Tung oil: An autonomous repairing agent for self-healing epoxy coatings

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1. Introduction

Most costs of corrosion protection methods are related to the coatings [1]. Coatings are exposed to mechanical and chemical attacks in their life that cause various types of defects in their structure. These defects, which diminish the life and protective properties of coatings, reduce the life of protected structure/equipment; because in addition to local corrosion, re-coating requires surface re-preparation and thickness loss. So, appearance of new technologies and more protective life of coatings can lead to service life time enhancement of structures/equipment with companionship of cost savings. These goals will be possible by improvement in coating quality and choice of proper and optimized protective coating system type.

In recent years the interest in self-healing materials witnessed strong growth and its successful laboratory design and synthesis provided a suitable base for achieving of smart/multi-functional materials. Various approaches were applied to create self-healing ability in bulk materials [2], but all of them were on a same principle. A healant material, usually in liquid phase, is stored in special spaces through the material body. After tearing of the space wall due to matrix scratch, the stored healant releases and causes to scratch repair by polymerization process. Among used approaches the micro/nanocapsule embedment through the material matrix was the main one for self-healing ability in coatings. In this system, the healant material is stored through the almost equal sized capsules. Fig. 1 shows a presentative schematic of self-healing process of this approach. The usual method for encapsulation process is in situ polymerization – oil in water emulsion [4]. Although poly urea–formaldehyde (PUF) was the prevalent shell of the synthesized capsules, but various material were used as the core (healant) material. Some of these tested materials as core were dicyclopentadiene (DCPD), Epon 828 and Epon 862 epoxy resin, chlorobenzene, phenylacetate, ethylphenylacetate and linseed oil [5]. Polymerization process of released DCPD from torn capsules requires catalyst, which must be dispersed into the coating matrix before applying. But linseed oil, as a drying oil, does not have this necessity; and air contacting is enough for polymerization to heal the scratch.

Chemically, drying oils are water-insoluble, unsaturated triglycerides of long chain fatty acids. Most of these oils contain less than 10% of any particular saturated fatty acid residue. The degree of double bond unsaturation controls the drying rate; the higher degree of unsaturation or iodine number, the faster the drying or polymerization of the oil. Reaction with oxygen is the most important reaction that drying oils undergo in the drying or polymerization process. Oxidation can result in trans isomer formation, cleavage of the carbon–carbon chain along with formation of volatile byproducts, and polymerization. These reactions can be catalyzed with metallic salts such as cobalt that promote free radical formation by reaction with hydroperoxides and other peroxides that are formed in the oxidation process.

Tung oil, as another drying oil, has some similar properties of linseed oil (for better comparison, see Tables 1–3). It is readily available as a major product from the seeds of the Tung tree [9]. For centuries, this oil has been used for paints and waterproof coatings, and as a component of caulk and mortar. Tung oil’s ability to dry quickly and polymerize into a tough, glossy, waterproof coating has made it especially valuable in paints, varnishes, linoleum,
Fig. 1. The autonomic healing concept. A micro/nanoencapsulated healing agent is embedded in a structural composite matrix containing a catalyst capable of polymerizing the healing agent. (a) Cracks form in the matrix wherever damage occurs; (b) The crack ruptures the microcapsules, releasing the healing agent into the crack plane through capillary action; (c) The healing agent contacts the catalyst, triggering polymerization that bonds the crack faces closed [3].

Table 1
Main unsaturated fatty acids found in drying oils.

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>No. of carbon atoms</th>
<th>No. of double bonds</th>
<th>Structural formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linolenic</td>
<td>18</td>
<td>3</td>
<td>HOOC(CH2)7CH=CHCH=CHCH=CHCH=CH3</td>
</tr>
<tr>
<td>Linoleic</td>
<td>18</td>
<td>2</td>
<td>HOOC(CH2)7CH=CHCH=CH(CH2)4CH3</td>
</tr>
<tr>
<td>Oleic</td>
<td>18</td>
<td>1</td>
<td>HOOC(CH2)7CH=CH(CH2)7CH3</td>
</tr>
<tr>
<td>Elaeostearic</td>
<td>18</td>
<td>3</td>
<td>HOOC(CH2)7CH=CH=CH=CH(CH2)3CH3</td>
</tr>
</tbody>
</table>

Table 2
Weight percentage of major unsaturated fatty acid residues in linseed and Tung oils [6,7] (remainder of oils is essentially all saturated fatty acid residues).

