Anti-corrosion Organic Coatings

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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

Scratch Machine

Materials Science

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

Scratch Distance (mm)

Deformation & Stretching
Pushing over
Compressing the pile-up

Scratch - Severe Damage
Mar-Scratch Transition
Scratch - Severe Damage
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:
  - **A** Barrier: 2D, nanoclay
  - **B** Sacrificial: Zn, Mn
  - **C** Anodic: Cr
  - **D** Smart: Self-healing

- 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%.

After exposure in salt spray for 500 h

![Images showing comparison between Epoxy, Epoxy/0.5 wt% GO, and Epoxy/2 wt% GO after exposure.](progress-in-organic-coatings-109-2017-126-134)

Research Focuses

1. Dispersion
2. Interface Design
3. Eco-friendly

Organic Nanocomposite Coatings
Relative Scale of Nanomaterials Studied

- **ZnO** (5 nm)
- **Polymer Radius of Gyration** (≈ 20 nm)
- **Block Copolymer** (15 nm; 200 x 15 nm)
- **Core-shell particles** (100 nm)
- **Natural/synthetic clay, graphene oxide, others** (≈ 100 x 1 nm)
- **CaCO₃** (30 nm)
- **MOF** (50 nm)
- **SWCNT** (≈ 300 x 1 nm)
- **MWCNT, Cu NW, Cellulose** (≈ 30 µm x 20 nm)
0-D ZnO Quantum Dots*

How to disperse ZnO QDs in epoxy without using organic surfactants?
HR-TEM
Particle size distribution

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

1. Aqueous suspension of CNTs → Dry
2. CNT aggregates and entanglements → Cannot redisperse
3. Nanoplatelet stacks and aggregates → Dry
4. Aqueous suspension of nanoplatelets
5. Aqueous suspension of CNTs and nanoplatelets → Dry
6. Entanglements of CNTs and nanoplatelets
7. Redispersion in organic solvents
8. Epoxy 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

<table>
<thead>
<tr>
<th></th>
<th>Neat Epoxy</th>
<th>Nanocomposite-1 (MWCNTs:0.2%;Clay:1.0%)</th>
<th>Nanocomposite-2 (MWCNTs:0.4%;Clay:2.0%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s Modulus (GPa)</td>
<td>3.04±0.04</td>
<td>3.40±0.06</td>
<td>4.27±0.07</td>
</tr>
<tr>
<td>Tensile Strength (MPa)</td>
<td>75.3±4.2</td>
<td>83.1±4.8</td>
<td>116±5.5</td>
</tr>
<tr>
<td>Elongation at Break (%)</td>
<td>3.7±0.1</td>
<td>3.9±0.3</td>
<td>4.3±0.4</td>
</tr>
</tbody>
</table>
TEM Showing the DN-4PB Crack Tip

Fractured Tip
Dispersion of MWCNT Using ZnO

In situ method

Mixing method

- Zinc ion
- Hydroxide
- ZnO nanoparticle
- Carbon nanotube
**Epoxy/MWCNT-ZnO Nanocomposite**

(1.7 wt.% and 3.4 wt.%)
Photocatalysis Application

First order reaction kinetics

\[ \ln \left( \frac{c}{c_0} \right) = K_{app} t \]

<table>
<thead>
<tr>
<th>Samples</th>
<th>( K_{app} ) (min(^{-1}))</th>
<th>( t_{1/2} ) (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>0.0089</td>
<td>77</td>
</tr>
<tr>
<td>MWCNT-ZnO</td>
<td>0.1452 ( \uparrow 16 \text{ times} )</td>
<td>4</td>
</tr>
</tbody>
</table>

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 HAuCl₄ aqueous solution with addition of reducing agent sodium citrate.

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.

Reflectance% vs Wavelength (nm)

Wavelength (nm)

330 (Ultraviolet) 380 430 480 530 580 630 680

140 - 240nm

White Light

Iridescence
Liquid Crystal Phase of ZrP in Epoxy (9.02 wt% = 4 vol%)
TEM-Tomography of Epoxy/ZrP (4 vol.\%)  
(Jinnai and Takahara, Kyushu Univ)
Epoxy/ZrP-8.2 vol%

- Highly aligned continuous films of ZrP nanoplatelets

Substrate
TEM and XRD of Epoxy/ZrP Nanocomposites

(a) Pristine ZrP
(b) Epoxy/ZrP-3.4 vol%
(c) Epoxy/ZrP-8.2 vol%
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.
In order to evaluate corrosion resistance performance, potentiodynamic polarization measurements were performed.

