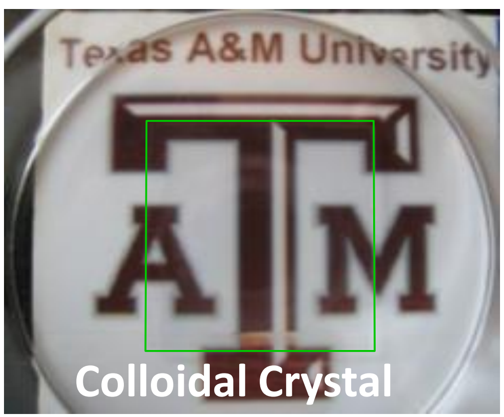
Relative Scale of Nanomaterials Studied



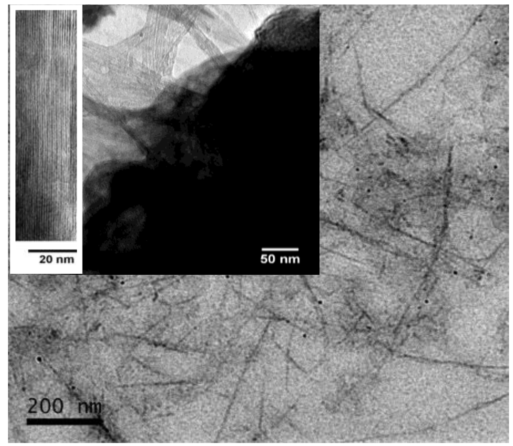
Nanomaterial Research
(Dispersion and Assembly)

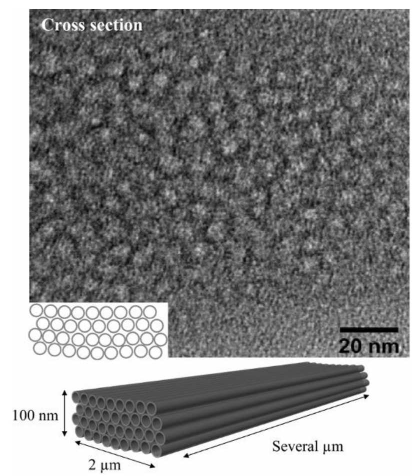
0-D nanomaterial
ZnO QDs



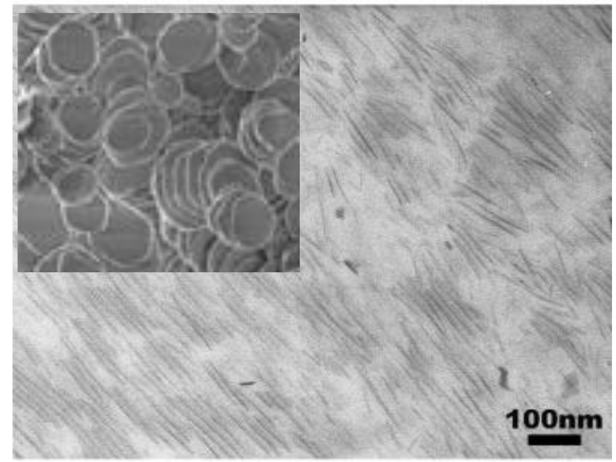


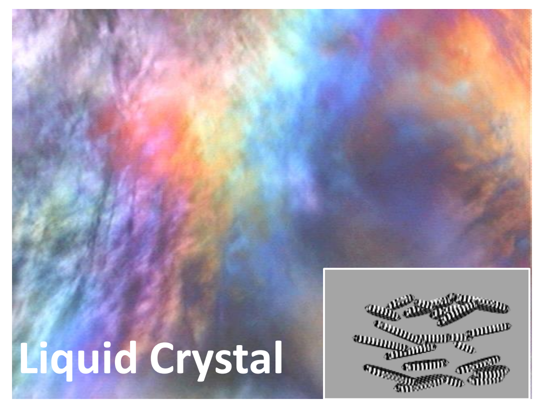
1-D nanomaterial
CNTs



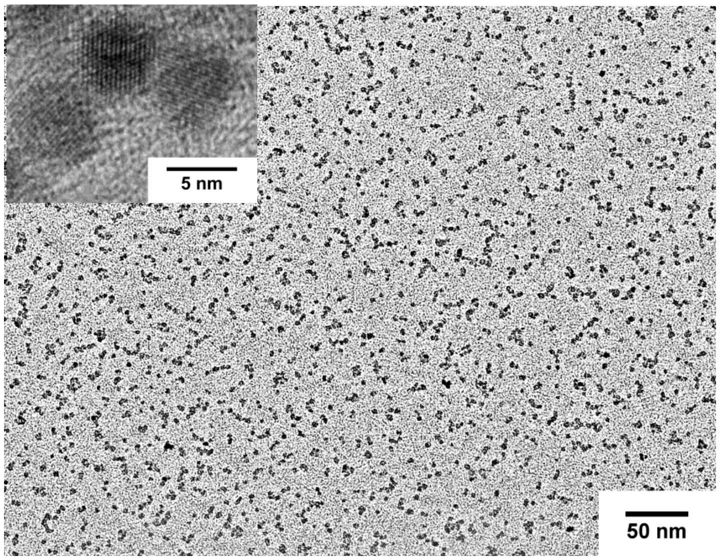


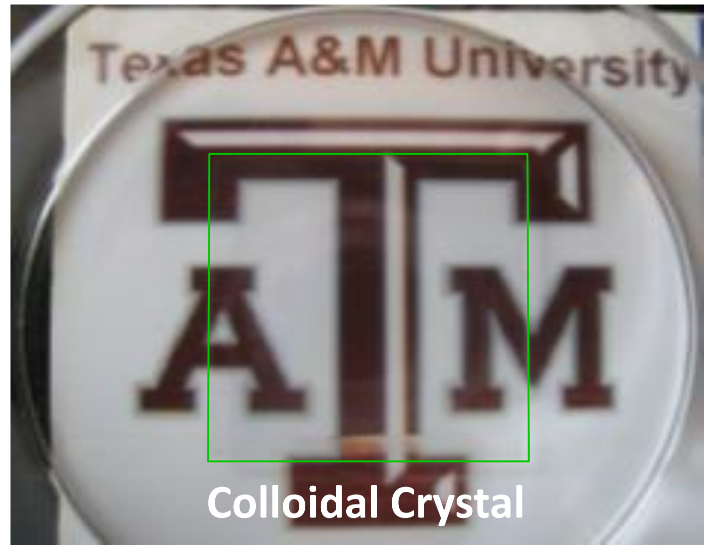
2-D nanomaterial
α-ZrP nanoplatelets





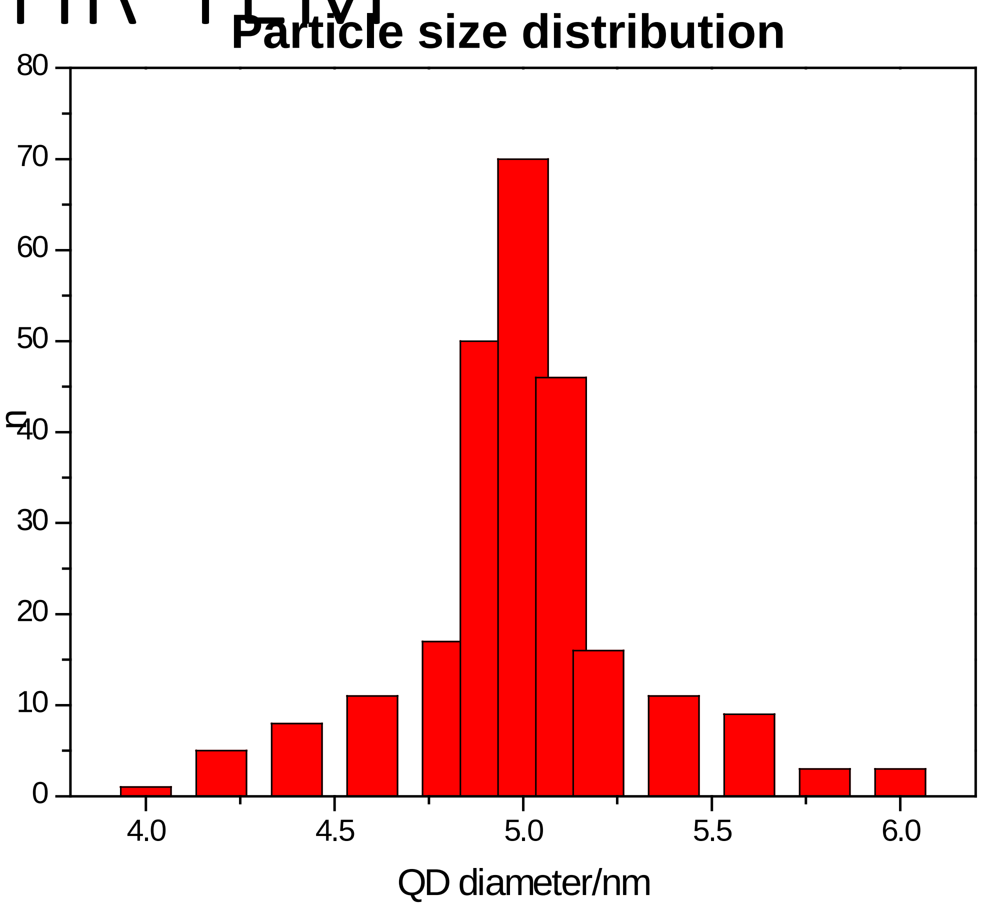
0-D ZnO Quantum Dots*

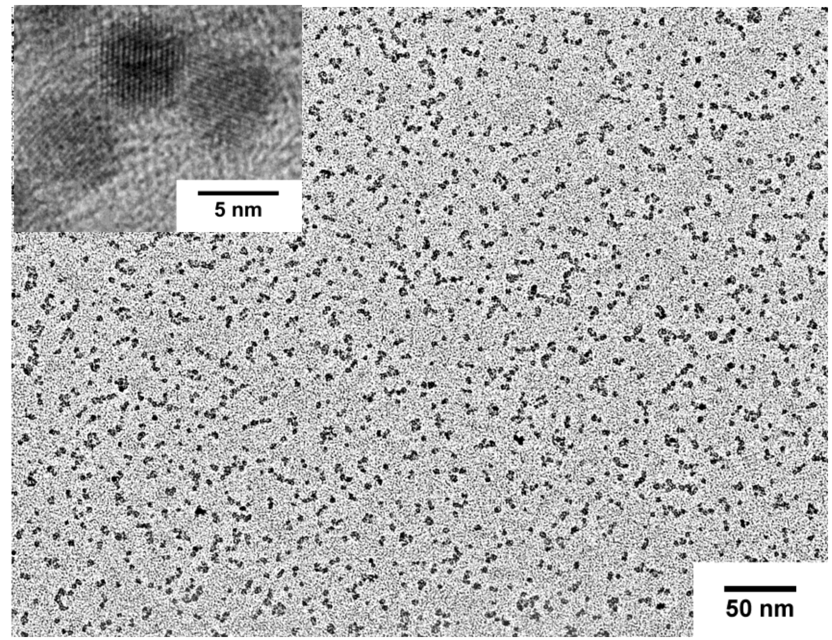


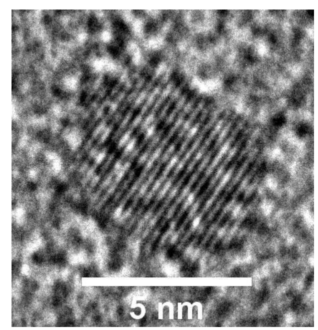


How to disperse ZnO QDs in epoxy without using organic surfactants?

HR-TEM

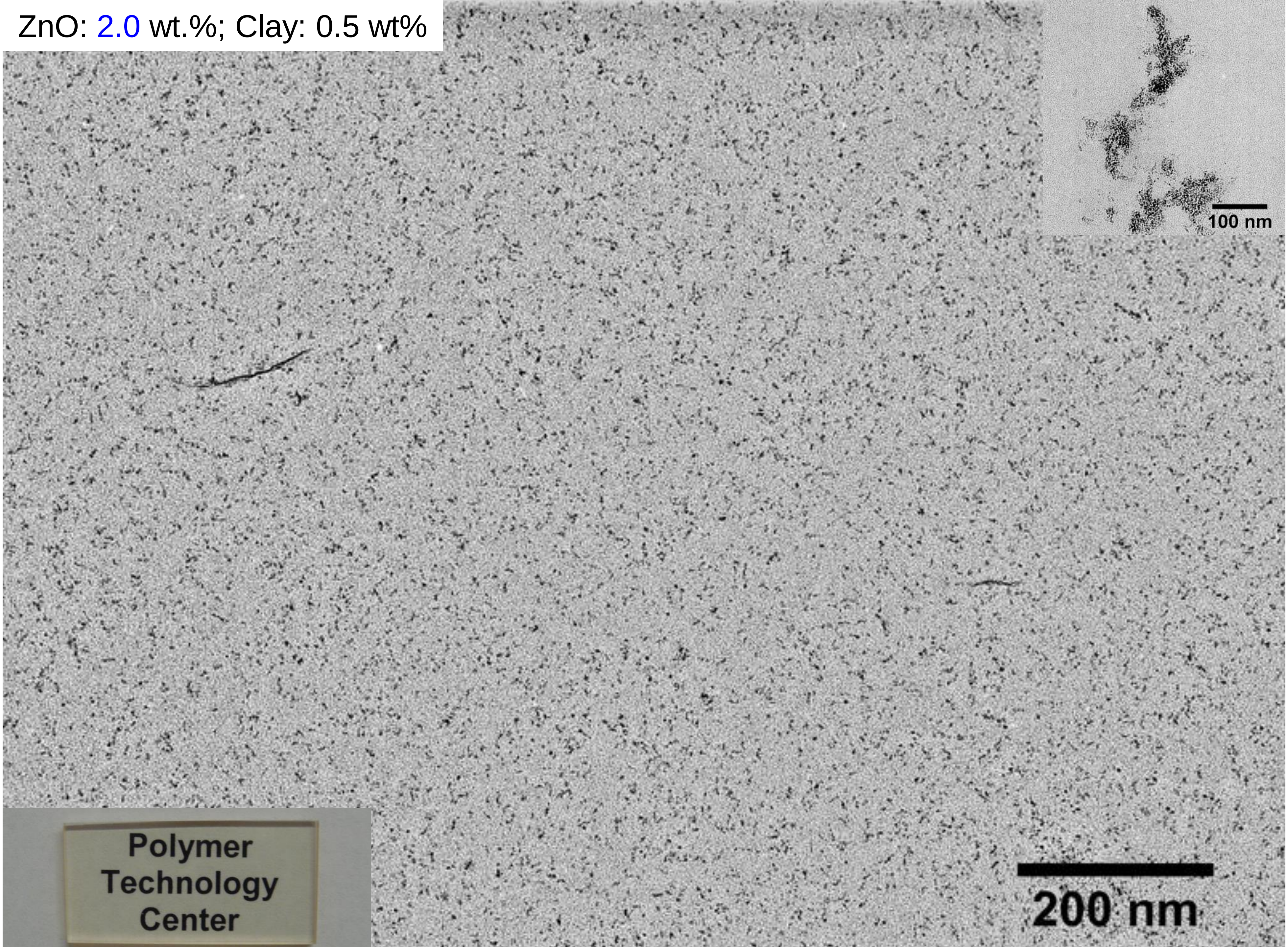




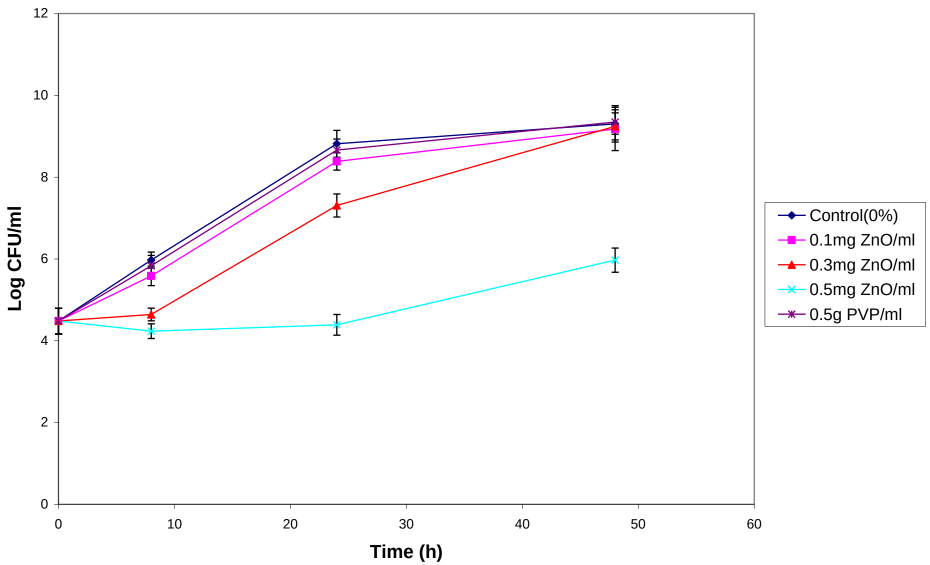


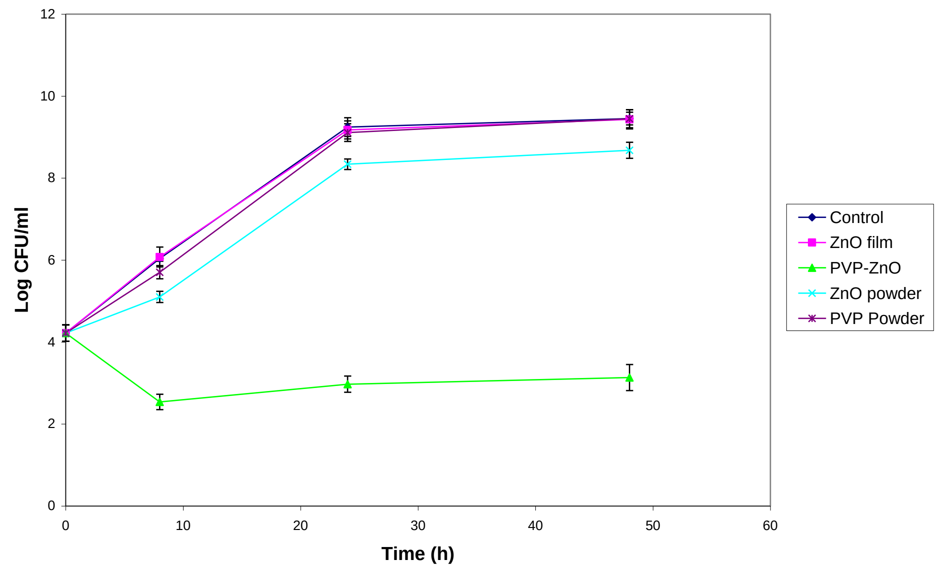
Average QD size : 5.0 nm; SD = 5.8% (Based on 250 QDs)

