Chemical functionalization of nanoparticles

Sérgio Eduardo Abud Filho

IPT – Institute for Technological Research

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1. Objectives
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Objectives

- Nanotechnology: chemical functionalization of nanoparticles
- Development of nanotechnology-based organic coating to enhance anticorrosion properties: incorporation of nanoparticles in organic coatings
- Characterization techniques of nanoparticle surface
Introduction

• **Nanotechnology**: study of materials in nanometric scale (nanoparticles, nanolayers, nanocoatings) – 1 nm to 100 nm

• **Advances in this area of science**: novel phenomena (physical, chemical and biological) materials when it's taken on the nanoscale

• **Chemical functionalization of nanoparticles**: modification of nanoparticle surface to apply in different areas: biological, medical, engineering, etc.
What’s chemical functionalization of nanoparticle?

Chemical modification of nanoparticle surface

Nanoparticle

Chemical functionalization

Active sites

Nanoparticles functionalized

Hydrophilic, hydrophobic, conductive, anticorrosive
Introduction

Development of nanotechnology-based organic coating to enhance anticorrosion properties (incorporation of nanoparticles)

- **Corrosion**: protection of metal structures from corrosion by organic coatings is a well known practice;
- **Commercial problems**: High toxicity of some components of the coating
- With the quest for new **developed coating** systems with low toxicity and high performance

Incorporation in the coating

Nanoparticles chemically functionalized
• The improvement in the properties of the nanocoatings is attributed to their nanoparticles functionalized;
• Nanomaterials mostly used in coating system: SiO₂, TiO₂, ZnO, Al₂O₃, Fe₂O₃, nano-aluminum, nano-titanium
Multi-functional hybrid coatings (inorganic and organic components) for scratch and corrosion resistance:

• the inorganic components (nanoparticle) contribute to increased the scratch and adhesion resistance on metallic substrate;

• the organic component (active site) increase the density and flexibility of the coating, and enhance functional compatibility with organic paint systems
• To improve UV-Blocking Coatings
• Inorganic nanoparticles, as alternative to UV-blockers in coating applications
• Nano-ZnO, nano-TiO₂, nano-CeO₂: **excellent photo- and thermal stability**
• **Example:** transparent ZnO/epoxy nanocomposite coating via in situ polymerization. Optical properties of the nanocomposite coating depends on ZnO particle size

• To develop anti-scratch and anti-abrasion coatings
• Nano-SiO₂, nano-Al₂O₃, nano-ZrO₂: improve the mechanical properties, increase the macro hardness, scratch resistance
Nanoparticles applications

• To develop anticorrosive coatings
• Development of nanoporous reservoir for storing of corrosion inhibitors on the metal/coating interface (nanostructure porous TiO$_2$ interlayer prepared on the aluminum alloy surface).
Nanoparticles applications

- To develop Super-Hydrophobic coatings
- Continuous demand for water-repellent or hydrophobic coatings in industry
Nanotechnology application for corrosion problems

• To develop SMART NANOCAPSULES containing inhibitors for corrosion protection
• Corrosion inhibitors are used extensively to prevent corrosion such as azoles group, amines and amino acids

Example: benzotriazole (BTA) is one of the most effective inhibitors for corrosion of copper and its alloys
• Copper surface is covered by a film identified as [Cu(I)BTA] complex

Corrosion Inhibition Techniques require
Maintaining a specific concentration of inhibiting reagent in the solution

Changes in the system
• pH
• temperature
• agitation rate

Development of SMART NANOCAPSULES
Nanosilica applications for corrosion problems

Multi-functional hybrid coating for scratch and corrosion resistance

- silica nanoparticles (increase scratch resistance, abrasion resistance, flexibility)
- anticorrosive acrylate resin

First step: functionalization of nanosilica surface with alkoxysilanes

Inorganic nanoparticles (very hydrophilic) → Cannot be dispersed → Acrylate resins (low polar)

PHOTOPOLYMERIZATION
Development of photocurable monomer
**Second step:** Synthesis of anticorrosive di-acrylate (anticorrosive)

\[
\text{1,4 - hydroquinone} + \text{aminopropyl ethanol} \xrightarrow{\text{CuCl}_2/O_2, \text{THF}} \text{1,4 - benzoquinone}
\]

\[
\xrightarrow{\text{Et}_3\text{N}, \text{DMF, 0°C}} \text{di-acrylate} \quad \text{(anticorrosive specimen)}
\]

\[
\xrightarrow{\text{methacrylic anhydride}}
\]
Nanosilica applications for corrosion problems

**Third step:** Syntheses of photocurable monomers

\[
\begin{align*}
\text{2,4,6,8-tetramethylcyclotetrasiloxane} & \quad + \quad \text{allyloxyethanol} & \quad \xrightarrow{\text{Pt, toluene}} & \quad \text{Intermediate} \\
\text{Methacrylic anhydride} & \quad \xrightarrow{\text{Et}_3\text{N}} & \quad \text{Tetrasiloxane acrylate} \quad \text{(PHOTOCURABLE MONOMER)}
\end{align*}
\]
Nanosilica applications for corrosion problems

