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Preparation and investigation of hybrid self-healing coatings containing linseed oil loaded nanocapsules, potassium ethyl xanthate and benzotriazole on copper surface

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ABSTRACT

The effectiveness of self-healing epoxy and polyurethane hybrid coatings filled with linseed oil (LO) containing nano-sized capsules, potassium ethyl xanthate and benzotriazole was investigated for self-healing and anti-corrosion performance on the copper metal films. The characteristics of synthesized nanocapsules were studied by fourier-transform infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA), field emission scanning electron microscopy (FESEM) for chemical structure, thermal stability and surface morphology investigations. Furthermore, size distribution of the prepared nanocapsules was investigated using dynamic light scattering (DLS). The anti-corrosion effect of coatings was studied by electrochemical impedance spectroscopy (EIS) and optical microscopy imaging. Taguchi method was used to reduce the number of experiments and anti-corrosion efficiency evaluations. The synthesized nanocapsules have 459–712 nm diameters. LO loading efficiency was almost 60%. Hybrid self-healing coatings which contain self-healing and anti-corrosion agents together showed synergistic effect at optimum levels (3 wt% LO and 5 wt% anti-corrosion agent). Adhesion pull-off test shows that higher amounts of nanocapsules, potassium ethyl xanthate and benzotriazole resulted in weaker adhesion for coatings.

1. Introduction

Copper and copper alloys are extensively used in various structures and materials in electrical and architectural engineering. The destruction of such structures and materials is time consuming and causes enormous economic losses. Corrosion is considered as one of the most important concerns that may lead to these losses [1,2].

There are several ways for protection against corrosion [3], which polymer paints and coatings are among the simplest and in some cases the cheapest methods that provide satisfied protection of the sub layer from corrosion [4]. While it can preserve the substance from corrosion agents, any mechanical damage on the coating during the performance, reduces the coating efficiency and consequently creates weak points on the coating and causes different types of corrosion such as general, pitting, galvanic, flow-assisted corrosion, etc. [5,6] to be started from these sites. In addition, maintenance of organic coating's elegance is another issue that may be desired and affect the cost and performance of coatings, so it has to be considered in designing coatings [7].

To solve such problems, since 1980, self-healing coatings are used to enhance the coating's anti-corrosion efficiency and lifespan by inspiration of biological systems [8]. Such coatings can heal the unobservable micro cracks and increase the lifespan and immunity of polymer components. For this purpose, several methods are used. One of the most efficient methods which provides self-healing properties for applied coating, include the addition of micro/nano sized polymeric capsules loaded with different compounds into the industrial resin based paints [9]. These loaded reagents are usually materials that react with another compound and are able to fill and repair the damaged area upon cracking and rupture of the capsules in the area of cracks causing release of the self-healing agents. Generally, the presence of another compound as catalyst is necessary for completion of healing reaction, but recently some air drying natural oils are utilized as self-healing agents, which do not need any catalyst and form the healing layer only in contact with atmospheric oxygen [10]. Drying natural oils are triglycerides, which are cured by a complicated chain of radical mechanism reactions and consequently, dry the oil. Linseed oil (LO), Tung oil, and rapeseed oil are some of these natural drying oils widely used as healing agents in designing self-healing coatings [11,12].

However, to enhance the performance of coatings, corrosion inhibitors should be used, too. Today, the application of hexavalent

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chromates as traditional inhibitors, have been restricted because of their severe toxicity and carcinogenic activity. Hence, recently, some other heterocyclic organic compounds such as benzotriazole (BTA) are widely used as corrosion inhibitor for copper and copper alloys, which exhibit lower toxicity. Another corrosion inhibitor, which is used as anti-corrosion agent with lower toxicity in comparison to heterocyclic compounds, is potassium ethyl xanthate (KEX) that has a profound anti-corrosion effect on copper due to its good interaction with surface of different metals such as copper [13–15].

In order to design some multi-functional coatings with great healing and anti-corrosion effects, some hybrid anti-corrosion coatings have been designed. Zheng et al. designed organic-inorganic hybrid coatings to achieve better efficiency [16]. They used some entrapped organic inhibitors in nanocontainer added to hybrid coatings to create hybrid anti-corrosion coatings [16]. Akid et al. used some hybrid sol-gel coatings in the presence of encapsulated corrosion inhibitors in order to design multi-functional anti-corrosion coating [17]. Siva et al. utilized mercaptobenzothiazole (MBT) and LO loaded nanocapsules to create a self-healing coating with dual active agents. Nonetheless, corrosion inhibitors can be added directly to the coating without encapsulation [18].

In this research, nano-sized poly(urea-formaldehyde) capsules were synthesized by in-situ polymerization in the presence of LO as a healing agent. Anti-corrosion agents, potassium ethyl xanthate (KEX) and benzotriazole (BTA) were embedded into the coating beside the nano-capsules. The performance of these hybrid coatings was investigated by different tests such as FESEM, electrochemical impedance spectroscopy (EIS) and adhesion strength test. For experimental design, Taguchi design of experiment (DOE) was used [19]. Taguchi is a statistical method developed by Genichi Taguchi [19] that is used to enhance the quality of products and can be applied to different fields such as engineering, marketing, etc. Taguchi design of experiment reduces the number of possible experiments, thus there will a reduction in the cost and time of experiment [20]. Beside the advantage of experimental designing with Taguchi method, the obtained results from any test can be analyzed with Taguchi. In this respect, S/N fraction is calculated and was used for determination of desired outcome such as larger is better, smaller is better, nominal is best and etc. Furthermore, calculated S/N for each factor in each level was applied to compute the difference between the largest and smallest fraction and was called Delta and thus, the largest amount of Delta (rank 1) is considered as the most effective factor among all studied factors.

