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Encapsulation of linseed oil and linseed oil based alkyd resin by urea formaldehyde shell for self-healing systems

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ABSTRACT

In the present study, linseed oil based alkyd resin and linseed oil have been encapsulated to propose the alkyd resin as a prospective material for being used in epoxy coating system for corrosion protection through self-healing.

The superiority of the present systems as Linseed oil and its alkyd resin evolves from the utilization of the environmentally friendliness thanks to their film formation by auto-oxidation. The encapsulation of healing agents by means of *in-situ* polymerization of urea formaldehyde has been studied with the parameters as the amount of surfactant and the rate of stirring. The experimental design has been modeled by using Response Surface Method to investigate the effect of surfactant (poly(vinyl alcohol), PVA) amount and stirring rate effect on the microcapsules (MC) size. Optical microscopy has been utilized to follow the reaction and size change of MCs. The chemical structure, thermal properties and capsule morphology has been illuminated by using FTIR spectroscopy, TGA and SEM analysis, respectively. The capsules obtained have had 51 and 56 μm diameter at high levels of the parameters (60 ml PVA, 1500 rpm stirring rate) and 97 and 261 μm diameter at low levels of the parameters (20 ml PVA, 800 rpm stirring rate) for LO and LO-Alkyd respectively.

1. Introduction

Corrosion is one of the important technological problems faced by all the industries such as manufacturing, chemical industries, automotive industries. Coating systems are applied to the metal surfaces as a barrier to protect corrosion which is the cheapest method, however the coating losses its protective behavior in the course of time [1].

A novel approach to the solution of the damaged coating problem is making use of capsule based self-healing (SH) systems through which the growing of crack is healed and thus the protection life of coating is improved [2]. Capsule based SH systems are obtained by addition of the capsules, having healing agent inside, through the coating material. Under damage of coating the capsules are ruptured and the healing agent inside diffuses with the capillary mechanism to fill the crack. The released healing agent repairs the crack *via* polymerization and forming a film on the surface in the presence of catalyst particles, formerly distributed through the polymer matrices or *via* oxidation upon contact with atmospheric oxygen [3–6].

The chemical, mechanical, thermal and morphological properties of capsules determine the success of the healing process. Poly (urea-formaldehyde) (PUF) is widely used as a microcapsule wall material since it gives good performances of seal, flexibility, penetration resistance, high-strength and impermeability [7]. The healing agent is encapsulated generally by *in situ* polymerization of urea and formaldehyde. This method which is free of solvent has a simple procedure, low costs and ease of industrialization when compared to the other encapsulation techniques. Another advantage of this method is the controllable size and shell thickness of the microcapsule [6].

The encapsulation process proceeds as the urea and formaldehyde react in water phase and form colloidal cross-linked particles, which deposit at the emulsified healing agent droplets. Thereby, the healing agent is covered by urea-formaldehyde (UF) shell wall [8].

Generally the microcapsule (MC) containing dicyclopentadiene (DCPD) agent is used in literature to prevent corrosion. However, the healing ability of DCPD is limited because of the necessity of catalyst that should be dispersed in the matrix [9]. Drying oils can be used instead of the catalyst involving systems to avoid corrosion, in green chemistry thanks to their auto-oxidation through the oxidation of unsaturated bonds [10].

They have the capacity to form a continuous film with good optical and mechanical properties after being spread out in a thin layer and cure in air without using a catalyst [11]. However, there are only a few studies using drying oils in anti-corrosion coatings [4,8,10–18].

Alkyd resins are preferred in paint industry as coating material

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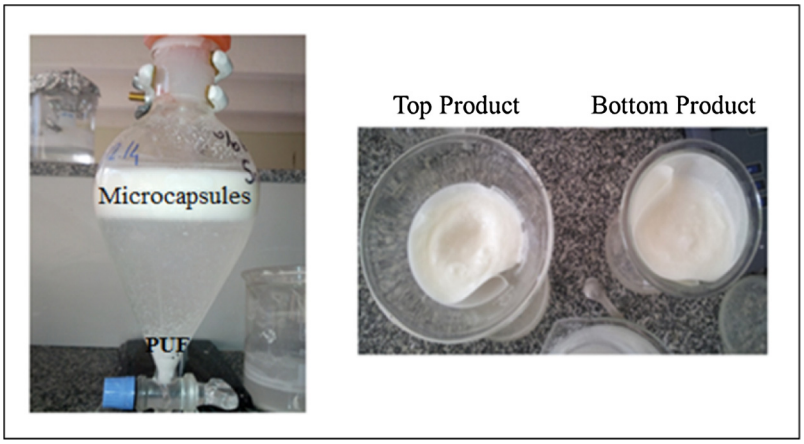

Fig. 1. Phase separation and filtering of the microcapsules.

because of their good corrosion protection and good adhesion properties [19]. The carboxyl and hydroxyl functional groups in alkyd resins react with epoxy functional groups which can act as healing process in the epoxy matrix [20]. By inspiring this behavior palm oil [21] and coconut oil [22] based alkyds were studied as healing agents. However the palm oil and coconut oil do not undergo auto-oxidation because of their low unsaturated fatty acid composition (2.6 and 8.0% by mass, respectively), healing occurs only when epoxy and alkyd reacts [21,22].

