Self-healing coatings with multiple functionalities for the corrosion protection of metals

Research consortium

VUB:
- For surface eng. & characterisation: Iris De Graeve, Herman Terryn
- For polymer science: Guy Van Assche, Bruno Van Mele
- Students: Alexander Lutz, Chiara Cordiola, Maria Mercedes Diaz, Gill Scheltjens, Thibault Muselle, Joost Brancart, Hilke Verbruggen

Collaborations: ....MANY...
Do self-healing coatings work in reality? **YES**

Current state-of-the-art
>> Works for black car
>> Only cosmetic repair

Concept of multiple action self-healing polymer coating

1. **Self-healing polymer systems**
2. **Corrosion inhibitors**
3. Healing metal through inhibitor release and activity = Autonomic, immediate response
4. Healing polymer, autonomic or induced = Delayed

Multiple action self-healing corrosion protection coatings
1. Proof of concept: Self-healing based on “shape memory polymer”

- PCL/PU block copolymer
- Physical network
  - Soft PCL matrix
  - Hard PU segments

Soft matrix
\[ T_{m,PCL} = 52^\circ C < T_{healing} < T_{m,PU} = 173^\circ C \]

Hard phases

Soft PCL segment (8000 g/mol)

Hard PU segment (variable length)

Polymer healing action

Atomic Force Microscopy on scratched coating

Before heating

After 60 mins at 120°C
Polymer healing action
AFM on scratched coating

Coating thickness 0.5 µm
Scratch width 15 µm

Polymer healing for corrosion protection
Scanning Vibrating Electrode Technique

Heating at 40°C
Heating at 80°C

2 days of immersion 1 day of immersion 6 days of immersion

Collaboration for local electrochemical methods:
Arjan Mol, Yaiza Gonzalez Garcia
Delft University of Technology
• UV-cure, polyester-urethane acrylate

• Nano phase separated high Tg polymer (dark zones) and polyester segments (light zones) = combination of extreme toughness with the ability to recover from mechanical damage by application of a thermal trigger

Collaboration for polymer synthesis:
Ghent University:
Philip Du Prez, Otto Van den Berg, Richard Hoogenboom, Lenny Voorhaar

Self-healing polymer efficiency?

Fresh coating  2 scratches  Healed coating

Major defect  During healing  Closed defect
Second approach: SH by capsules for autonomous healing

1\textsuperscript{st} generation of Melamine Formaldehyde (MF) capsules

\(~90\%\) plasticizer content

Scale bar 100 µm

Robust microcapsules

Scale bar: 10 µm

Very Thin Shells

Concept of multiple action self-healing polymer coating

Self-healing polymer systems

Corrosion inhibitors

Metal

Damage

Healing of metal through inhibitor release and activity

= Autonomic, immediate response

Metal

Healing of the polymer, autonomic or induced = Delayed

Metal

Multiple action self-healing corrosion protection coatings
2. Inhibitor selection and incorporation

Case: galvanized steel

Aim: durable protection, (partial) replacement of zinc

Q1: Which inhibitor is best suited for galvanized steel?
Q2: How bring it into the coating for controlled release?
Q3: How monitor the leaching?

Q1: Inhibitor selection

Literature and electrochemical assessment

Example of linear sweep voltammetry:

Influence of adding corrosion inhibitor to the electrolyte

⇒ Best results for MBT already at $10^{-5}$ M
Q2: Inhibitor incorporation into coatings

Mercaptobenzothiazole (MBT)

- Dissolved in the coating
- Encapsulated in
  - Porous nanocapsules
  - Layered Double Hydroxides (LDH)

For inhibitor encapsulation: Aveiro University: Michael Zheludkevich, A.C. Bastos

SiNC (+MBT)
FEG-SEM and TEM

TEM: Antwerp University: Artem Abakumov, Tyché Perkisas
Q3: Inhibitor leaching out of the nanocontainers when in solution?