ZnO: 2.0 wt.%; Clay: 0.5 wt%

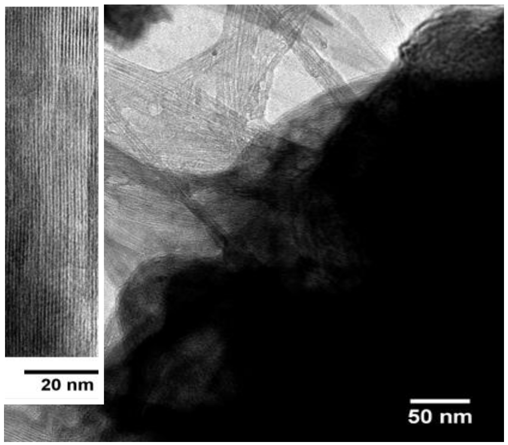


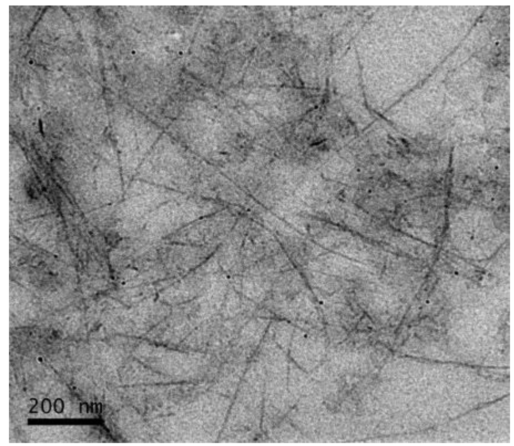
Antimicrobial Activity of Zinc Oxide Quantum Dots against *Listeria monocytogenes, Salmonella* Enteritidis and *Escherichia coli* O157:H7 (Project with USDA)

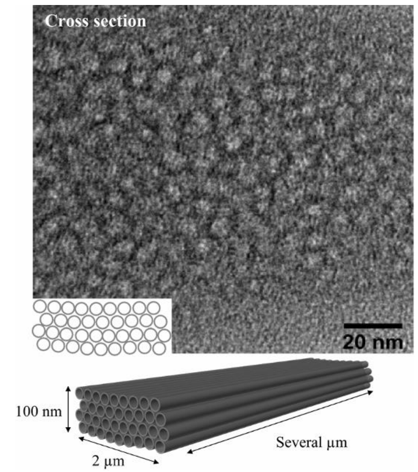




1-D Carbon Nanotubes

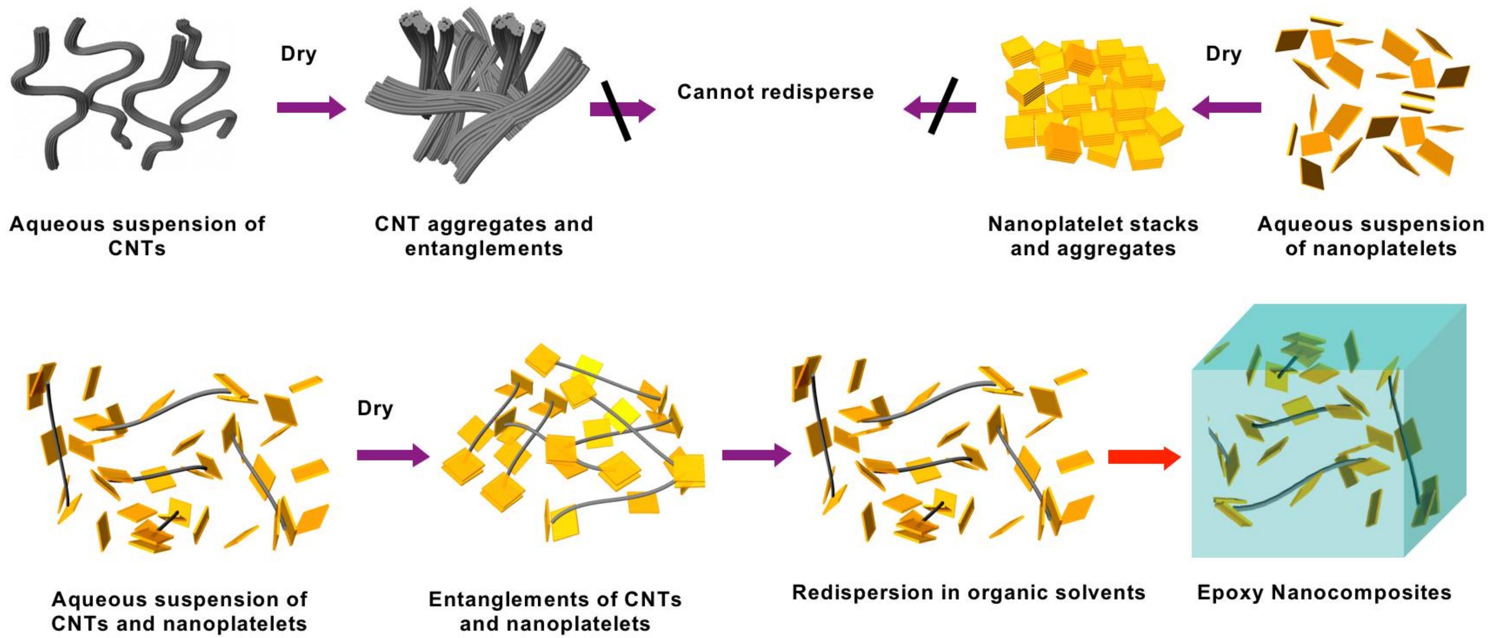






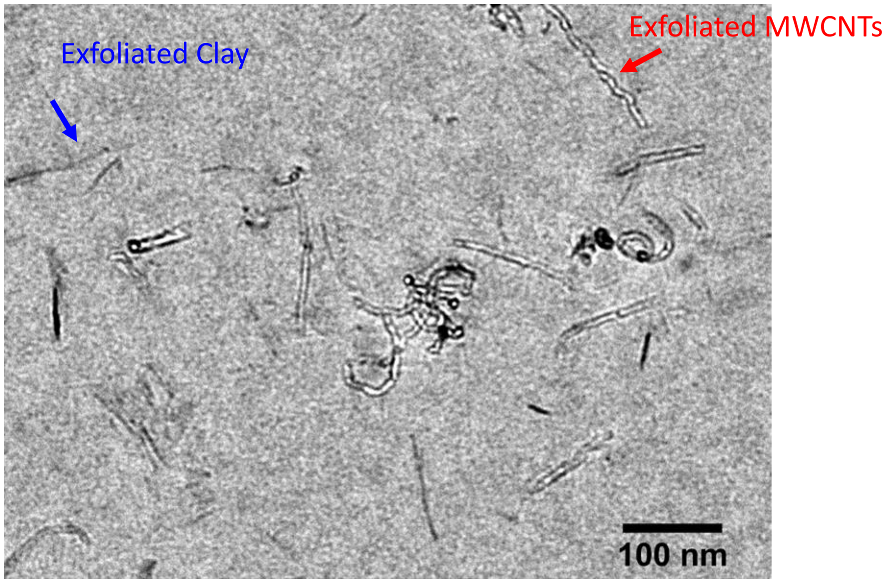
How to exfoliate SWCNTs in epoxy?

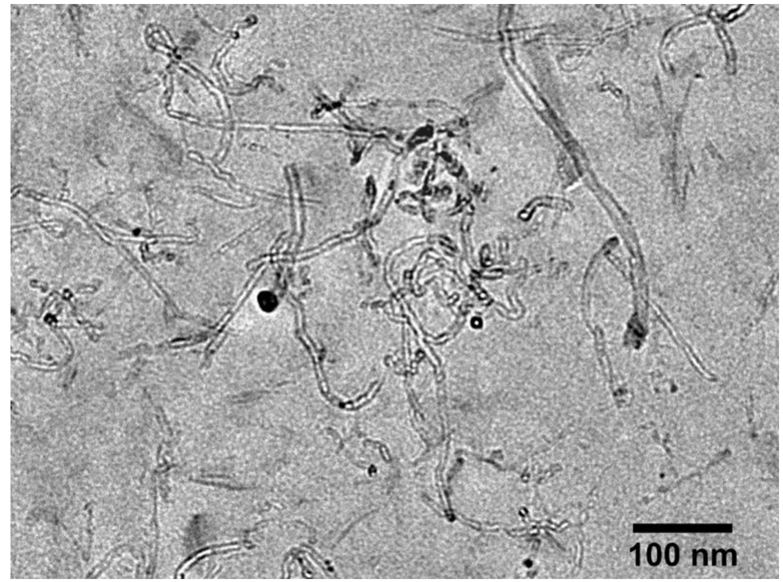
Our Approach for Preparing Nanocomposites



