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Fabrication of microcapsules containing dual-functional tung oil and properties suitable for self-healing and self-lubricating coatings

Haiyan Li, Yexiang Cui, Zhike Li, Yanji Zhu, Huaiyuan Wang*

Provincial Key Laboratory of Oil & Gas Chemical Technology, College of Chemistry & Chemical Engineering, Northeast Petroleum University, Daqing 163318, PR China

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ABSTRACT

Tung oil-loaded microcapsules with the protection of Poly(urea-formaldehyde) (PUF) shells were prepared by in-situ polymerization method. Microcapsules keep the spherical shape with core content of more than 80.0 wt%. The average diameter was approximately 105 μm. Microcapsules exhibit excellent thermal stability. Dual-functional coatings were prepared by incorporating tung oil-loaded microcapsules into epoxy. Self-healing and self-lubricating function of coatings were realized by the releasing of tung oil from microcapsules under the scarp or wear condition. Tung oil has excellent film-forming property when they contact with oxygen. self-healing anti-corrosion and self-lubricating anti-wear properties were evaluated by salt-immersed corrosion tests and wear tests. Results demonstrated the coatings have an excellent corrosion resistance performance, the corrosion resistance get better as the increasing of microcapsules content. Besides, epoxy coatings demonstrated a favorable self-lubricating performance with the add of microcapsules. The friction coefficient and wear rate were the lowest at the microcapsules content of 10 wt%, there were 17.3% and 78.6% decrease respectively compared to the pure epoxy. The self-healing and self-lubricating mechanism were also discussed.

1. Introduction

Self-healing and self-lubricating functional coatings have drawn great attention in recent years due to their ability to heal damage automatically and improve the anti-wear properties without the need for external intervention. The self-healing and self-lubricating function of coatings can be achieved by embedding microcapsules. Corrosion protective self-healing coatings based on microcapsules have been investigated intensively. Several self-healing agents, such as dicyclopentadiene (DCPD) [1], epoxy [2,3], tung oil [4,5], linseed oil [6–11], perfluorooctyl triethoxy-silane(POT) [12] isophorone diisocyanate (IPDI) [13–15], hexamethylene diisocyanate (HDI) [16], corrosion inhibitors [17,18], have been microencapsulated successfully and then added into a polymer to prepare self-healing corrosion coatings. When damage occurred in coating surface, the self-healing agent was released from microcapsules and subsequently polymerized in the presence of catalyst, oxygen or H_2O. The cross-linked polymer film was formed automatically to retard corrosion.

Self-lubricating materials based on lubricant-loaded microcapsules has also been reported widely. Several self-lubricating agent, such as paraffin wax [19–22], lubricant oil [23–25], sulfureted fatty [26], and hexamethylene disocyanate (HDI) [27], ionic liquid [28–30] have been microencapsulated and incorporated into polymers to prepared self-lubricating materials. When friction occurred in polymer surface, liquid lubricants from crushed microcapsules are released to the surface. The boundary lubricating film formed and significantly decreased the friction coefficients and wear rates.

It is a new idea to fabricate a dual-function coating with self-healing and self-lubricating functions at the same time. In this study, a dual-function coating was fabricated by incorporating poly(urea-formaldehyde) (PUF) microcapsules containing tung oil into epoxy matrix. Tung oil is a kind of excellent self-healing agent because the excellent film-forming property when they contact with oxygen. Tung oil is water-insoluble, unsaturated glycerides of long chain fatty acids. The main constituent is a glyceride of an elaeostearic acid, a conjugated triene. Reaction with oxygen is the most important reaction in the polymerization process. This highly unsaturated and conjugated system are largely responsible for the rapid polymerization. Oxidation can result in cleavage of the carbon–carbon chain and polymerization. The cross linking of the tung oil's molecules forms solid film which makes the surface waterproof and impermeable to many chemicals. This gives the materials an anti-corrosion function. As tung oil dries and cures, the molecules join together in a tight complex formation, the bonding also gives flexibility to the surface, making it capable of withstanding wear and tear [4]. At the same time, tung oil has excellent thermal stability and similar viscosity compared to lubricant oil, which make it can be

* Corresponding author.
E-mail address: wanghyjiji@163.com (H. Wang).

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used as lubricant. In this paper, tung oil can be considered as self-healing agent and self-lubricant, the tung oil −loaded microcapsules were prepared and characterized. The self-healing and self-lubricating properties of dual-functional epoxy coatings were evaluated by corrosion and tribological test.

2. Experimental

2.1. Materials

Tung oil (410 m Pa s, 25 °C) was obtained from Guangzhou Hanhao Chemical Co. Ltd. Urea, formaldehyde (37 wt% aqueous solution), sodium chloride (NaCl), ethanol and *n*-Octanol were purchased from Tianjin Damao Chemical Reagent Co. Lignosufonic acid (Reax 88A) was bought from MeadWestvaco Corporation. Triethanolamine (TEA) and resorcinol were provided by Macklin. Hydrochloric acid (HCl) was obtained from Beijing Chemical Factory. E-51 epoxy resin (Bisphenol-A) and harder tetraethylenepentamine(TEPA) were provieded by Heilongjiang chemical Engineering Institute Co. Ltd. The water used in the study was deionized water and all chemicals were used as received with no further purification.