Third step: Preparation of hybrid coatings

- Functionalized silica nanoparticles
- Anticorrosive di-acrylate

The coating formulations were **dip-coated** on iron substrates and **photopolymerized by UV irradiation** for 5 min (thicknesses from 10 µm – 12 µm).
**RESULTS - Composition of the formulations**

<table>
<thead>
<tr>
<th></th>
<th>Coating 1</th>
<th>Coating 2</th>
<th>Coating 3</th>
<th>Coating 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urethane acrylate</td>
<td>100</td>
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**Corrosion studies by Electrochemical Impedance Spectroscopy (EIS)**

To evaluate the corrosion protection performance of the prepared coatings
# Nanosilica applications for corrosion problems

## Table of Coatings

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## Diagrams

**Graph 1:**
- Initial impedance: $10^8 \ \Omega \text{cm}^{-2}$

**Graph 2:**
- Phase angle: $90^0$
Nanosilica applications for corrosion problems

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The electrolyte diffused through the coatings 1 and 2
Nanosilica applications for corrosion problems

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AFTER 50 DAYS

10^8 Ω cm\(^{-2}\)

90°
• Modification of epoxy coatings by adding various levels of ZrO₂ nanoparticles (1, 2 and 3 wt%)
• To promote chemical interactions between nanoparticles and polymeric coatings, the surface of the nanoparticles

Chemical functionalization

Aminopropyl trimethoxy silane (APS)

ZrO₂ nanoparticles

ZrO₂ functionalized nanoparticle
Corrosion performance of EPOXY COATINGS containing ZrO$_2$ nanoparticles

**FTIR VIBRATION SURFACE CHARACTERIZATION**

A – aminopropyl trimethoxy silane (APS)  
B – untreated ZrO$_2$ nanoparticles  
C – APS – treated ZrO$_2$ nanoparticles

<table>
<thead>
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<th>Wavenumber (cm$^{-1}$)</th>
<th>Functionality</th>
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<tbody>
<tr>
<td>490</td>
<td>Stretch vibration band of Si - O</td>
</tr>
<tr>
<td>510</td>
<td>Stretch vibration band of Zr – O - Zr</td>
</tr>
<tr>
<td>964</td>
<td>Stretch vibration band of Zr – O - Si</td>
</tr>
<tr>
<td>1000 - 1300</td>
<td>O – Si asymmetric vibration</td>
</tr>
<tr>
<td>1570</td>
<td>Si – O bonds</td>
</tr>
<tr>
<td>2870</td>
<td>Symmetric Stretch vibration of [-$(CH_2)_n$] and –$(CH_3)$</td>
</tr>
<tr>
<td>2930</td>
<td>Asymmetric Stretch vibration of [-$(CH_2)_n$] and –$(CH_3)$</td>
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<tr>
<td>3430</td>
<td>Vibration band of -OH</td>
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</tbody>
</table>
Corrosion performance of EPOXY COATINGS containing ZrO₂ nanoparticles

TRANSMISSION ELECTRON MICROSCOPY RESULTS

Aggregation size

- Relatively dispersed at the scale of 100 – 170 nm
- Some aggregates particles can be observed (-OH: hydrogen bonding)
Corrosion performance of EPOXY COATINGS containing ZrO$_2$ nanoparticles

SALT SPRAY TEST RESULTS (2000 hours)

Without nanoparticles

2 wt% ZrO$_2$ (corrosion was not evident even after 2000 h)

1 wt% ZrO$_2$

3 wt% ZrO$_2$ (corrosion was not evident even after 2000 h)
Characterizations techniques

- **NMR** (Nuclear Magnetic Resonance) spectroscopy $^1$H and $^{13}$C;
- **FTIR** (Fourier Transform Infrared in the transmission mode at 400 – 4000 cm$^{-1}$ – degree of modification of the nanoparticles;
- **RAMAN SPECTROSCOPY**
- **TEM** (Transmission Electron Microscopy) images – effect of modification of nanoparticles on their dispersion properties;
- **EIS** (Electrochemical Impedance Spectroscopy) – estimate the corrosion protection performance of the prepared coatings
Conclusions

• Functionalized nanoparticles have been used in anticorrosive coatings
• Development of multi-functional hybrid coating for scratch and corrosion resistance: inorganic (nanoparticle) and organic component (active site)
• Functionalized nanoparticles can be applied in different areas: engineering, medical, biological, etc.
  Its necessary optimize the active sites on the nanoparticle surface (hydrophilic, hydrophobic, conductive etc)
• Characterization technique of nanoparticles surface: NMR, FTIR, Raman, TEM;
• Coating characterization: EIS, salt spray
Thank you !!!