Epoxy/MWCNT/Clay Nanocomposites

MWCNTs

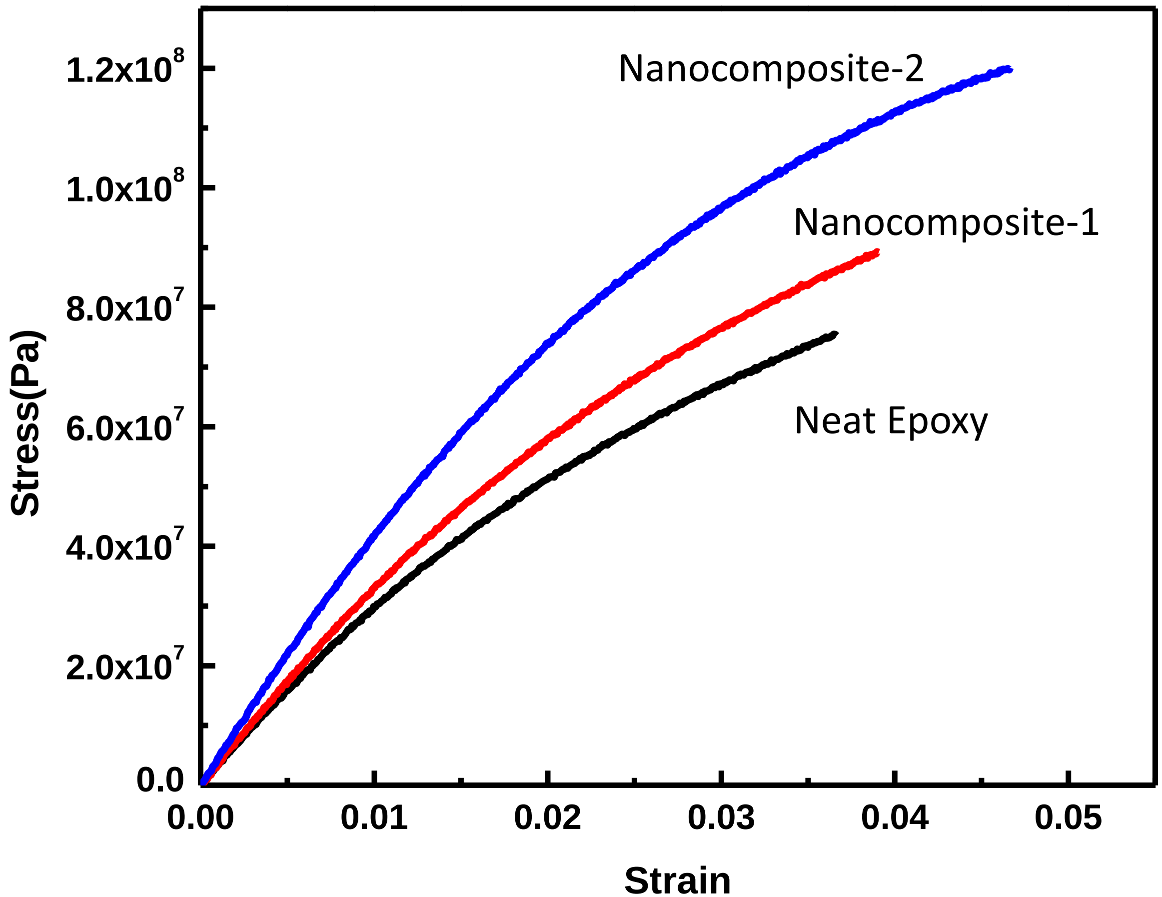


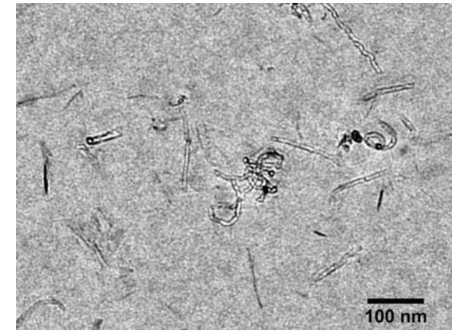


MWCNTs: 0.2 wt.%
Clay: 1.0 wt.%

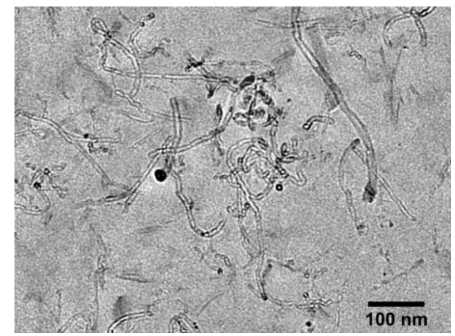
MWCNTs: 0.4 wt.%
Clay: 2.0 wt.%

Epoxy/MWCNT/Clay Nanocomposites





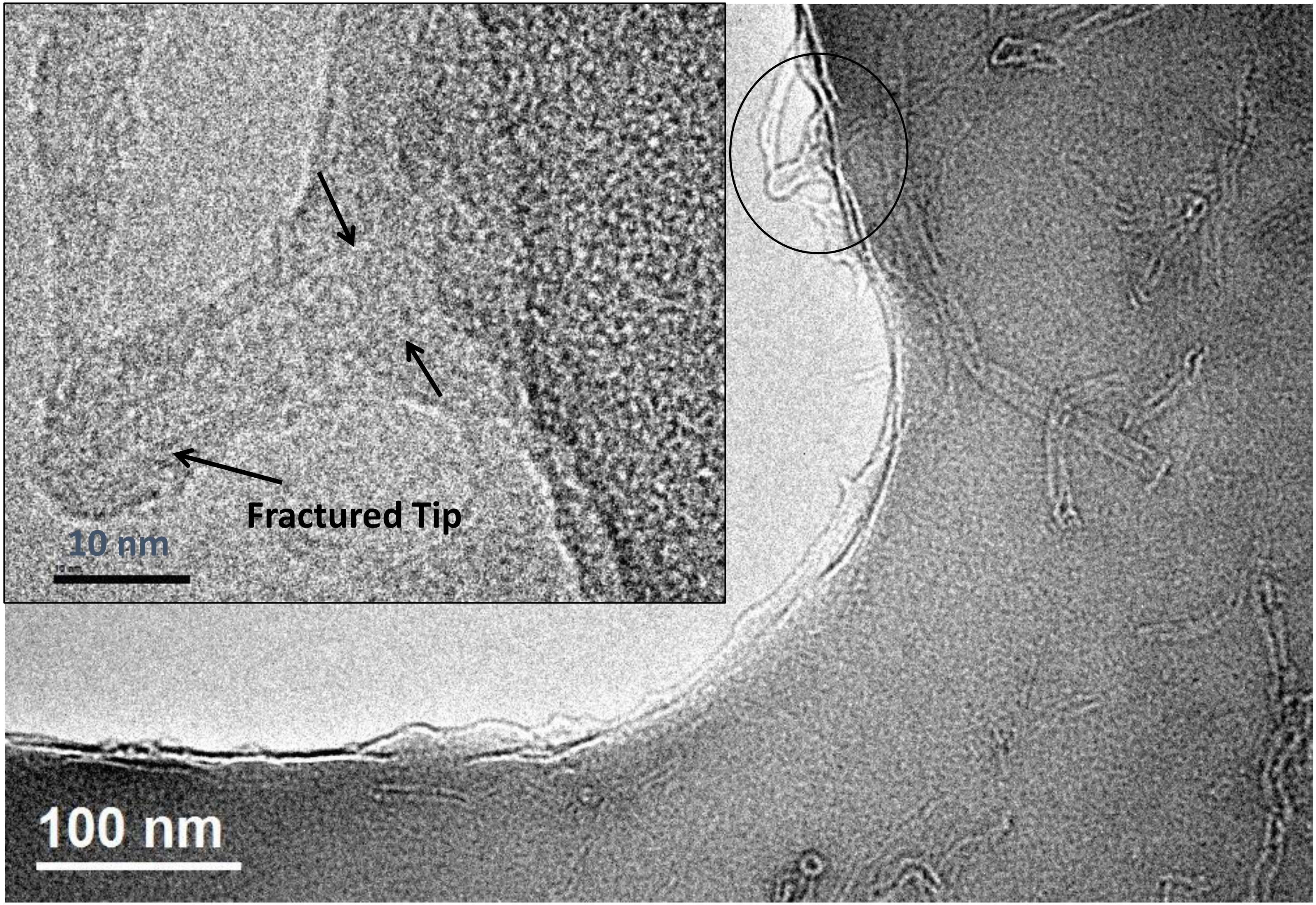
MWCNTs:0.2%;Clay:1.0%



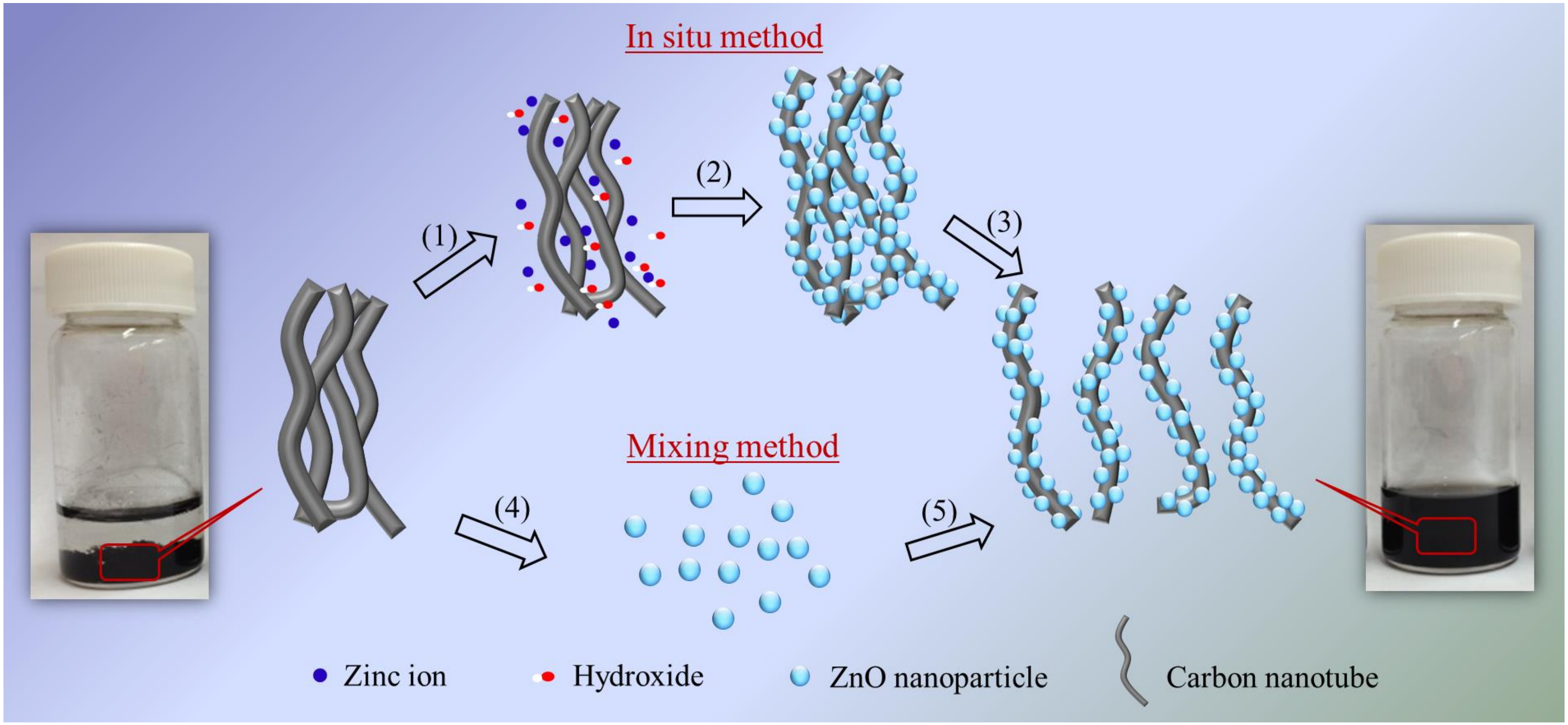
MWCNTs:0.4%;Clay:2.0%

	Neat Epoxy	Nanocomposite-1 (MWCNTs:0.2%;Clay:1.0%)	Nanocomposite-2 (MWCNTs:0.4%;Clay:2.0%)	
Young's Modulus (GPa)	3.04±0.04	3.40±0.06	4.27±0.07	41%
Tensile Strength (MPa)	75.3±4.2	83.1±4.8	116±5.5	55%
Elongation at Break (%)	3.7±0.1	3.9±0.3	4.3±0.4	24%

TEM Showing the DN-4PB Crack Tip

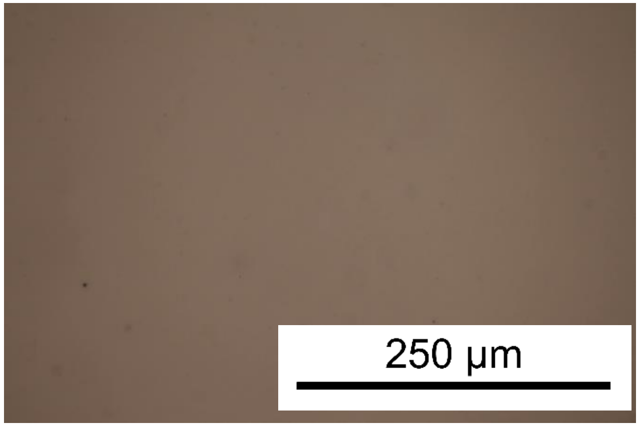


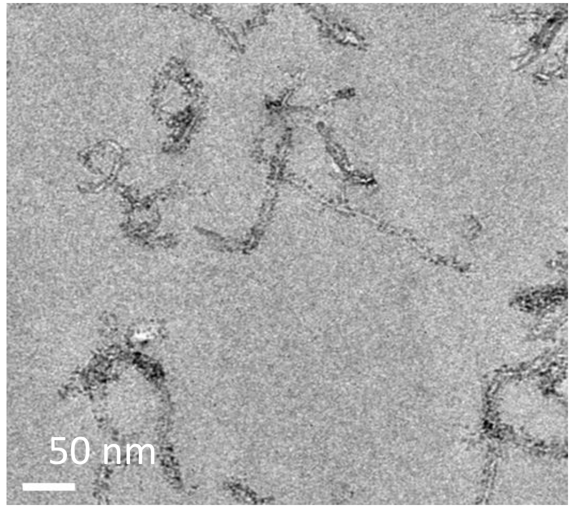
Dispersion of MWCNT Using ZnO

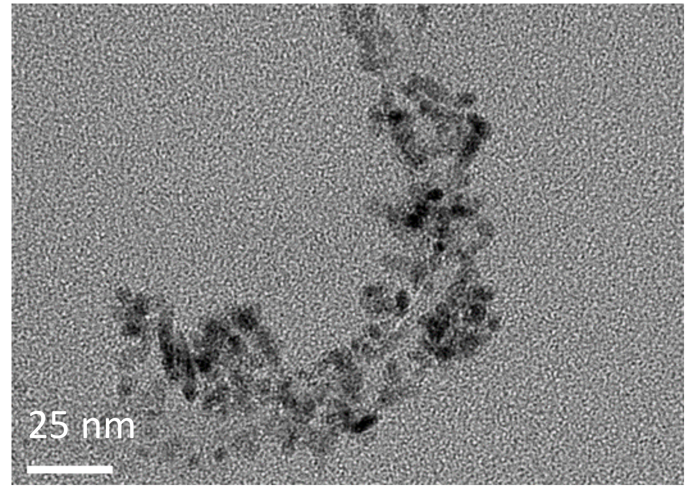


Epoxy/MWCNT-ZnO Nanocomposite

(1.7 wt.% and 3.4 wt.%)

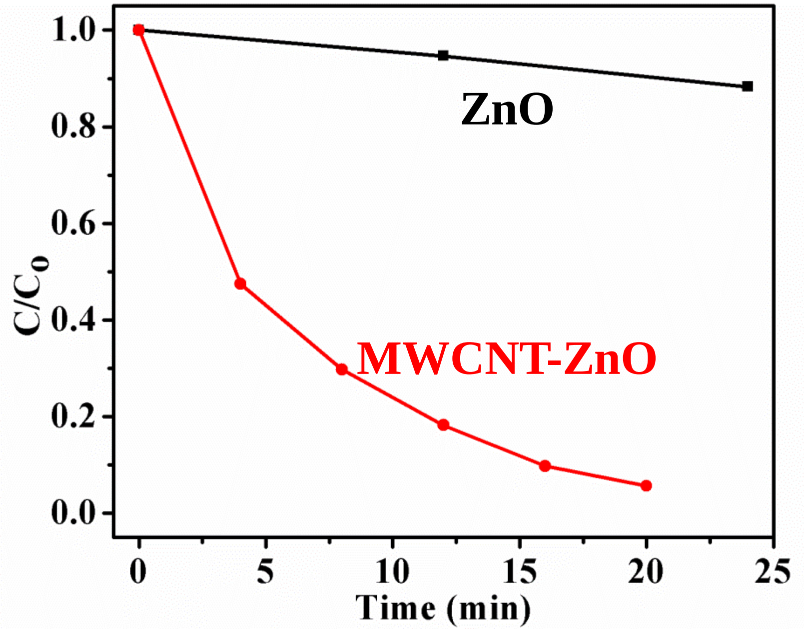






Samples	E [GPa]	σ_{UT} [MPa]	ε_B [%]	σ [S/m]
Epoxy	**2.71 ± 0.04**	**51 ± 5**	**2.7 ± 0.4**	NA
Epoxy/P-MWCNT	3.01 ± 0.04	41 ± 10	1.5 ± 0.4	2.923E-02
Epoxy/O-MWCNT	2.53 ± 0.09	41 ± 13	1.8 ± 0.7	NA
Epoxy/ZnO/P-MWCNT	**3.59 ± 0.12**	**61 ± 1**	**3.0 ± 0.2**	6.142E-01
Epoxy/ZnO/O-MWCNT	**4.10 ± 0.09**	**62 ± 8**	**3.0 ± 0.8**	NA

Photocatalysis Application



First order reaction kinetics

$$ln\left(\frac{c}{c_o}\right) = K_{app}t$$

Samples	K_{app} (min^{-1})	$t_{1/2}$ (min)
ZnO	0.0089	77
MWCNT-ZnO	0.1452 ↑ 16 times	4

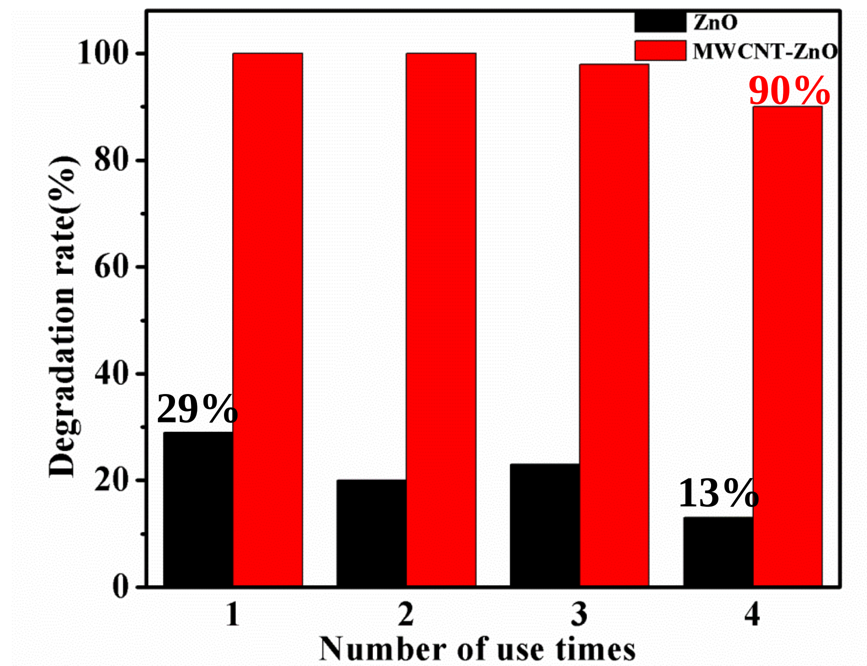
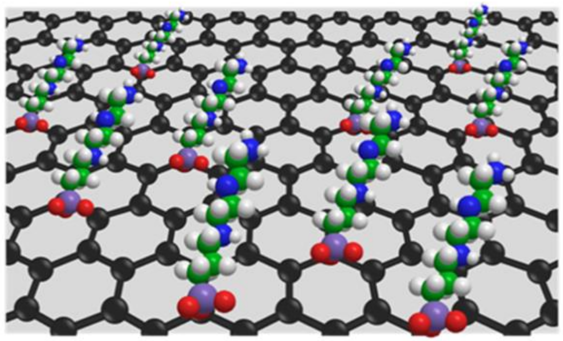


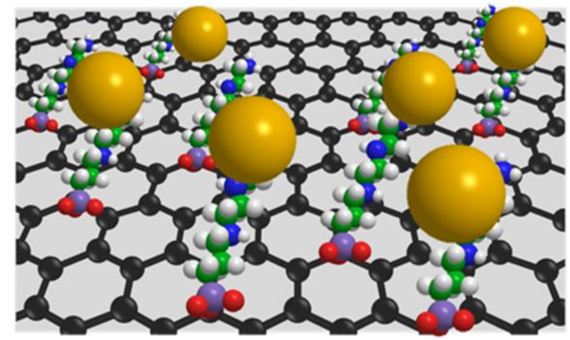
Photo-stability of the catalyst

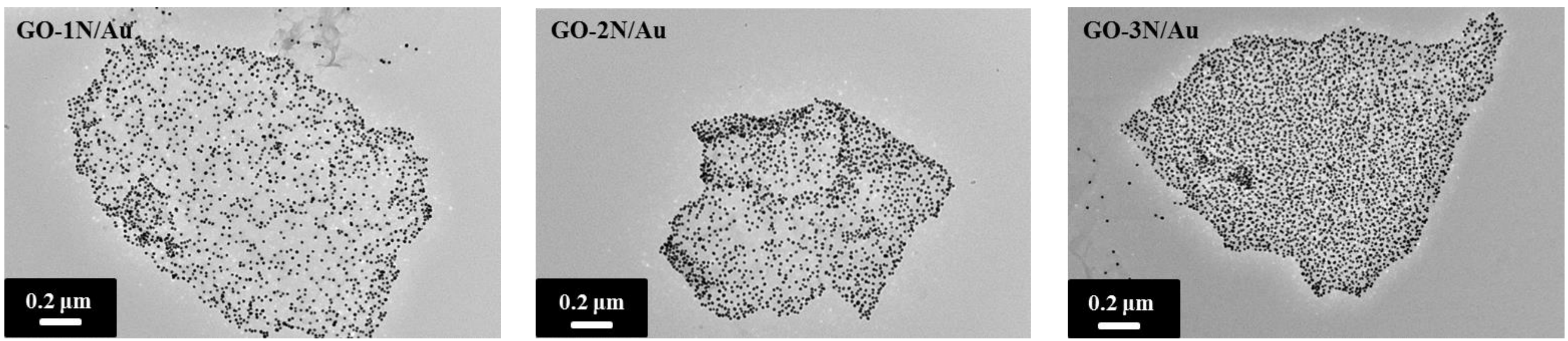
ZnO retains 45% of activity for degradation of RhB after 4 usages, while MWCNT-ZnO retains 90% of activity.