<table>
<thead>
<tr>
<th>Oil</th>
<th>Linolenic</th>
<th>Linoleic</th>
<th>Oleic</th>
<th>Eleostearic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linseed</td>
<td>52</td>
<td>16</td>
<td>22</td>
<td>–</td>
</tr>
<tr>
<td>Tung</td>
<td>3</td>
<td>4</td>
<td>8</td>
<td>80</td>
</tr>
</tbody>
</table>

Table 3
Physical characteristics of linseed and Tung oils [8].

<table>
<thead>
<tr>
<th>Oil</th>
<th>Specific gravity 25.5/25.5 °C</th>
<th>Iodine value</th>
<th>Saponification value</th>
<th>Acid value</th>
<th>Refractive index 25 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linseed</td>
<td>0.926</td>
<td>180</td>
<td>190</td>
<td>3.0</td>
<td>1.478</td>
</tr>
<tr>
<td>Tung</td>
<td>0.915</td>
<td>170</td>
<td>192</td>
<td>0.2</td>
<td>1.517</td>
</tr>
</tbody>
</table>

2. Experimental

2.1. Materials

Urea, formaldehyde, ammonium chloride, octanol, resorcinol and sodium chloride were procured in high purification from Merck Co. Epoxy resin (epoxy equivalent = 183–189 g/equiv.), its reactive diluents (epoxy equivalent = 299–328 g/equiv.) and (cycloaliphatic polyamine) hardener (H+ active equivalent = 115 g/equiv.) were purchased from Bajak paint and resin Co. and dodecyl sulphate. Tung oil (commercial grade) was purchased from Sigma–Aldrich. All chemicals/materials were used without any purification.

2.2. Microcapsules’ synthesis

Numerous preparation technologies available for the encapsulation of core material have been reported [11,12]. But here microcapsules were prepared by in situ polymerization – oil in water emulsion process. The distinguishing characteristic of in situ polymerization rather than other polymerization process for encapsulation is that no reactants are included in the core material. All polymerization occurs in the continuous phase, rather than on both sides of the interface between the continuous phase and the core material.
The encapsulation process was inspired by the works of Brown et al. [4] and Suryanarayana et al. [5]. The process is presented here in details.

At room temperature, 260 ml of deionized water with 10 ml of 5 wt% dodecyl sulphate solution were mixed in 1000 ml beaker which was suspended in a temperature-controlled water bath. The solution was agitated with a digital mixer driving a three-bladed, low-shear mixing propeller placed just above the bottom of the beaker.

Under 200 rpm agitation 5 g urea, 0.5 g ammonium chloride and 0.5 g resorcinol were dissolved in solution. The pH was adjusted to approximately 3.0 using 1 wt% solution of hydrochloric acid in deionized water. After 10 min of agitation 50 ml of Tung oil was added slowly to form an emulsion and allowed to stabilize for 15 min under agitation. After stabilization, 13 g of 37 wt% aqueous solution of formaldehyde was added. The emulsion was covered and slowly heated and maintained at 60 °C for 12 h.

2.3. SEM analysis of synthesized capsules

Capsule samples were coated with an ultrathin layer of Ag coating by a sputter coater (POLARON SC7620) to provide a conductive surface for capsule samples and prevent the accumulation of static electric charge on the specimen during electron irradiation. Morphology of synthesized microcapsules was observed by a scanning electron microscope (LEO 1455VP), while their maximum and minimum sizes were measured.