2.2. Preparation of tung oil-loaded microcapsules

2.2.1. Preparation of the pre-polymer of urea-formaldehyde (pre-UF)

The pre-UF was synthetized by two-step in-situ polymerization method. 5 g urea was dissolved in 10 g formaldehyde (37 wt%) in a 50 mL beaker with a magnetic stirrer in a temperature-controlled water bath. Keep stirring until the urea completely dissolved, control the pH to 8–9 with TEA, heat up the system temperature to 70 °C for 1 h, after which the pre-UF was obtained and stored for further experiments.

2.2.2. Preparation of tung oil microcapsules

Resorcinol(0.5 g), 10 g tung oil and Reax 88A acting as an emulsion dispersant were added into 60 mL deionized water in a 250 mL three-neck flask. Mechanically emulsified for 20 min at room temperature resulting in a stable O/W emulsion with a Reax 88A concentration of approximately 1 g/L. Then, the 5 g pre-UF mentioned above was added into the mixture at 800 rpm, further stirred about 5 min, dropped *n*-octanol for defoaming the foam generated in the system and adjusted the pH of the emulsion to 2–3 with 1 mol/L HCl. The temperature was raised to 60 °C and further reaction conducted for 2.5 h. After the experiment, the tung oil loaded microcapsules were isolated by filtering and washing alternatively with deionized water and ethanol. Finally dried in a vacuum oven.

2.3. Characterizations of microcapsules

2.3.1. Chemical composition

The chemical composition and functional groups of the PUF, tung oil and prepared-microcapsules were performed by Tensor 27 FTIR in the wavelength range of 4000–450 cm^{-1}. The PUF shells were achieved after that the tung oil was extracted from broken microcapsules with acetone and then washed with distilled water at least 3 times respectively. Finally, filtrated and dried.

2.3.2. Morphology, shell thickness and size distribution

The inner/outer surface, shell thickness and size of the microcapsules were monitored with a scanning electron microscopy (SEM, Zeiss SIGMA). For the mean diameter, at least 200 individuals of microcapsules were measured and calculated from the optical microscope (OM) pictures.

2.3.3. Thermal stability

Thermal gravimetric analysis (TGA, Pyris America) was employed to evaluate the thermal stability of microcapsules and the temperature range from 25 to 600 °C at a heating rate of 10 °C/min under the protection of N_2 atmosphere.

2.3.4. Core fraction and microencapsulation efficiency

The core content of tung oil in the microcapsules was measured using acetone immersion method and could be calculated by $[(W_1\text{-}W_2)/W_1] \times 100\%$. Where W_1 is the weight of microcapsules randomly selected (g), W_2 is the weight of the aforementioned microcapsules' shell (g) which was collected by separating the tung oil from the crushed microcapsules in the way of immersed in acetone. Microencapsulation efficiency was calculated from the weight of the resultant microcapsules (W_m) over the initial weight of all reactants (tung oil and pre-UF), the formula is as follows: microencapsulation efficiency = $[W_m/(W_{tungoil} + W_{pre\text{-}UF})] \times 100\%$.

2.4. Fabrication of dual-functional epoxy coatings

Self-healing anti-corrosion coatings were prepared by incorporating different concentration of microcapsules (5, 10, 15 and 20 wt%) into epoxy resin. Firstly, the synthesized microcapsules were gradually dispersed into E-51 epoxy resin followed by addition of 12 wt% TEA as hardener. Then the mixture was removed to vacuum drying chamber for 15 min at 55 °C for the removal of trapped air. Prior to the preparation of the coatings, the steel panel (80 × 80 × 1 mm) was first polished with a 600 and 1000 mesh sandpapers, ultrasonically washed with deionized water and acetone to remove the dust and grease on its surface. Afterward the epoxy mixture was coated on one side of each dried steel, the thickness was about 300 μm and another side of steel was coated with a wax. The coating was initially cured 3 h at ambient temperature and then 80 °C last for 6 h for the further polymerization. After the coatings were completely cured, an induced crossing scratches were manufactured on the coating using a razor blade. It is worth taking notice of that each notch was deep enough to reach the steel substrate. The scratched coatings were laid aside for a certain period of time for the crosslinking curing reaction of the tung oil which released from the broken microcapsules. Similar process was carried out to prepare microcapsules-free neat epoxy coatings with the same thickness for comparison. Self-lubricating anti-wear coatings were fabricated with the same manner expect for the size of steel is (7 × 8 × 1 mm) and no scratch in the outer surface of coatings.

2.5. Evaluation of dual-functional coatings

Both microcapsules filled and free epoxy coatings were immersed in corrosion medium (10 wt% NaCl solution) for different times to inspect the self-healing anticorrosion performance. The steel panels. A camera for visual inspection was used to record the corrosion state of various microcapsules percentage of coatings in different immersion time. The self-lubricating properties was investigated by friction and wear tests via a pin-on-disc frictional apparatus (MPX-2000, China), details refer to our former research [5]. Besides, the scratched areas and wear surface were observed by SEM.

2.6. Adhesion test

For investigation of the influence of microcapsules on composite coating adhesion, cross-cut tests were carried out according to standard ASTM D3359 2009e2. An X-cut was made through the clean and dry coatings with a razor. One more attention, the scribe length on these panels coatings should be 40 mm long that intersect closing to their middle with the angle between 30° and 45°. And the tape must be pressed and pulled rapidly to remove the coating from the surface within 90 ± 30 s as an angle of 180°.