2. Materials and methods

2.1. Materials

Urea, formaldehyde, ammonium chloride, resorcinol, sodium dodecyl sulfate (SDS), xylene, octanol, hydrochloric acid, benzotriazole and ammonium chloride were all purchased in high purity from Merck. For synthesis of potassium ethyl xanthate, ethanol, carbon disulfide, diethyl ether and potassium hydroxide were purchased from Sigma-Aldrich. Epoxy resin (Epikote8, epoxy equivalent = 183–189 g/equiv) and related hardener (EpiqureF205, cycloaliphatic polyamine with H^+ active equivalent = 115 g/equiv), polyurethane and its hardener (Bajatan, code: 55210) were obtained from Bajak paint and resin Co. Industrial sample of LO was prepared from the local market and was used as received.

2.2. Encapsulation process

Among various methods available for synthesizing microcapsules [21], in the current research, capsules were prepared by an in situ polymerization process, which was inspired by the works of Suryanarayana et al. [8] and Brown et al. [22]. First, 130 ml of distilled water and 5 ml of 5 wt.% aqueous solution of sodium dodecyl sulfate (SDS) were mixed at room temperature. To this solution, 2.5 g urea, 0.25 g ammonium chloride and 0.25 g resorcinol were added and stirred at 400 rpm with mechanical mixer to obtain a clear solution. Then the pH of this solution was adjusted to 3 with 1 M hydrochloric acid aqueous solution and 30 ml of LO was added slowly under stirring to form stable emulsion. Before adding second monomer to start polymerization, and to obtain nano-sized capsules, ultrasonic hielscher UP100H probe was used at amplitude of 100% for 120 s to break LO drops to smaller sizes. After using ultrasonic probe, stirring rate was increased to 600 rpm and 6 ml of 37 wt.% formaldehyde solution was added to the mixture. Temperature was increased to 55 °C and the mixture was stirred for 5 h. Then the mixture was cooled to ambient temperature. Obtained nanocapsules (white powder) were centrifuged and separated from solution and washed and rinsed 3 times with distilled water. Finally, nanocapsules were washed several times with xylene to remove the suspended LO and then were dried under vacuum at 40 °C for 2 days.

2.3. Potassium ethyl xanthate synthesis

To synthesize potassium ethyl xanthate (KEX), 2.5 g of KOH was dissolved in 20 ml of ethanol to obtain a clear solution, 10 ml of carbon disulfide was added to the solution and was kept under stirring at room temperature for 12 h to complete the reaction. Yellow product was rinsed by diethyl ether and was dried at 40 °C for 1 day [14].

2.4. Soxhlet extraction and infrared spectroscopy

The separation of core and shell materials of the synthesized nanocapsules was carried out by soxhlet extraction. 0.5 g of the nanocapsules (W_c) was crushed using pestle and mortar and transferred to a thimble. Weight of thimble (W_{ti}) was recorded. Extraction was carried out using xylene as a solvent for LO. After 3 h of extraction at an approximate temperature of 145 °C, the thimble was carefully taken out and after completely draining the solvent; it was dried at 40 °C in an oven for 24 h and the weight of thimble was recorded again (W_{fi}).

To identify the separated core and shell, their spectra were recorded by Fourier transform infrared (FTIR) spectrophotometer. In addition, the percentage of encapsulated LO was calculated by the following equation. The structure of KEX was also characterized by FTIR.

$$\text{Weight of linseed oil } (\%) = \frac{(W_c + W_{ti}) - W_{fi}}{W_c} \times 100 \tag{1}$$

In this equation W_c, W_{ti} and W_{fi} were related to weight of nanocapsule, weight of thimble after extraction and drying respectively.

2.5. FESEM, TGA, DLS and optical microscopy analysis

Surface morphology, shape and size of the synthesized nanocapsules were investigated by Field Emission Scanning Electron Microscopy (FESEM). Moreover, healing of the cracks in the place of intentionally created scratches were studied by FESEM either.

To analyze the thermal stability of the synthesized nanocapsules, thermal gravimetric analysis (TGA) was used. Core-shell structure of capsules can be confirmed by TGA, too.

To investigate the size distribution of prepared capsules, Dynamic Light Scattering (DLS) analysis was utilized.

Healing process and crack filling of the cross-cut coatings were investigated by optical microscope. Samples were studied during 30 days and the data were collected on 1st, 7th, 14th and 30th days.

2.6. Taguchi design of experiment (DOE)

For designing different experiments and in order to evaluate the efficiency of various hybrid coatings, mixed 2–4 level design was used. In this respect, variable factors that were considered are: weight