2.4. Soxhlet extraction and infrared spectroscopy

Amount of Tung oil present in microcapsules was determined by extracting oil in a Soxhlet apparatus and xylene was used as solvent to extract Tung oil. In current project, a known weight of micro/nanocapsules (W FC) was crushed using pestle and mortar and transferred to a thimble. Pestle and mortar were rinsed with xylene and added to thimble. Extraction was carried out using xylene as a solvent for Tung oil. After 5 h of extraction, thimble was carefully taken out of the Soxhlet apparatus and after completely draining the solvent, it was dried in oven. The final weight of the remaining material (W E) was noted and the core content of synthesized capsules can be calculated by:

$$W_{ic} = W_{fc} - W_{e}$$ (1)

To specify the core and shell material of synthesized capsules, their spectra were recorded on Fourier transform infrared spectrophotometer.

2.5. Dispersion of capsules into epoxy and paint applying

Three mentioned epoxy coating component (See Section 2.1) were mixed in stoichiometric amount for curing. Considering mentioned points in a study [13], the microcapsules were incorporated into the paint formulations at the time of application.

Microcapsules were added under slow agitation (200 rpm with mechanical mixer) to epoxy resin solution at ambient temperature in concentrations of 12 wt%.

Clean C-steel panels, size 60 mm × 60 mm × 2 mm were blasted with sand to the sa2 1/2 grade (according to ISO 8501) and then coated on one side by applicator to obtain an average dry film thickness of approximately 150 μm DFT. After 14 days of curing in the air, cross-cut was made on panels and kept at ambient (−25 °C) for 24 h. A composition without capsules was prepared as a control sample.

2.6. Corrosion resistance investigation

The capsule incorporated coating sample was kept in the air (−25 °C) for 24 h, after cross-cutting by a razor blade. In fact the sample was allowed to do its probable healing process.

The corrosion resistances of scratched neat and capsule incorporated coating and also unscratched neat epoxy coated C-steel samples were monitored during two weeks and data was gained three days (one, seven and fourteen days after start of immersion) by electrochemical impedance spectroscopy (EIS) and compared to each other. The samples were in touch with aqueous solution of 3.5 wt% NaCl, during these two weeks.

The exposed samples surface area of 17.0 cm² acted as the working electrode. An Ag/AgCl electrode was employed as reference electrode and a large stainless steel (AISI-316) counter electrode positioned parallel to the exposed sample completed the cell. The cell was filled with 3.5 wt% NaCl aqueous solution and remained open to the air. The samples were in touch with the electrolyte, during these two weeks. The measurements were carried at ambient temperature.

EIS measurements were carried out at the Ecorr potential of the samples in the frequency range 0.01–100,000 Hz. The frequency values are spaced logarithmically, and the rms width of the sinusoidal voltage signal applied to the system was 10 mV. EIS data were plotted in terms of Bode magnitude (logarithm of the impedance modulus, |Z|, as a function of the logarithm of the frequency) diagrams. AutoLab potentiostat/galvanostat (PGSTAT 302N) was used for all these electrochemical tests.

Also corrosion resistance of similar samples was tested through salt water immersion. The salt concentration of the solution was 3.5 wt%, as the same as EIS test.

2.7. Adhesion test

For investigation of probable negative effects of capsule embedding on coating adhesion, pull-off test was done for three coated samples coated by capsule incorporated epoxy coating. In this way, adhesion is quantified in terms of the forces employed to detach the test dollys glued to the paint film from the underlying metal. These tests were conducted according to ASTM D4541-09.

3. Results and discussion

The encapsulation process of Tung oil was successful and the product was analyzed under SEM. The SEM images (Fig. 2) revealed that the capsules were spherical in shape, and had a rough and non-porous exterior shell wall. Rough morphology of capsules ensures their good mechanical bonding to coating matrix. Their spherical shape guarantees the storage role of capsules and easy dispersion into the coating before applying. All of synthesized capsules were in the 40–100 μm diameter range.