The corrosion potential ($E_{corr}$), electromotive force in electrochemistry, 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>
<thead>
<tr>
<th></th>
<th>$E_{corr}$ (V)</th>
<th>$I_{corr}$ ($\mu$A/cm$^2$)</th>
<th>CR (mm year$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare Al</td>
<td>-0.825</td>
<td>29.41</td>
<td>3.21×10$^{-1}$</td>
</tr>
<tr>
<td>Neat epoxy coated Al</td>
<td>0.102</td>
<td>1.98</td>
<td>2.16×10$^{-2}$</td>
</tr>
<tr>
<td>Smectic epoxy/ZrP coated Al</td>
<td>1.068</td>
<td>0.36</td>
<td>3.93×10$^{-3}$</td>
</tr>
</tbody>
</table>
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

- Low Load (1 N)
- Scratch Direction
- High Load (50 N)

1. Mar Zone: Ironing & Roughening
2. Scratch Zone: “Fish-Scale” due to Ductile Drawing
3. Material Removal: Rupture & Cracking
Visual Assessment of Scratch Damage

Scratch Direction

$F_N \approx 10 \text{ N}$

$F_N \approx 17 \text{ N}$

$F_N \approx 5 \text{ N}$

$F_N \approx 44 \text{ N}$

1 N to 120 N

Bulk epoxy

Neat epoxy Coating

Epoxy-M1000 Coating

Epoxy/ZrP-M1000 Coating

0 10 20 30 40 50 60 70 80 90 100 mm

$F_N \approx 10 \text{ N}$

$F_N \approx 17 \text{ N}$

$F_N \approx 5 \text{ N}$

$F_N \approx 44 \text{ N}$
Subsurface Deformation and Damage

Laser Scanning Confocal Microscopy

Scratch depth (um)
Normal load (N)

-65
-60
-10
0
40 45 50 55 60 65 70

coating cracking
coating removal
OM micrographs in the longitudinal section of the scratch (Scratch direction: from left to right).

(a) $F_N \approx 60 \text{ N}$  
(b) $F_N \approx 60 \text{ N}$  

(c) $F_N \approx 63 \text{ N}$  
(d) $F_N \approx 63 \text{ N}$
Wet Coating Adhesive Strength Evaluation
(Funded by DOT, 3M, Shawcor, Dow Chemical)
Critical Strength for Various Coating Damage Modes

<table>
<thead>
<tr>
<th>Damage Mode</th>
<th>Transition Load (N)</th>
<th>Damage Strength (MPa)</th>
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</thead>
<tbody>
<tr>
<td>Delamination</td>
<td>18.3 N</td>
<td>36</td>
</tr>
<tr>
<td>Transverse cracking</td>
<td>34.5 N</td>
<td>51</td>
</tr>
<tr>
<td>Buckling</td>
<td>39.8 N</td>
<td>136</td>
</tr>
</tbody>
</table>

Transition Load (N): 1 N to 50 N

Damage Strength (MPa): 1 N to 50 N
Debonding Mechanism

Cross-section view

Center of tip

Debonding

Coating

Substrate
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 1 day hot-water immersion)
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

<table>
<thead>
<tr>
<th>Immersion Time (days)</th>
<th>Onset Load of Delamination (N)</th>
<th>Adhesive Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>~</td>
<td>~</td>
</tr>
<tr>
<td>1</td>
<td>42</td>
<td>36</td>
</tr>
<tr>
<td>3</td>
<td>33</td>
<td>25</td>
</tr>
<tr>
<td>5</td>
<td>26</td>
<td>17</td>
</tr>
<tr>
<td>7</td>
<td>20</td>
<td>14</td>
</tr>
</tbody>
</table>

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 \textit{nano-dispersion} of inorganic nanoparticles in polymers without utilization of organic surfactants.

• It is possible to greatly \textit{improve mechanical properties, barrier properties, electrical conductivity, and other multi-functionality} using well-dispersed nanoparticles.

• The \textit{ASTM scratch tests} can serve as an effective quantitative tool to determine coating adhesive strength and mechanical integrity.