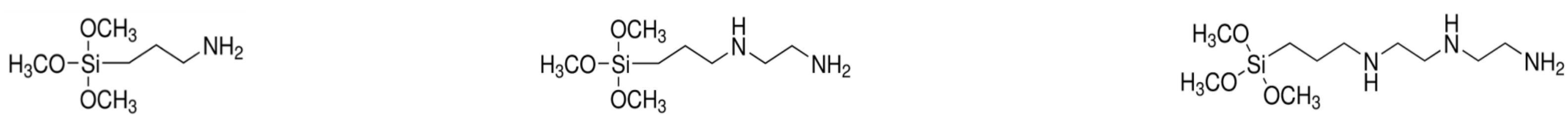
GO-Au Nanocomposites



Mixing with pre-synthesized Au nanoparticles





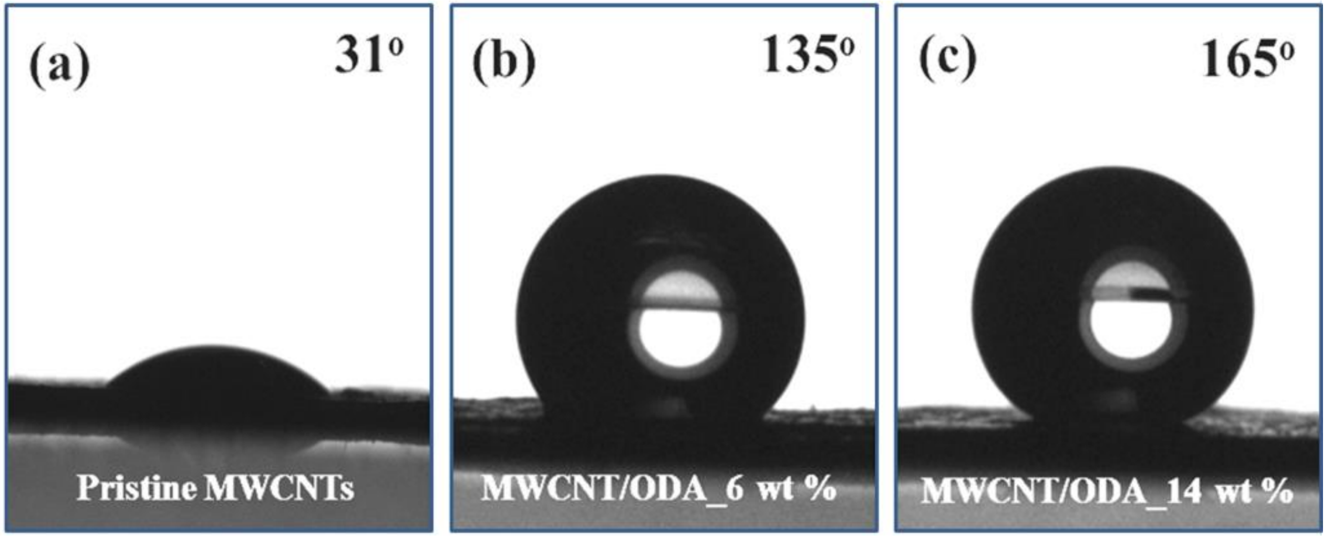


The spatial coverage of nanoparticles is controlled by varying functional groups.

Note: Au nanoparticles were synthesized from $HAuCl_4$ aqueous solution with addition of reducing agent sodium citrate.

H. Yao et al. J. Mater. Chem. A, 2013, 1, 10783–10789
H. Yao et al. RSC Advances, 2014, 4, 61823-61830

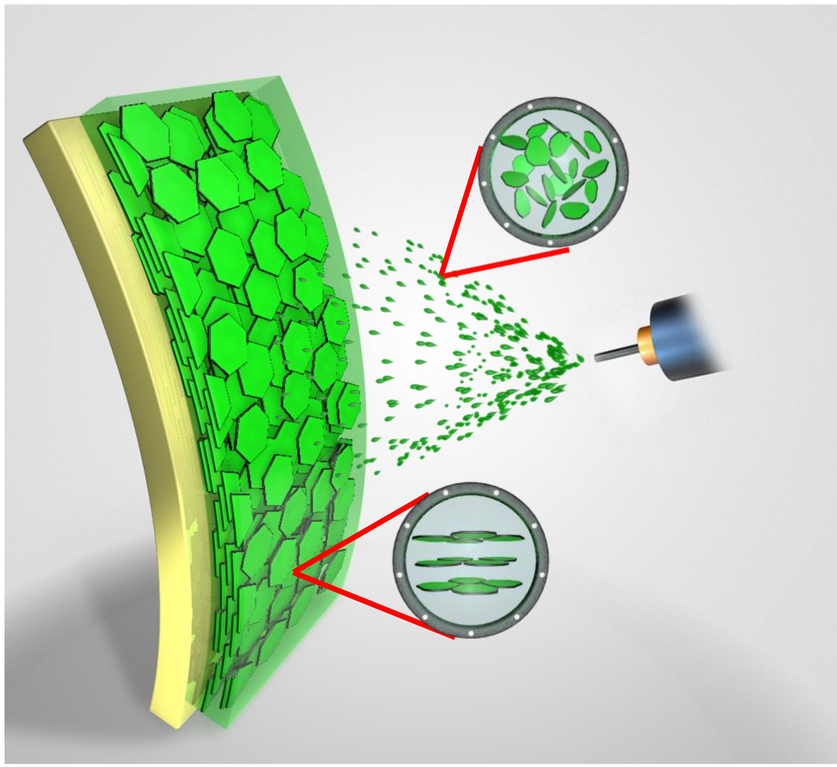
Superhydrophobic Surfaces



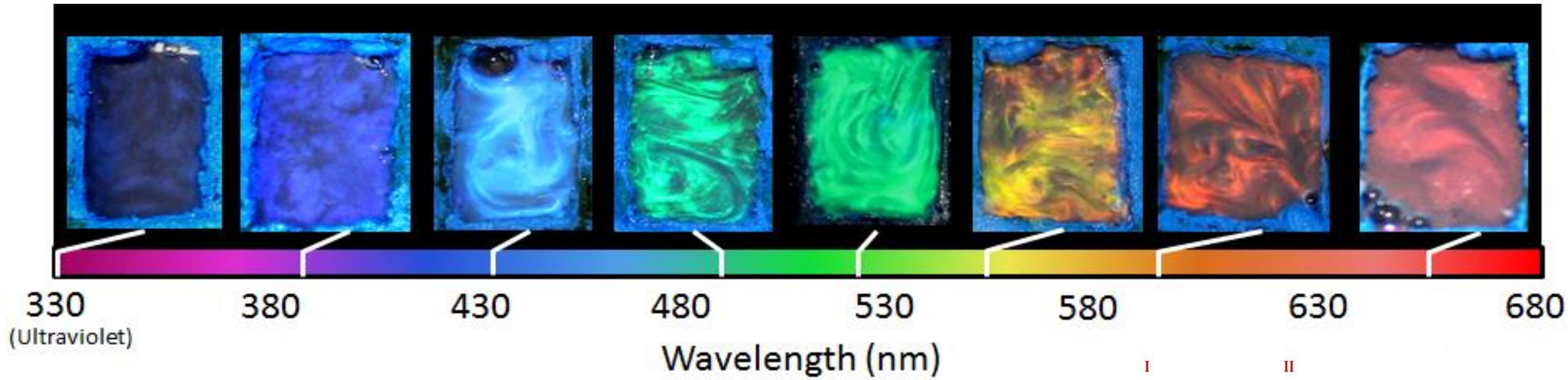
Profile of a water droplet on (a) pristine MWCNT film with CA of 31±1°, (b) MWCNT/ODA-6 wt. % with CA of 135±1°, and (c) MWCNT/ODA-14 wt. % with CA of 165±2°.

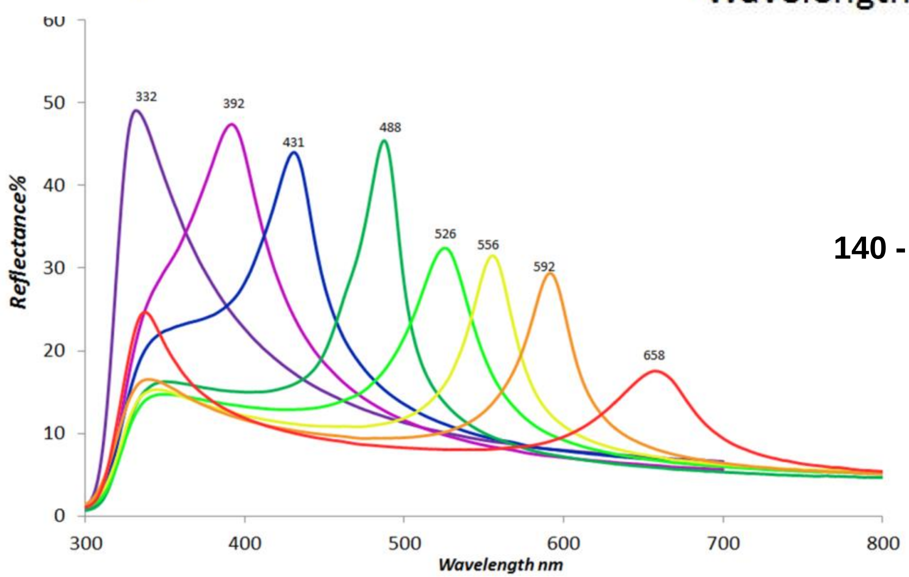
The wettability of MWCNT/ODA films can be tuned by the level of functionalization using ODA.

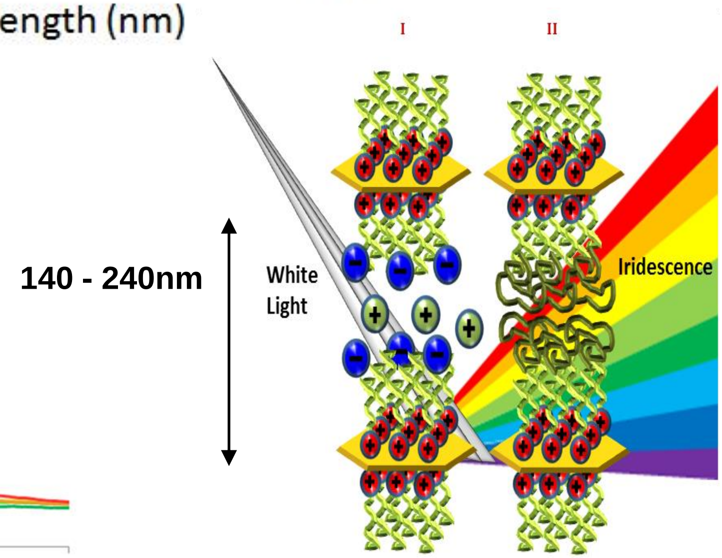
Spray-coatable Smectic 2D Crystals in Epoxy Coating



Liquid Crystalline Order of Nanoplatelets in Acetone

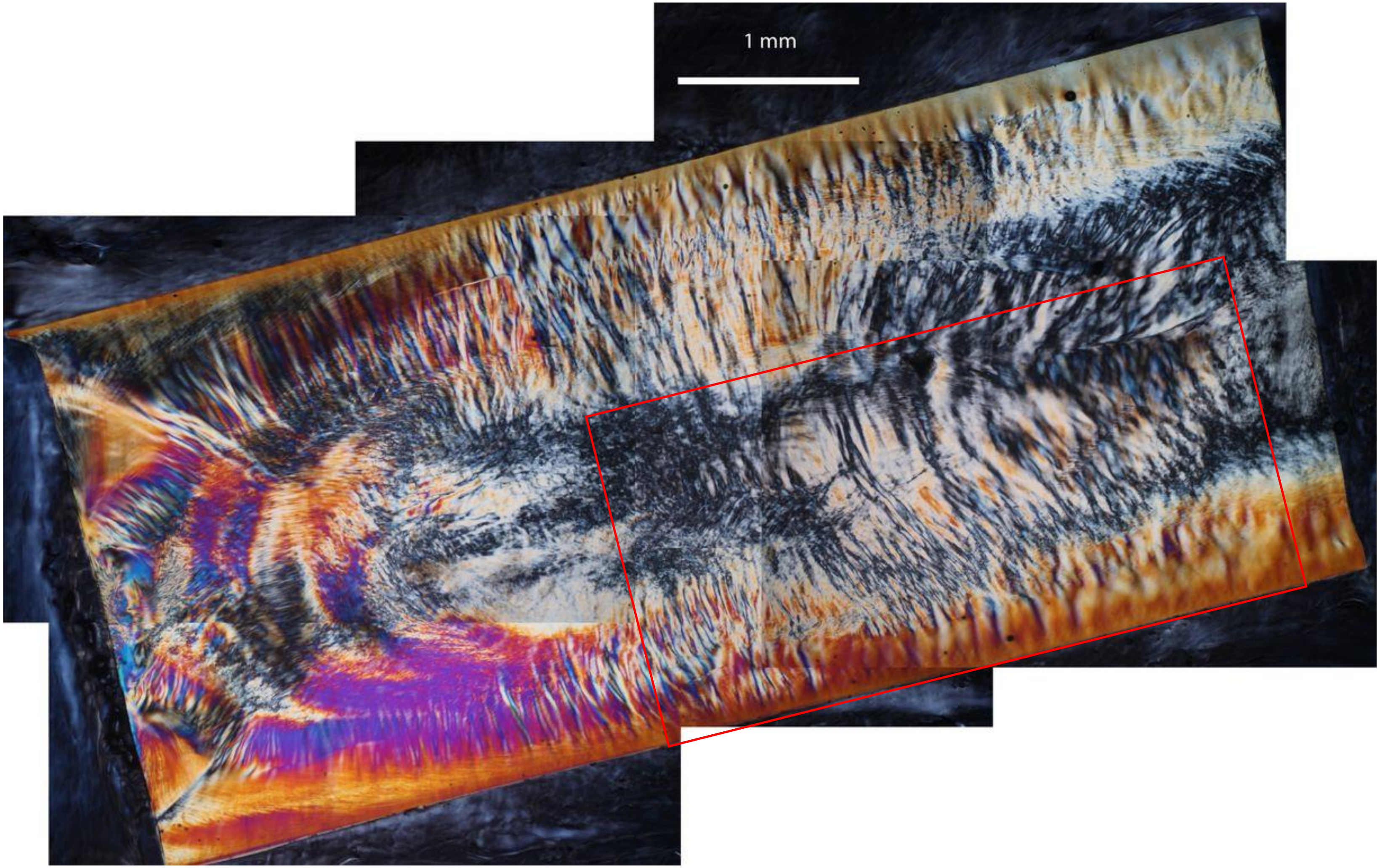






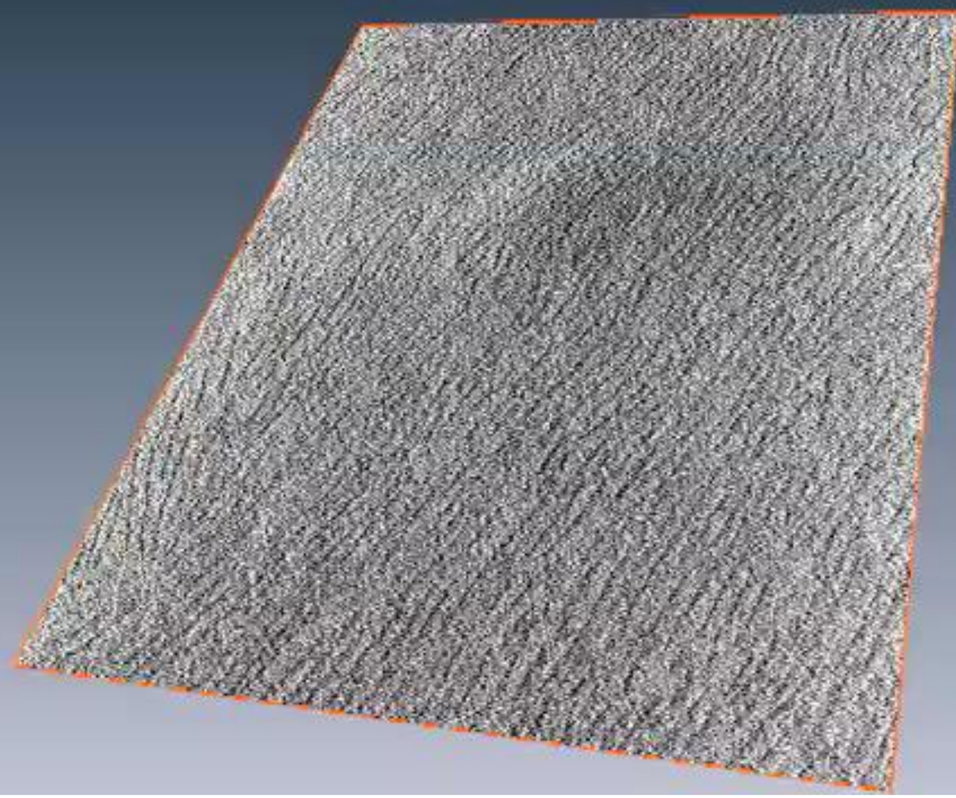
Color of reflected light depends on d-spacing of smectic phase