Core and shell of the capsules were separated by Soxhlet extraction and FTIR spectra was recorded. It is seen from the FTIR spectra of urea–formaldehyde resin (presented in Refs. [14,15]) and shell material that both are closely matching at characteristic peaks of a N–H stretching vibration at 3350 cm⁻¹, a C=O stretching vibration at 1639 cm⁻¹, and a C–H stretching vibration at 1458 cm⁻¹. C–N stretching vibrations are shown at 1250 and 1134 cm⁻¹. This spectrum confirms that shell material is made of urea–formaldehyde polymer. Spectra of Tung oil (presented in Ref. [16]) and core material have also been found matching at characteristic peaks for C=O stretching vibration at 1742 cm⁻¹ and C=C stretching vibrations at...
Fig. 2. Surface and shell morphology of synthesized PUF microcapsules containing Tung oil.

Fig. 3. Bode magnitude plot of EIS data of samples after 1 day of immersion in 3.5 wt% NaCl aqueous solution.

2041 cm\(^{-1}\), C–H peaks at 1456 cm\(^{-1}\) and in 2924 cm\(^{-1}\) peaks is the O–H band.

In view of above it is established that Tung oil has been successfully encapsulated in urea–formaldehyde shell. The mean core content of two synthesized capsule samples was around 75 wt% by Eq. (1).

To investigate the corrosion resistance of Tung oil capsule incorporated coating, cross-cut was made on a sample by a razor blade and impedance of the coating was monitored through two weeks, by EIS. Also the same procedure was repeated for scratched and un-scratched neat epoxy with the same thickness. The results are shown in Figs. 3–5. According to these figures, scratching of neat epoxy led to severe decline in corrosion resistance of coating and in last day of EIS study, the scratched one was degraded completely. But the capsule incorporated coating was stronger in preservation of its primary corrosion resistance, although there was a little decrease in its corrosion behavior, along test days.

In fact this film is found to provide a very high level of protection to the underlying metal in the case of scratched neat coat.

It reveals that Tung oil release from incorporated microcapsules and polymerization phenomenon occurred in contact of the air. It is obvious that the mechanical properties of healed area are not the same as epoxy structure, but creation of a barrier between air and substrate can extend the coating life against corrosive media.

Fig. 6 shows the final images of the samples after ten days immersion. The results of immersion tests also confirmed the EIS investigation outcome. After 20 h of immersion, metal rusting was completely obvious and accelerated next hours, especially at edges of scratches, in neat epoxy coated sample. But capsule embedded coat showed quite different behavior. Even after 180 h, there was not any visible evidence of corrosion on the coating surface.

Two coated samples, neat and capsule incorporated, were scratched and the capsule incorporated panel was given 24 h time to heal itself. The SEM images of scratched areas are shown through Fig. 7. By comparing of below images, it is obvious that the scratch line was healed successfully and corrosion protection of the substrate has been continued by the applied coating.

The results of adhesion test are shown in Table 4. There is no significant difference between the mean values. The results show that the control sample (without microcapsules) had better adhesion than the coatings with microcapsules. Thus, it appears that some coating adhesion will may be sacrificed by addition of microcapsules.
Fig. 6. Immersed samples in 3.5 wt% NaCl solution after 10 days ((a) neat coat and (b) encapsulated coat).

Fig. 7. (a) SEM image of artificial scratch on epoxy coating; (b) SEM image of healed scratch on epoxy coating.

Table 4
Adhesion strength of pull off tests.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Adhesion strength of samples (psi)</th>
<th>Mean adhesion strength (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat epoxy coating</td>
<td>628, 615, 631</td>
<td>625</td>
</tr>
<tr>
<td>Tung oil capsule incorporated epoxy coating</td>
<td>590, 586, 618</td>
<td>598</td>
</tr>
</tbody>
</table>

4. Conclusions

1. The used encapsulation process (in situ polymerization, oil in water emulsion) was successful for Tung oil in PUF shell.
2. Synthesized microcapsules in paint films released healing material, which during scratching healed scratch efficiently with satisfactory anticorrosive properties.
3. Incorporated Tung oil capsules through epoxy structure provided self-healing ability for coating without any catalyst requirement.

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References