Most widely used drying oils for the production of air drying alkyds are linseed oil, soybean oil, tung oil, safflower oil and *etc*. [23]. Alkyds containing drying oils easily form a non-tacky film as they have high molecular weight and their curing takes place without catalyst in a short time by oxidative polymerization to produce film [24].

Linseed oil alkyd (LO-Alkyd) dries by auto-oxidation thanks to its high (52 wt.%) linolenic acid content in LO fatty acid composition [25]. Besides, the reaction between alkyd functional groups and epoxies which occurs similar to that in palm and coconut oil based alkyds [20] expected to improve the healing behavior as compared to LO. In addition, LO-Alkyds offer good adhesion properties [19] and thus it is most likely that they would provide longer protection of the coating as compared to the present ones.

In the present study Linseed oil (LO) and as a new type of healing agent LO-Alkyd have been encapsulated employing parameters as surfactant (poly(vinyl alcohol), PVA) amount and stirring rate to compare with each other in terms of their MC properties such as capsule size, thermal stability, and morphology.

2. Materials and methods

2.1. Materials

Urea (99.5 wt.%) and formaldehyde (37 wt.% aq.) which are the main shell components and resorcinol (99 wt.%) which is used as the cross-linker are products of Merck KgaA (Germany) while ammonium chloride (99.8 wt.%)) which is used as hardener is a product of Horasan Chemical Co (Turkey). LO was kindly supplied by Kanat Paints and Coatings Co (Turkey). LO-alkyd resin was kindly supplied by DYO Paints Manufacturing and Trading Co (Turkey). Polyvinyl alcohol (PVA, Mowiol-10, 60,000 g/mole) is a product of Sigma Aldrich (Germany).

2.2. Encapsulation of healing agent

Microencapsulation of the healing agent in urea-formaldehyde was carried out by using *in situ* polymerization in a glass vessel particularly sealed by using a Teflon lid and jacketed for water circulation to maintain the temperature.

2.2.1. Preparation of reaction medium

Firstly, 260 ml of deionized water and surfactant (PVA: 20–60 ml) were mixed in 500 ml reaction vessel under stirring at 800–1500 rpm for 10 min to homogenize the system (t = 0 min) meanwhile the reaction temperature is maintained at 55 °C. Thereafter, at about fifteenth minute, urea, resorcinol and ammonium chloride were added into the reactor 7.5 g, 0.75 g, and 0.75 g respectively. The molar ratio of Resorcinol to NH_4Cl was 0.007/0.0009 per one mol of urea.

After the reactants are dispersed homogeneously in the solution, the 25 ml of healing agent (LO or LO-alkyd) was injected into the reactor.

2.2.2. Commencement of reaction

Incorporation of formaldehyde (14 ml; 0.15 mol per mole urea) was performed at about 30th minute of HA addition as the homogeneous reaction medium is maintained. The Optical Microscope (OM, Nikon 150 LV) pictures were taken just before the formaldehyde addition and after that, at every 30 min throughout the reaction which takes about 4 h, to follow the progress of microcapsule-formation. The pH of the medium was in the vicinity of 3.0 ± 0.5 throughout the reaction.

2.2.3. Separation of capsules from the bulk

after making sure the completion of reaction (t = 300 min), the content of the reactor was put into a separation funnel to rest about 20 h. Following a phase separation having a visible bottom and top products, each product was separately filtered. Each product was washed on filter paper about eight times with deionized water (Fig. 1) to remove residual resin and surfactant prior to drying at the ambient conditions about one week. The encapsulation process steps are given in Fig. 2.

2.3. Design of experiments

Response Surface Model (RSM) was used to investigate the effect of PVA amount (X_1) and stirring rate (X_2) on microcapsule size (Fig. 3).

The experiments were planned using a composite central design (CCD) and the program “Minitab 17”, which is a statistical program, has been used. The experimental designs were created with 2^2 factorial design and faced center ($\alpha = 1$), and the repeatability was increased with five center points. The low and high levels of parameters were determined as X_1:20–60 ml for PVA amount and X_2:800–1500 rpm stirring rate, respectively. The experimental points are given in Table 1. The experimental code of the capsules is given as “Healing agent type-PVA amount/Stirring rate”. For example LO-30/1500 indicates linseed oil encapsulated by using 30 ml amount of PVA at 1500 rpm.