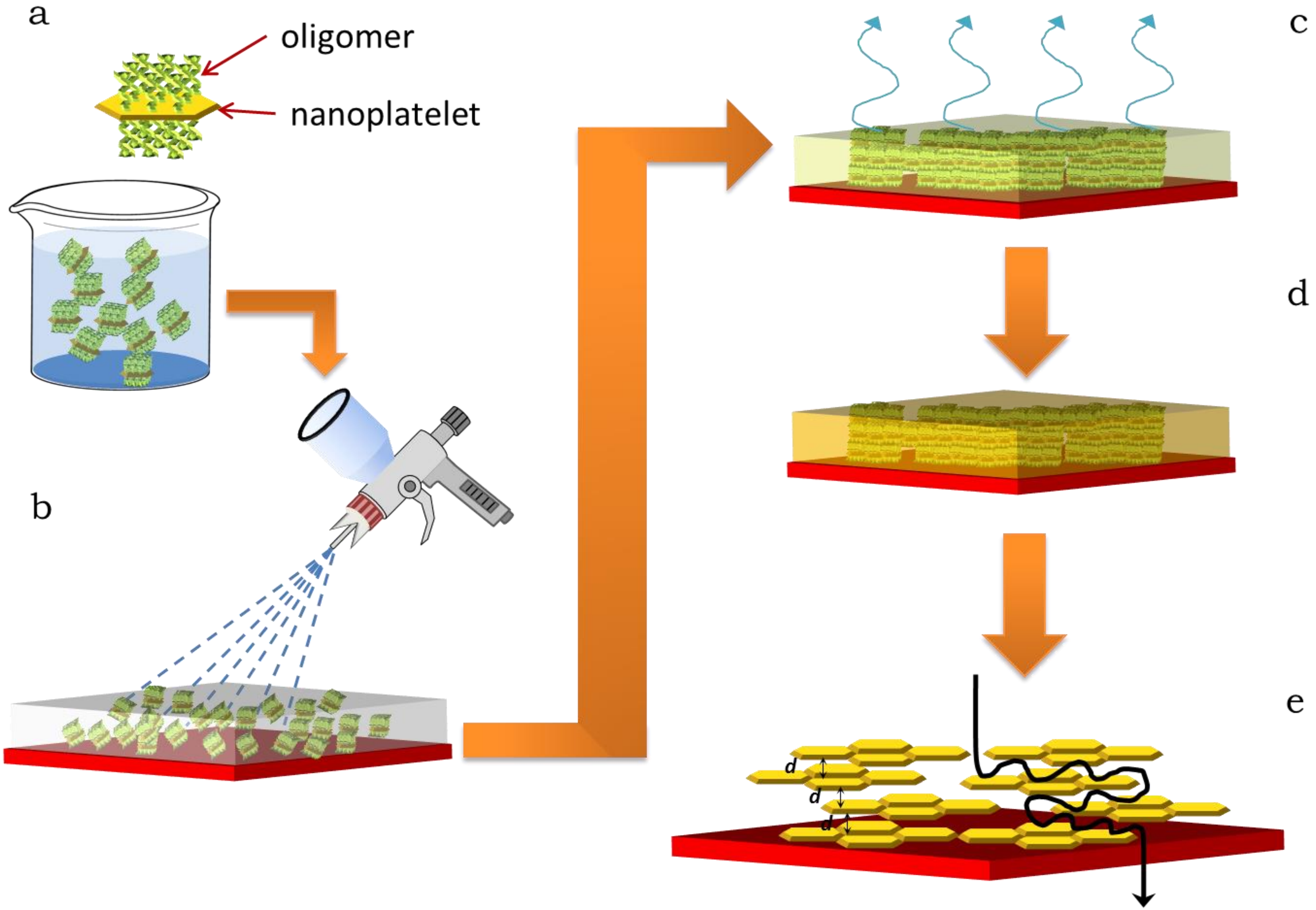
Liquid Crystal Phase of ZrP in Epoxy (9.02 wt% = 4 vol%)

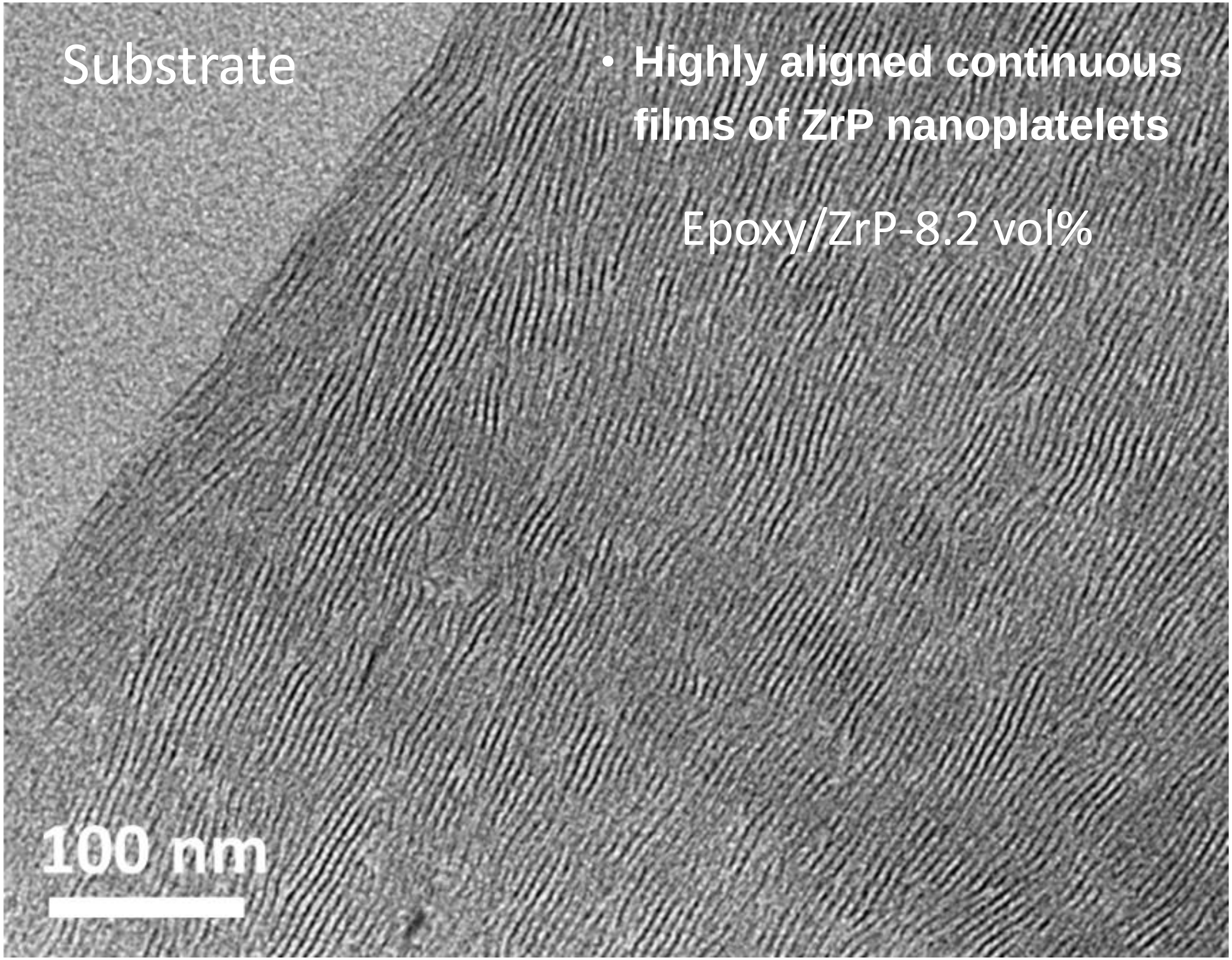


TEM-Tomography of Epoxy/ZrP (4 vol.%)

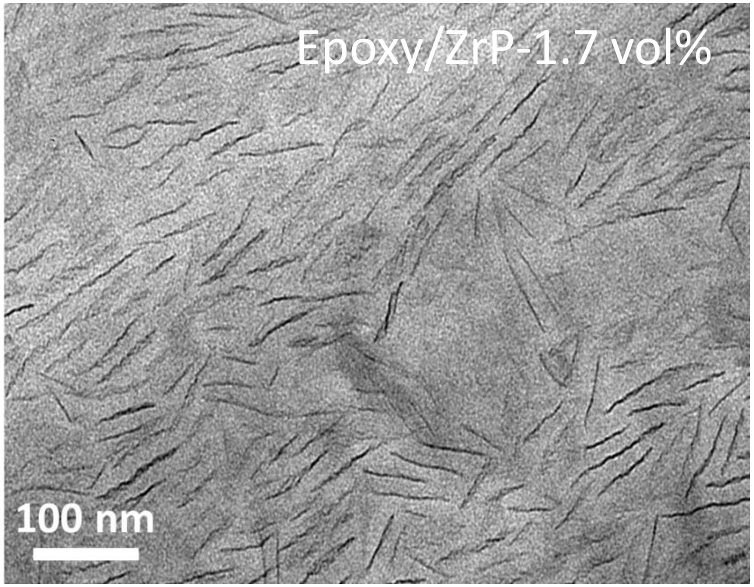
(Jinnai and Takahara, Kyushu Univ)

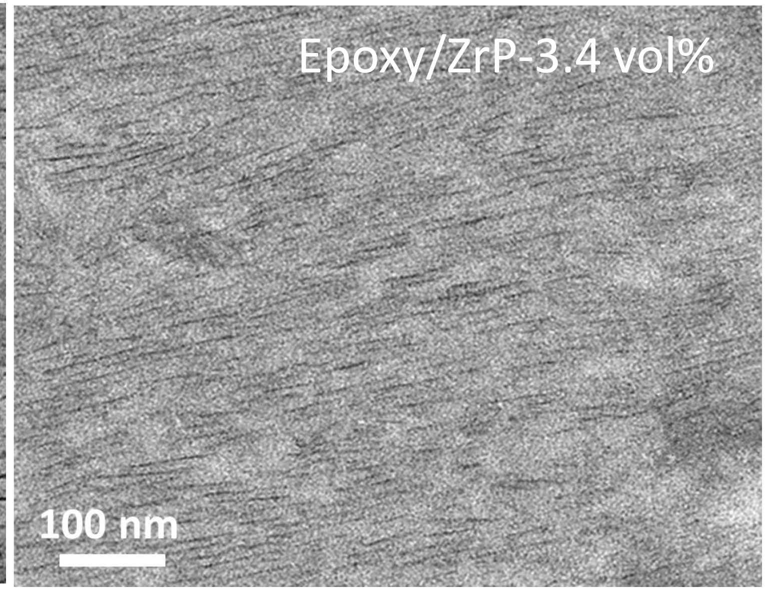


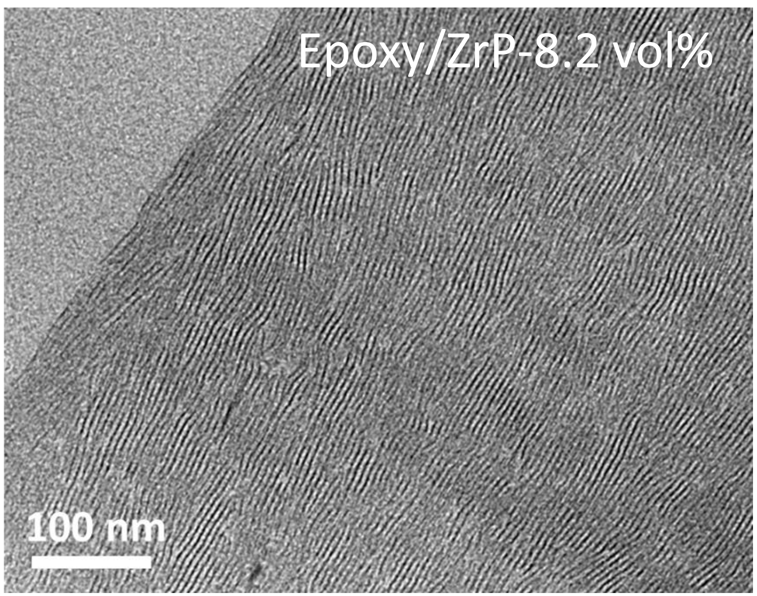

a
oligomer
nanoplatelet
b
c
d
e
d
d
d

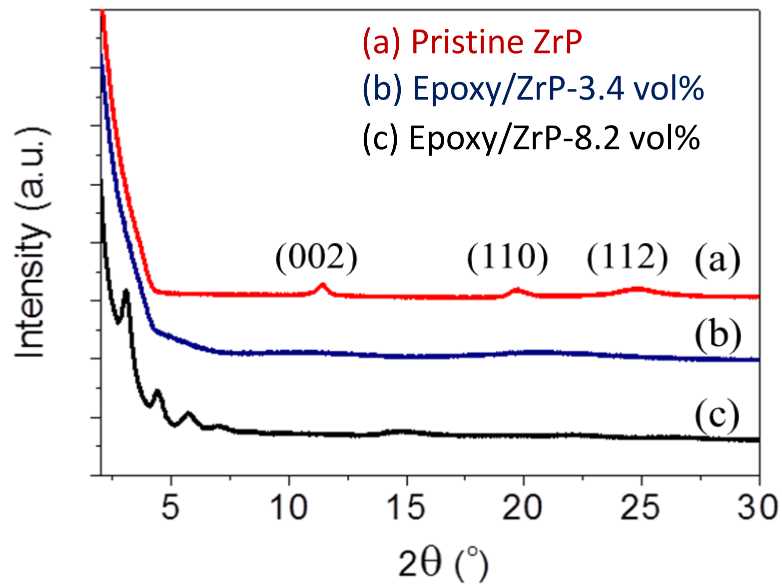

Substrate
• Highly aligned continuous films of ZrP nanoplatelets
Epoxy/ZrP-8.2 vol%
100 nm