LSV on HDG steel

Blanc 0.05M NaCl - A
Blanc 0.05M NaCl – C
SiNC+MBT - A
SiNC+MBT – C
LDH+MBT - A
LDH+MBT - C
Q3: Inhibitor leaching out of the nanocontainers?
Surface Enhanced Raman Spectroscopy

LDH+MBT on AgProbe
SiNC+MBT on AgProbe
Blanc AgProbe

After rinsing of the AgProbe

Concept of multiple action self-healing polymer coating

Self-healing polymer systems

Corrosion inhibitors

3. Healing of metal through inhibitor release and activity
   = Autonomic, immediate response

Healing of the polymer, autonomic or induced = Delayed

Multiple action self-healing corrosion protection coatings
3. Evaluation of the inhibitor activity in the coating
Experimental setup

- Epoxy-Amine thermoset (non self-healing)
- Inhibitor (0.4 wt%) added to unreacted components
  - Dissolved
  - In porous nanocapsules
  - In LDH
- Bar coater on HDG → 50 µm thick coatings

SVET on coating without inhibitors

⇒ In-situ optical imaging and SVET mapping above two micro-drill defects

0 hr of immersion 4 hr of immersion
SVET on coating with **dissolved MBT**

4 h

4 hr of immersion

Lower currents, but coating delamination!

3-5-2013

SVET on coating with **SiNC + MBT**

For 4 hr of immersion

**Corrosion inhibition and no coating delamination**

3-5-2013
SVET on coating with LDH + MBT

For 4 hr of immersion

Corrosion inhibition and no coating delamination

Next step

➢ Incorporation into a SELF-HEALING polymer coating !!!!
SH coating with X+MBT
FEG-SEM

SH coating with SiNC+MBT

SH coating with LDH+MBT

SH coating with X+MBT: leaching of the inhibitor from the scratched coating? SERS on AgProbe

Coating + SiNC+MBT
Coating+ LDH+MBT
Coating + LDH+MBT
Coating without inhibitor
SH coating with LDH+MBT
XPS on multiple scratched coating

>> Evidence of inhibitor (S of MBT) confirms leaching mechanism into scratches
>> BUT: very low concentration is difficult to detect….

Concept of multiple action self-healing polymer coating

Self-healing polymer systems

Corrosion inhibitors

Healing of metal through inhibitor release and activity = Autonomic, immediate response

Healing of the polymer, autonomic or induced = Delayed

Multiple action self-healing corrosion protection coatings
4. Multiple action self-healing???
EIS on SH coating with LDH+MBT

Undamaged coating
Scratched coating
Scratched coating
Thermally healed coating
Thermally healed coating

>> Inhibitor action at low frequencies + polymer healing action at mid-high frequencies

Conclusions

• Polymer healing action
  – Healing temperature is very dependent on the chemistry
  – Defect healing monitored with AFM, optical imaging, local electrochemical methods (SVET, SECM)

• Inhibitor activity from nanocontainers
  – LSV, SERS Raman: leaching from the nanocontainers in a solution and from the coating
  – SVET, SECM: inhibition in coating defects
  – XPS: inhibitor deposition in the scratch

• Multiple-action self-healing studied with EIS
  >>> Autonomous metal passivation
  >>> Thermally induced recovery of barrier properties
Acknowledgements

Papers

Gonzalez-Garcia Y., Mol J.M.C., Muselle T., De Graeve I., Van Assche G., Scheltjens G., Van Mele B., Terryn H.,
SECM study of defect repair in self-healing polymer coatings on metals,
Electrochemistry Communications, 13 (2011) 169-173

Gonzalez-Garcia Y., Mol J.M.C, Muselle T., De Graeve I., Van Assche G., Scheltjens, G., Van Mele B., Terryn H.,
A combined mechanical, microscopic and local electrochemical evaluation of self-healing properties of shape-memory polyurethane coatings,
Electrochimica Acta 56 (2011) 9619– 9626

Scheltjens G., J. Brancart, De Graeve I., Van Mele, B., Terryn H., Van Assche G.,
Self-healing property characterization of reversible thermoset coatings,
Journal Of Thermal Analysis And Calorimetry 105 (3) (2011) 805-809

Investigation of the self-healing properties of shape memory polyurethane coatings with the ‘odd random phase multisine’ electrochemical impedance spectroscopy,
Proof of concept demonstrated on VUB logo

Top view of SMPU coating, locally 'damaged' with VUB logo using nanolithographic AFM tip during heating to 80 °C >> flow of soft phases >> fading of the contours after healing procedure >> stitching of the logo >>> healing of damage!

Future?

Meet us in June 2013 for the International Self-Healing Materials conference in Ghent – Belgium!