TEM and XRD of Epoxy/ZrP Nanocomposites



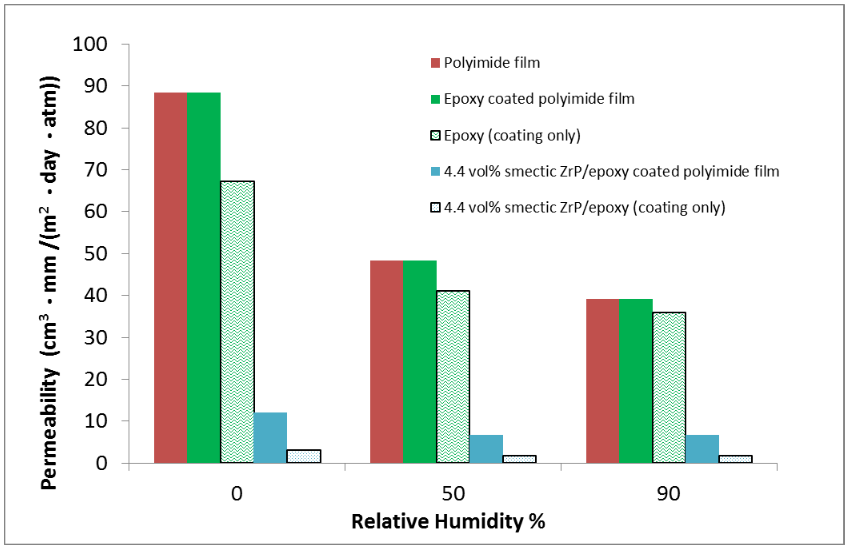




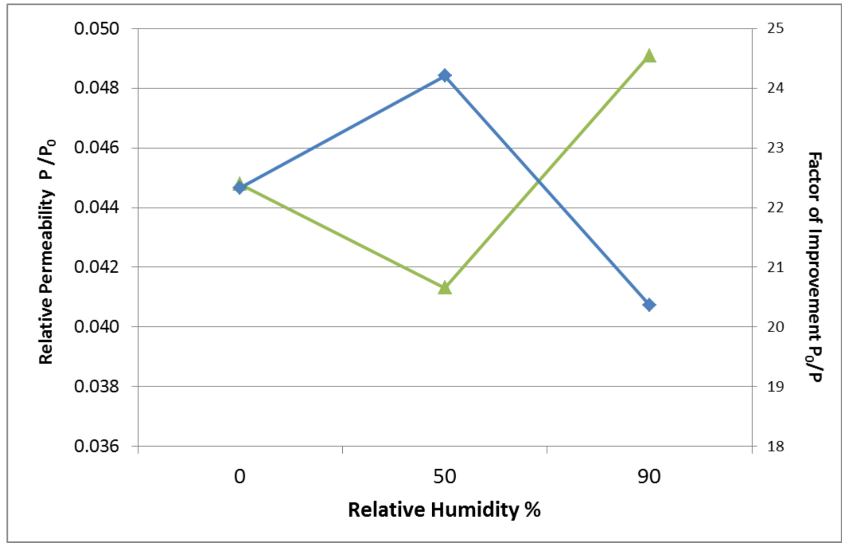


Barrier Property*

Permeability



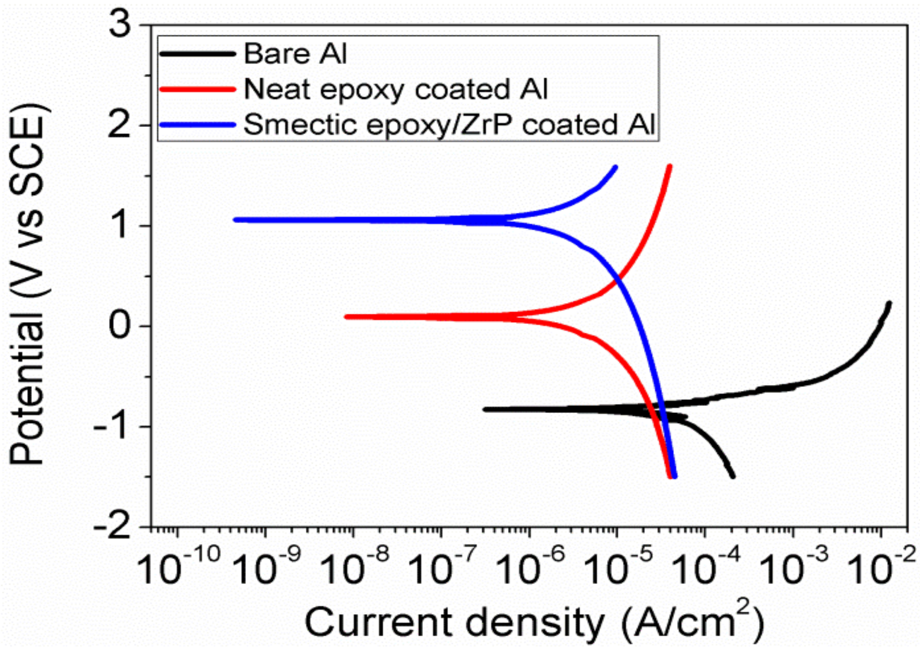
Humidity Effect



- **Ten times reduction in OTR in polyimide film achieved by just 8 μm of liquid crystalline nanocomposite coating.**
- **A factor of twenty times reduction in permeability observed in the LC nanocomposite film compared to neat epoxy.**

***Courtesy of Dow Chemical Company.**

Anticorrosion Properties of Smectic Epoxy/ZrP Coating on Al Substrate



- In order to evaluate corrosion resistance performance, potentiodynamic polarization measurements were performed.

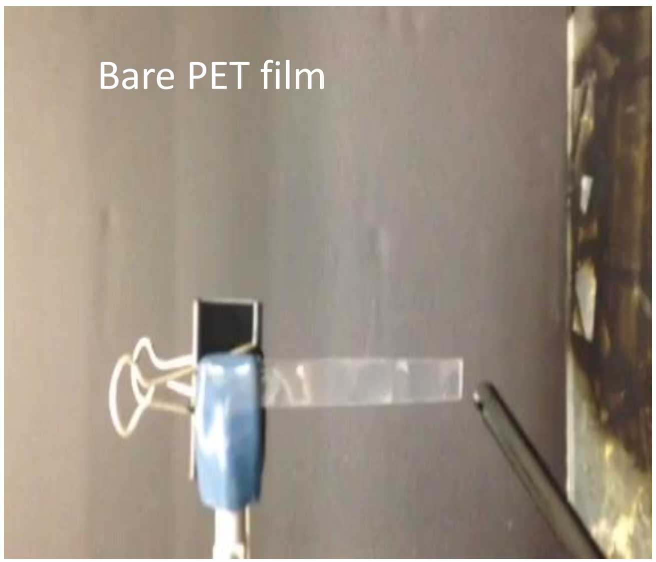
- The corrosion potential (E_{corr}), eletromotive force in eletrochemstry, helps to predict the intensity of a corrosion process. The higher E_{corr} and lower corrosion current density (I_{corr}) indicate better anticorrosion properties.

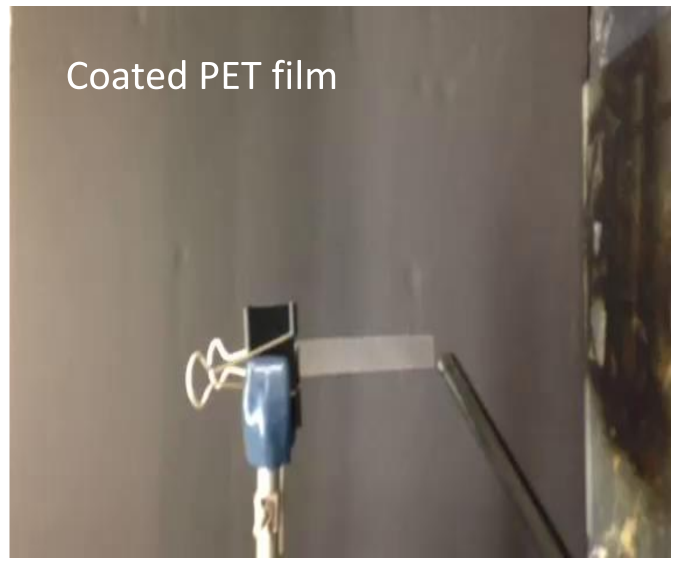
Table: Corrosion parameters from potentiodynamic plots using Tafel fitting

	E_{corr} (V)	I_{corr} ($\mu A/cm^2$)	**CR** (mm year^{-1})
Bare Al	-0.825	29.41	3.21×10^{-1}
Neat epoxy coated Al	0.102	1.98	2.16×10^{-2}
Smectic epoxy/ZrP coated Al	1.068	0.36	3.93×10^{-3}

Fire Retardation of Epoxy/ZrP Coated Polymers (11 Wt.%)

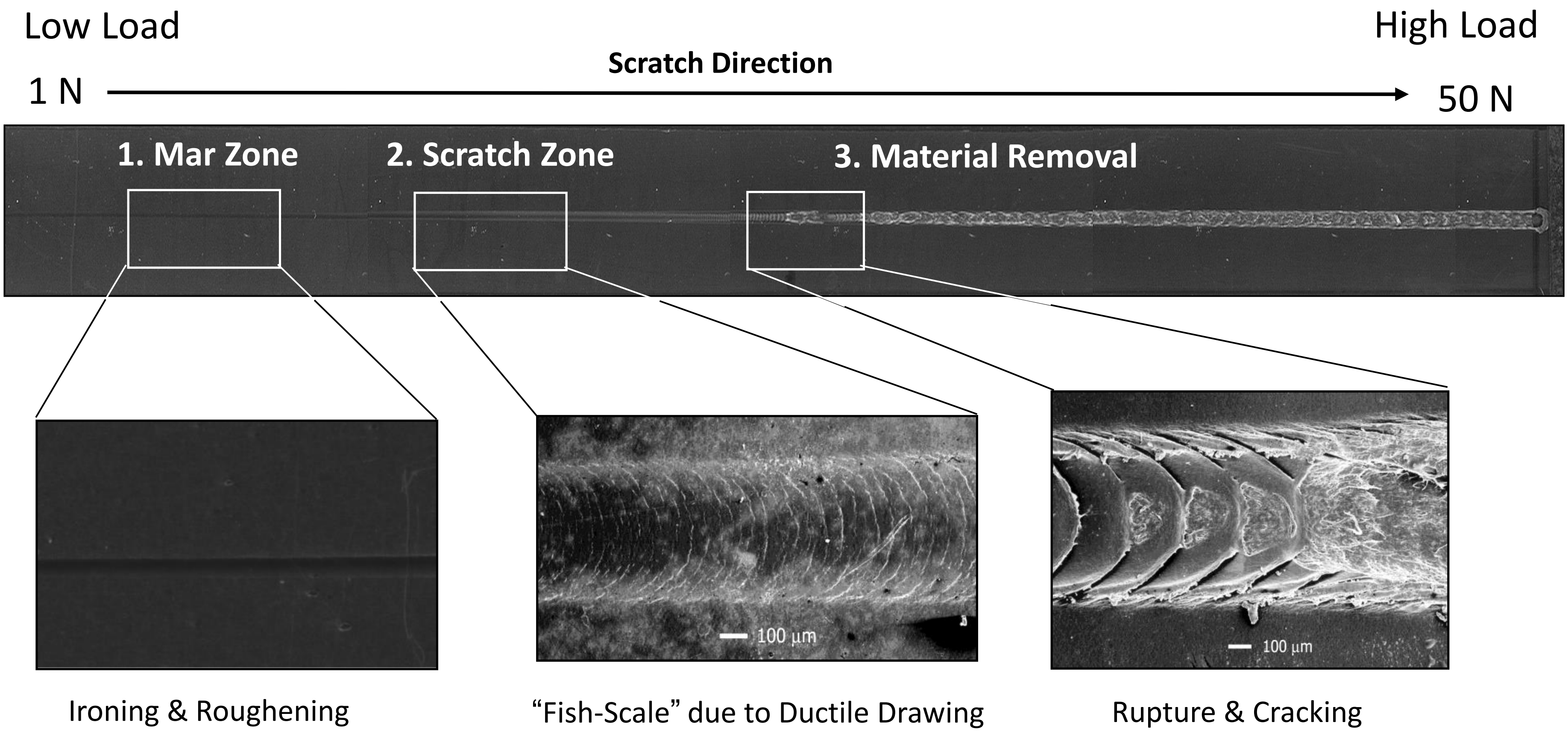
- PET itself exhibits significant melt-dripping during combustion and forms limited char.
- The coated PET forms char and does drip.



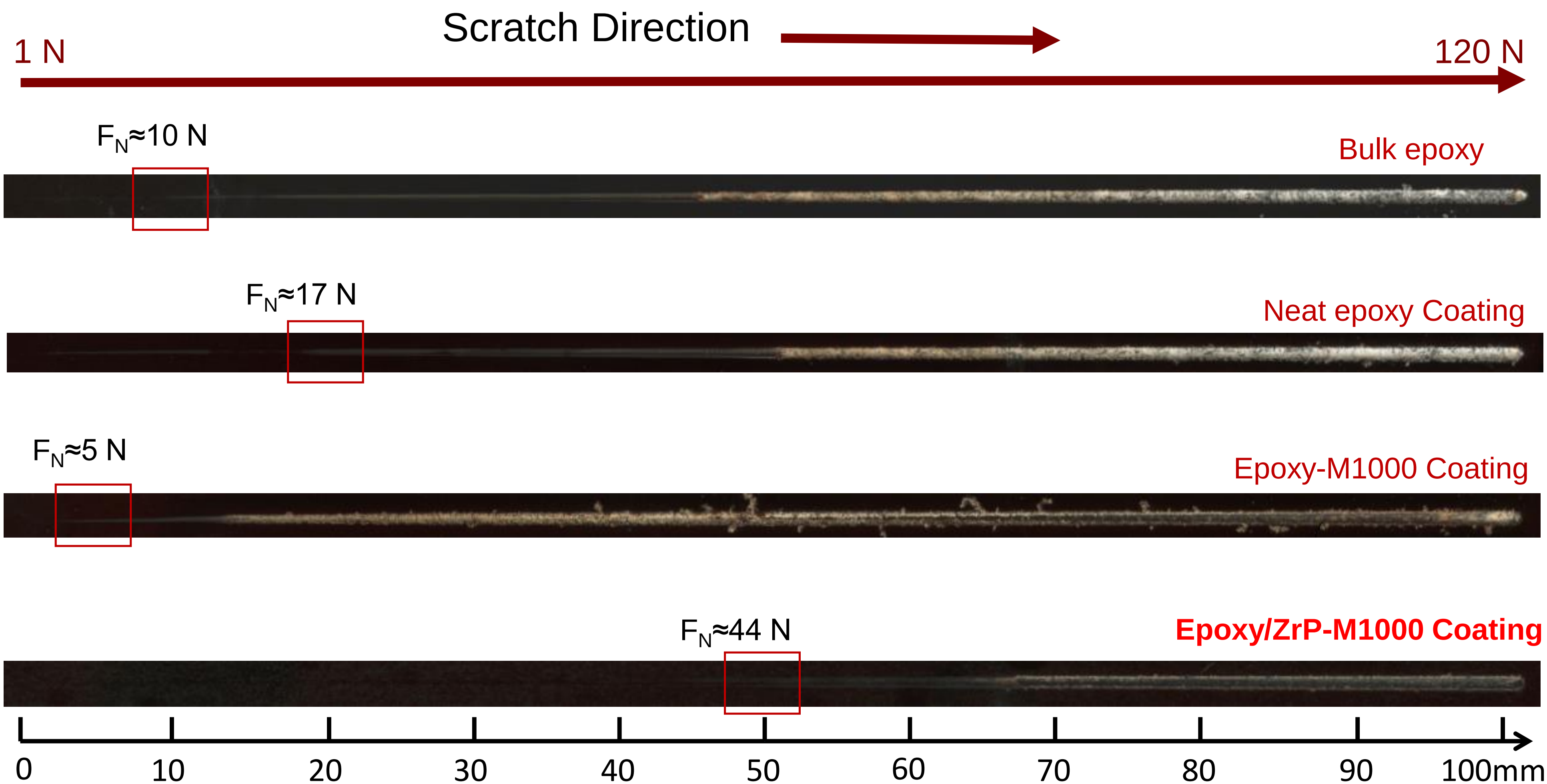


Scratch Resistance

ASTM D7027-13

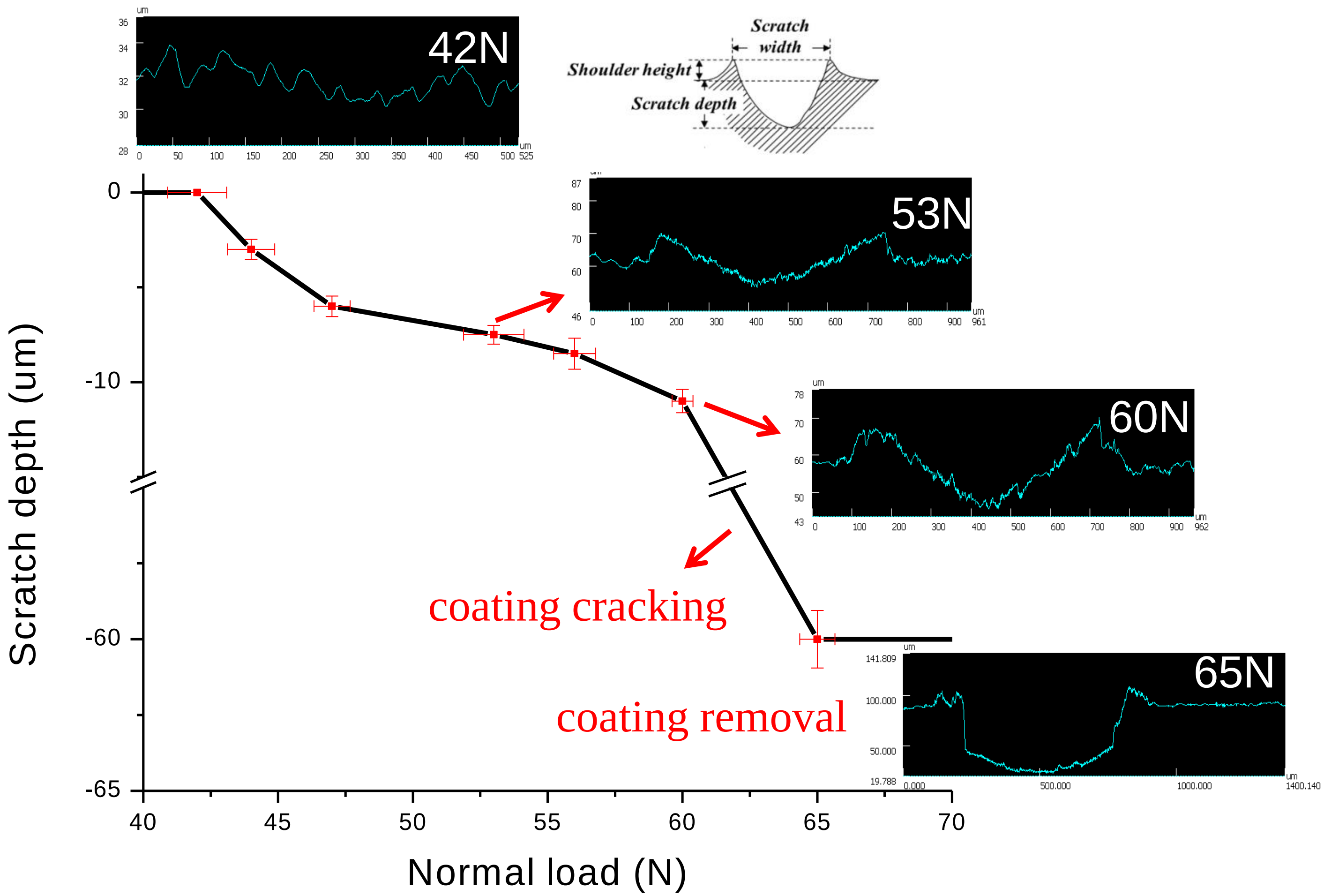


Visual Assessment of Scratch Damage



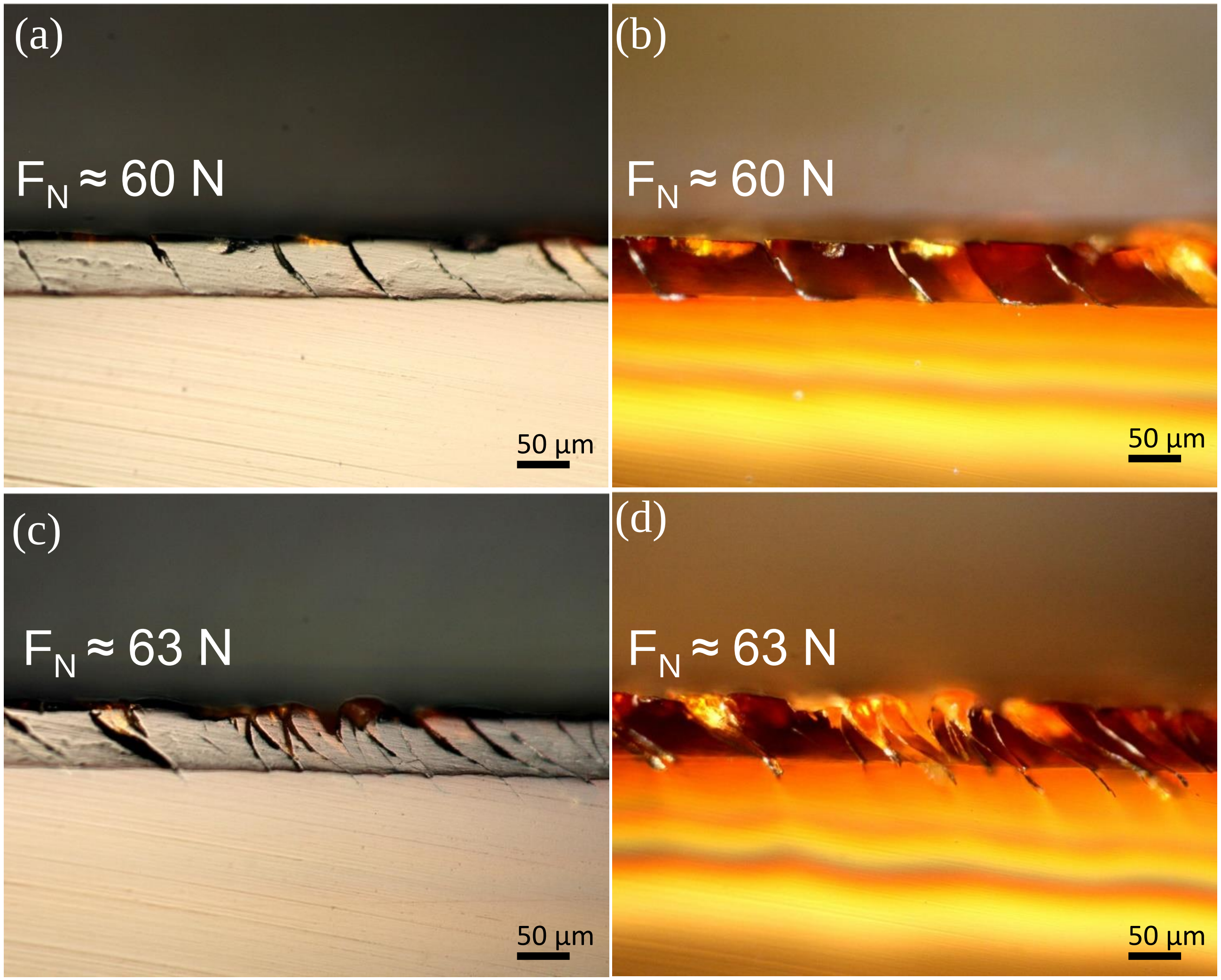
Subsurface Deformation and Damage

Laser Scanning Confocal Microscopy



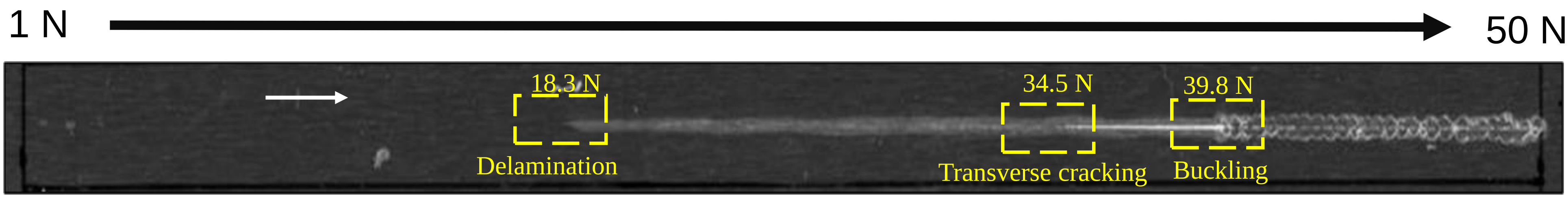
OM micrographs in the longitudinal section of the scratch

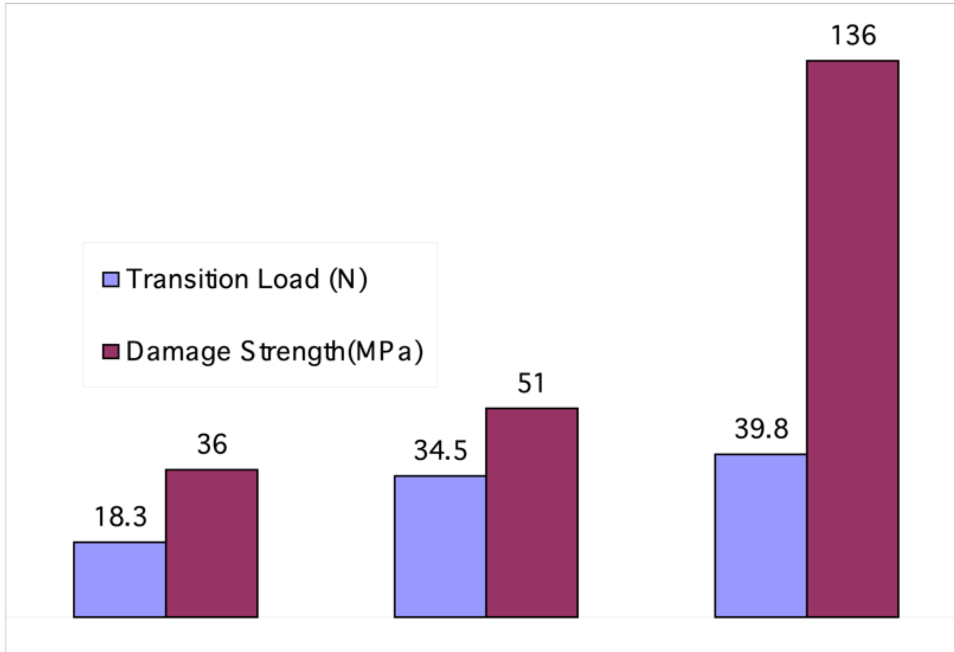
(Scratch direction: from left to right).



Wet Coating Adhesive Strength Evaluation
(Funded by DOT, 3M, Shawcor, Dow Chemical)

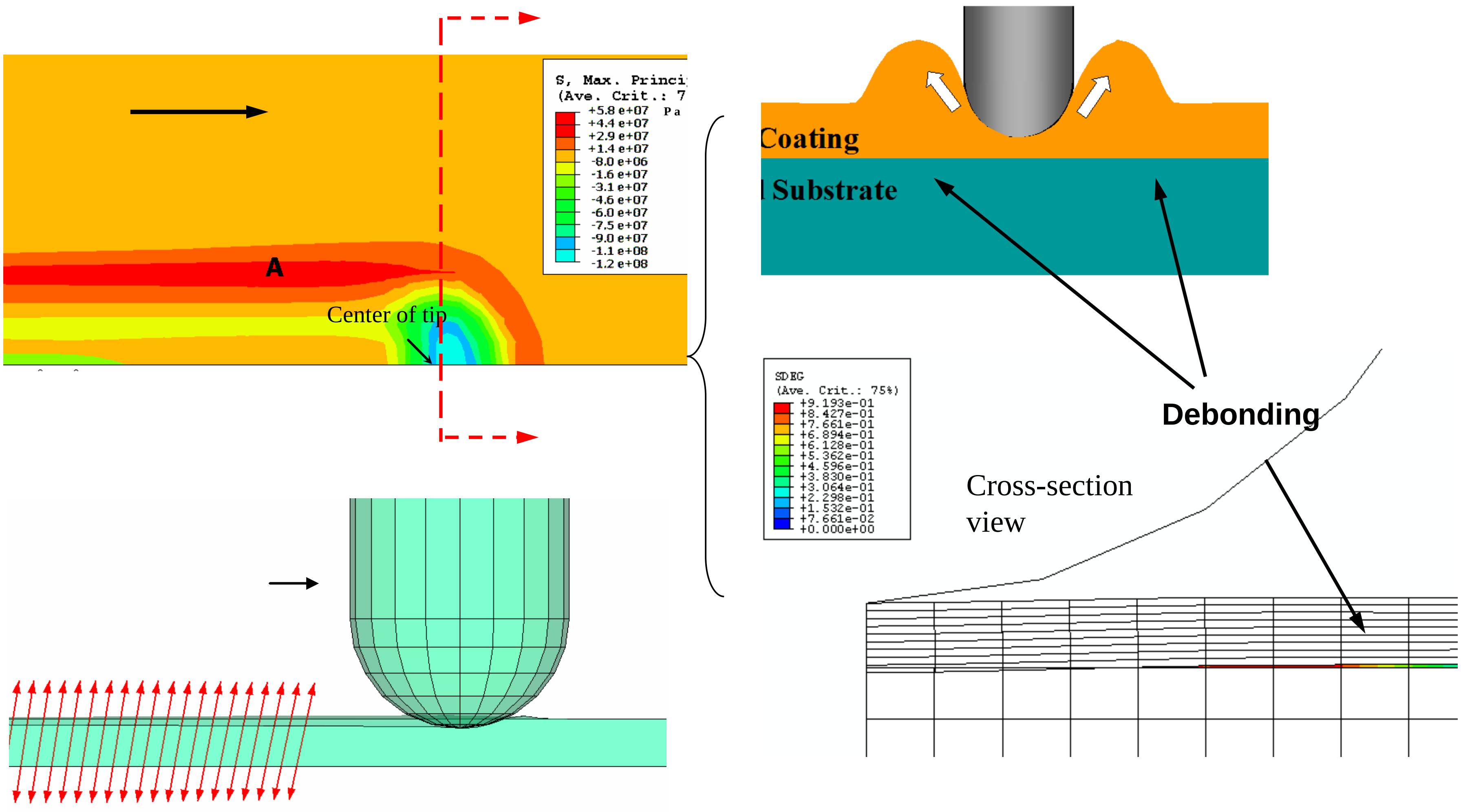
Critical Strength for Various Coating Damage Modes



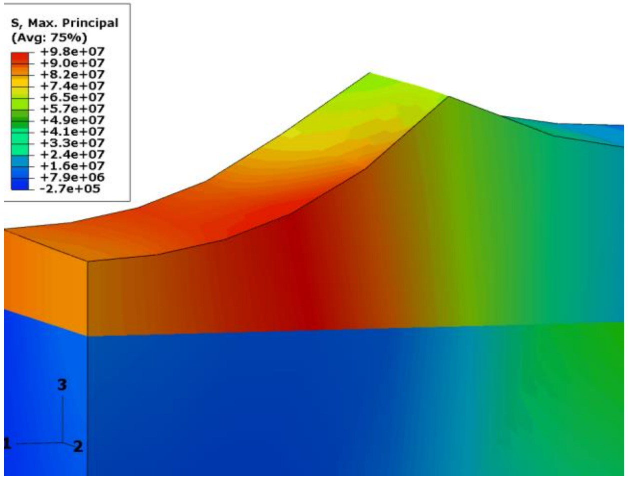


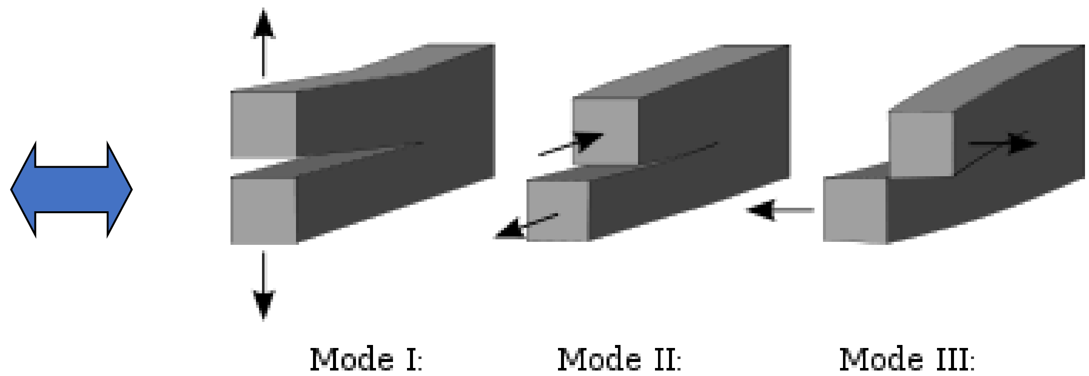
	Delamination	Transverse Cracking	Buckling
Transition Load (N)	18.3	34.5	39.8
Damage Strength(MPa)	36	51	136

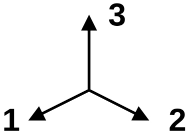
Debonding Mechanism

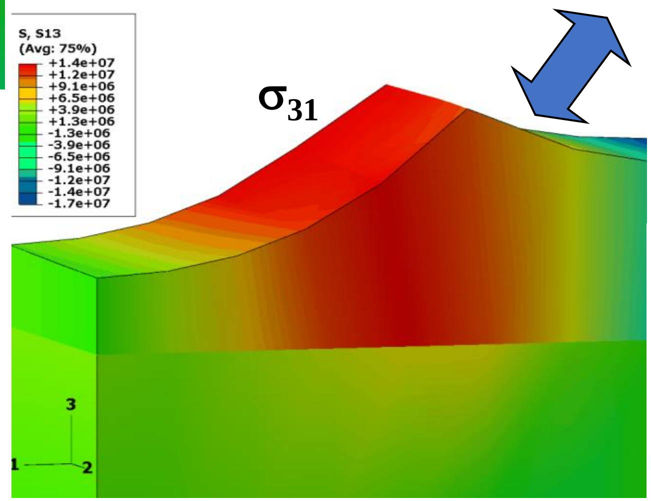


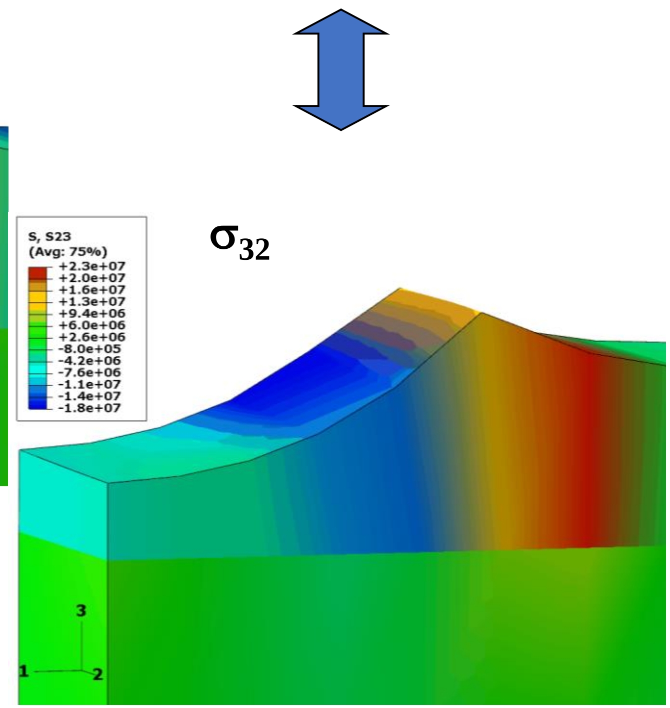
Debonding is Mode-I Dominant









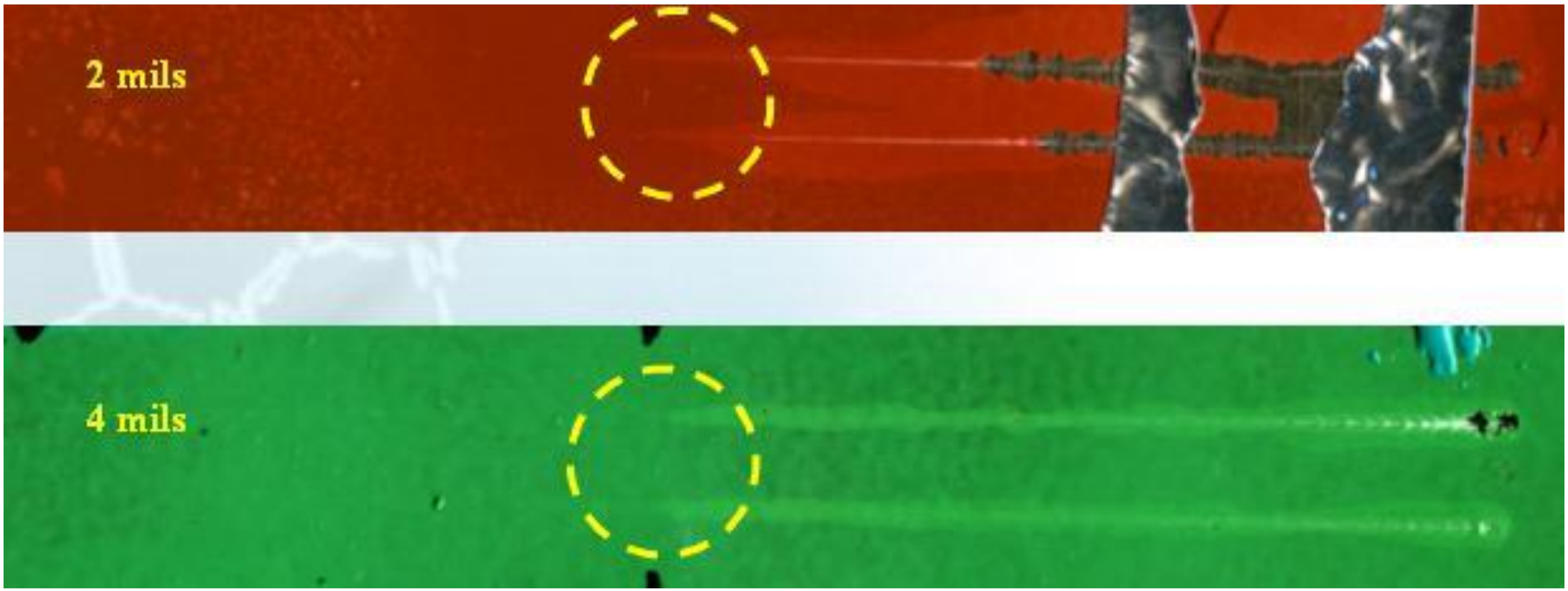


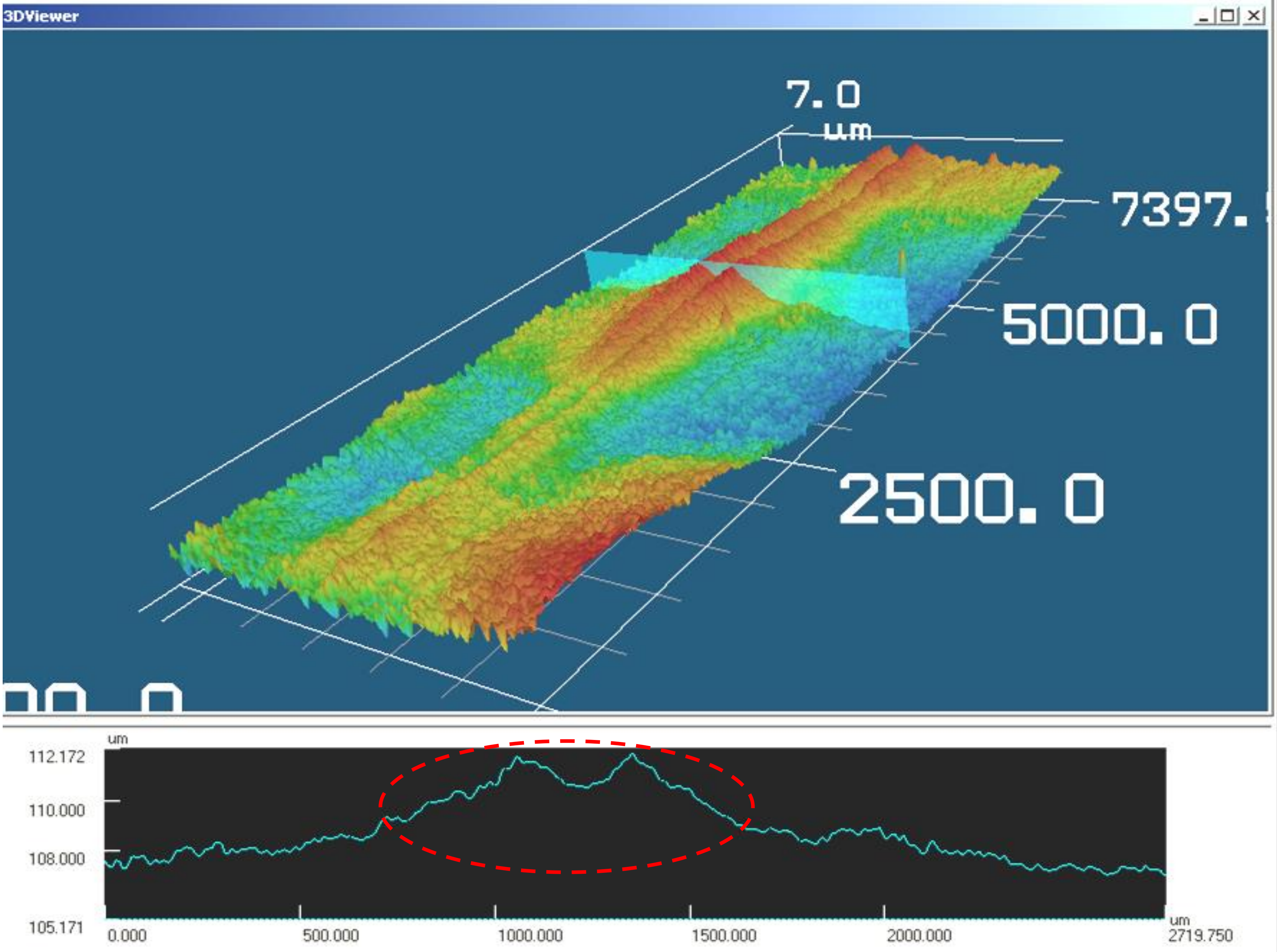
Although the scratch-induced coating debonding is mix-mode in nature, the stress magnitude of Mode I component is almost an order of magnitude higher than Mode II & Mode III stresses.

Identification of Onset of Delamination

☑ **Directly Observable on Thin Coatings**

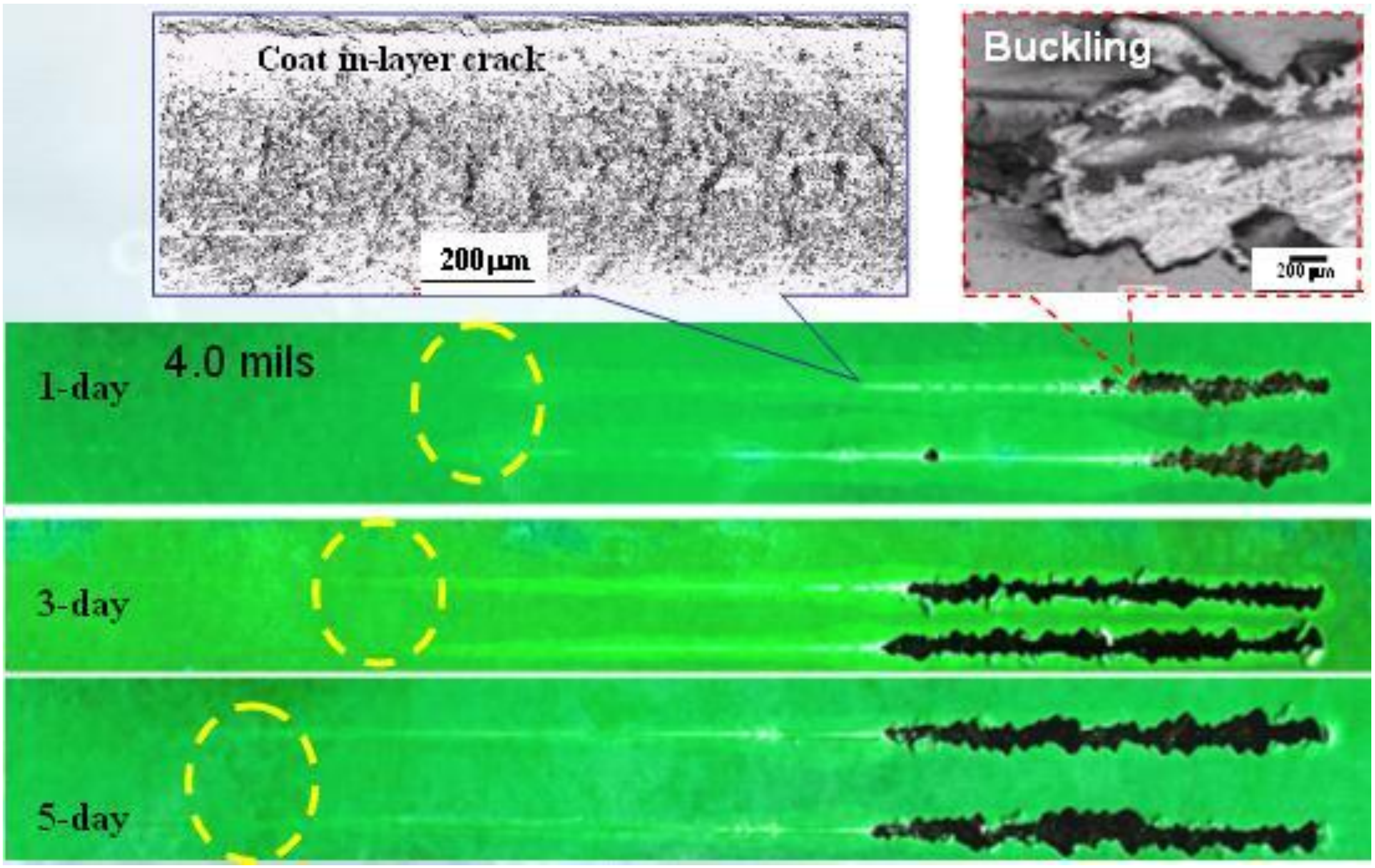
(after 1day hot-water immersion)





3DViewer
7.0
um
7397.
5000.0
2500.0
um
112.172
110.000
108.000
105.171
0.000
500.000
1000.000
1500.000
2000.000
um
2719.750

Adhesive Degradation in Water at 90° C



1) Interfacial Adhesion weakens as a function of immersion time.

2) Onset of delamination is observed.

3) Scratch test results are consistent with expectation.

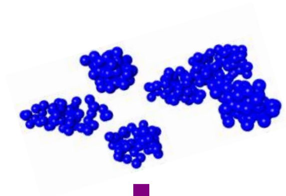
Wet-Adhesive Strength from FEM Modeling

Immersion Time (days)	Onset Load of Delamination (N)	Adhesive Strength (MPa)
0	~	~
1	42	36
3	33	25
5	26	17
7	20	14

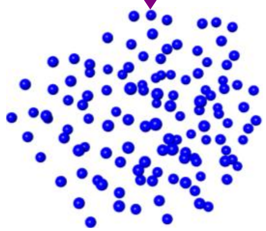
Effects of coating formulation, coating thickness, steel surface treatment, and environmental factors can all be evaluated directly.

Summary

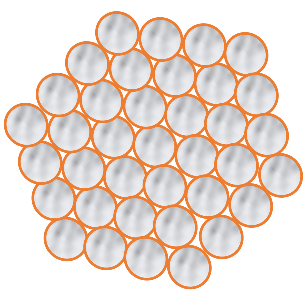
0D – Quantum Dots



Exfoliation

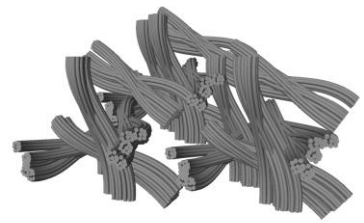


Assembly

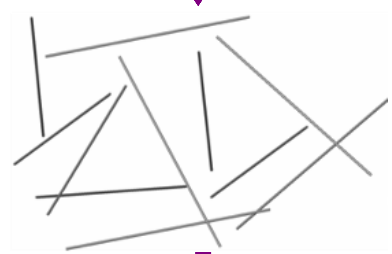


Colloidal Crystal

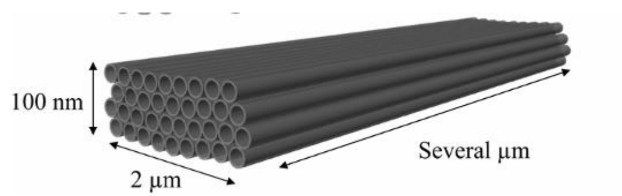
1D - Nanotubes



Exfoliation

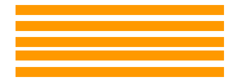


Assembly

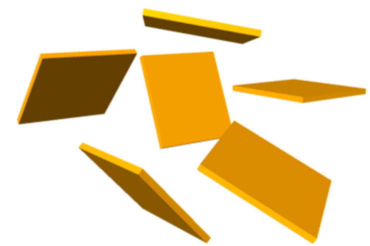


Aligned Tubes

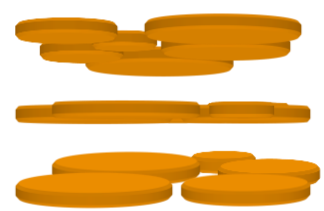
2D - Nanoplatelets



Exfoliation



Assembly



Liquid Crystal

Summary (Cont.)

- It is possible to achieve *nano-dispersion* of inorganic nanoparticles in polymers without utilization of organic surfactants

- It is possible to greatly *improve mechanical properties*, *barrier properties*, *electrical conductivity*, and *other multi-functionality* using well-dispersed nanoparticles.

- The *ASTM scratch tests* can serve as an effective quantitative tool to determine coating adhesive strength and mechanical integrity.