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Self healing coatings containing dual active agent loaded urea formaldehyde (UF) microcapsules

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ABSTRACT

Urea formaldehyde (UF) microcapsules loaded with linseed oil and mercaptobenzothiazole (MBT) as core materials have been synthesized by in situ emulsion polymerization. The capsules were characterized by FTIR. Surface morphology of microcapsules was analyzed using scanning electron microscope. The thermal stability of the microcapsules is in the temperature range around 600 °C as confirmed by TG analysis. The open circuit potential measurements have shown that the coatings with microcapsules maintain the potential in the noble range (≈−0.390 V vs. SCE) while the coating without microcapsules exhibit potentials in the active range. EIS studies at the artificial defect area have shown that the coating containing microcapsules is able to protect steel in neutral media since the impedance values remained at $10^7\ \Omega\,cm^2$ even after 15 days exposure where as the coatings without microcapsules have lost their protection ability. The self healing ability of the coating containing microcapsules was studied by SVET.

1. Introduction

Anticorrosive coatings are always in the high risk of being damaged at micro-level during service period. Such damages are hard to detect and the corrosion process due to small anode–large cathode configuration gets initiated and spreads. The concept of self healing in protective coatings is developing very fast in the last decade due to the strong industrial demand [1–3]. One of the main strategies is the incorporation of inhibitor compounds directly into the polymer, hybrid or inorganic layers [4,5]. Even though hexavalent chromates are successful in this regard, their usage is restricted due to the high toxicity. While exploring the new environmentally friendly alternative inhibitors, greater attention was paid to the organic heterocyclic compounds like thiazole derivatives [6,7]. The mechanism of action of such inhibitors is not fully understood; however, the adsorption properties are expected to explain their anticorrosion effect [8,9]. The 2-mercaptobenzothiazole (MBT) is the most widely used corrosion inhibitors for metals [10].

Modern technology demands the usage of multifunctional additives for improved performance of organic coatings. This includes use of smart reservoirs [11], microcapsules [12], graphene [13–15], functional polymers [16], etc. In recent years many self healing chemistries and material systems have been developed to address this issue [17–22]. However, with the concern of compromised system integrity after introducing healing agent carriers in matrix materials, self healing concepts have attracted more interests in the corrosion resistant coating applications where mechanical strength is not a major concern [23–30]. Self healing concept was successfully proved to autonomously repair microcracks in the epoxy resin with incorporation of dicyclopentadiene microcapsules and Grubbs' catalyst particles [31].

The microcapsules are tiny particles with diameters in the range of nanometers to micrometer consisting of core materials and covering shell [32]. Microcapsules can encapsulate various substances including gases, liquids, solids, etc. Encapsulating shell material can also be selected from a wide variety of natural or synthetic polymers depending on the desired characteristics of the microcapsules. By tuning the composition of core materials, it is possible to endow microcapsules with a variety of functions. Recently the microencapsulation technology exhibited significant promise by providing "smart" functionality for applications such as self healing composites [33]. Urea formaldehyde (UF), a rigid and slowly degradable polymer which can be prepared by in situ polymerization in aqueous solutions is an appropriate shell material [34]. Linseed oil is one of the most widely used drying oils in paints formulation. Drying oils are natural triglycerides containing high percentage of polyunsaturated fatty acids with air-drying property. These polyunsaturated fatty acids readily oxidize to form a three-dimensional network [35,36].

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In this paper, we have reported the synthesis of urea formaldehyde microcapsules loaded with linseed oil and MBT (mercaptobenzothiazole) [LO/MBT] and self healing behavior of this microcapsules containing epoxy coating. Our interest is devoted for a better understanding of the reaction parameters that influence the micro-encapsulability of the core material. The UF wall material was opted as it avoids leakage and diffusion of the encapsulated active agent for a prolonged time. In order to evaluate the relation between the experimental conditions and the encapsulation yield, a set of urea formaldehyde microcapsules containing an LO/MBT was prepared in which reaction time, temperature and stirring speed were modulated. Scanning electron microscopy (SEM) was used to investigate the microcapsule size and surface morphology. Optical microscopic observation and scanning vibrating electrode technique (SVET) were used to evaluate the self healing properties of microcapsules containing coating.

2. Experimental

2.1. Materials

Linseed oil was purchased from Hindustan Produce Company, Kolkata, and mercaptobenzothiazole (MBT) was purchased from Sigma Aldrich Chemicals, Mumbai. Urea and formaldehyde aqueous solutions, acting as shell forming monomers, were obtained from TCI Chemical Reagent Co. Ltd., Mumbai. Ammonium chloride (NH_4Cl), and resorcinol used to maintain the pH (base condition) were purchased from Fisher Scientific Chemicals, Mumbai. Dodecylbenzenesulphonic acid (DBSA) purchased from Sigma Aldrich Chemicals, Mumbai was used as an emulsifier. Hydrochloric acid (HCl) purchased from Merck; Mumbai, was used to control the pH of solution (acid condition). Commercial grade epoxy resin 6071 (CibaGeigy India Ltd.), polyamide hardener (Synpol-125), Methyl isobutyl ketone (MIBK), xylene and acetone were used without further purification. All solutions were prepared using Millipore double distilled water having resistivity 18.2 MΩ cm.

2.2. Preparation of microcapsules

Microencapsulation is a technique through which liquid materials either aqueous or non-aqueous in nature is encapsulated with in solid shell. The nature of shell wall materials is a function of the material to be encapsulated, the coating application process. Microcapsules were prepared by in situ polymerization in oil/water emulsion. In a typical procedure, 10 mL DBSA dissolved in 250 mL water was taken in a three neck round bottom flask and agitated for 20 min using a high speed homogenizer at 1200 rpm. 5 g of urea, 0.5 g of ammonium chloride and 0.5 g of resorcinol were mixed thoroughly using a magnetic stirrer at room temperature. After the urea was completely dissolved, the pH of the solution was adjusted to 8–9 with 1.0 M NaOH and the temperature was kept at 50–55 °C for 30 min. A slow stream of prepared mixture (5:1) of LO (25 g)/MBT (5 g) was added to form an emulsion and allowed to stabilize for 10 min. After stabilization, the pH of the emulsion was adjusted to 2–3.5 by the slow addition of hydrochloric acid. 12.76 mL aqueous solution of formaldehyde (1.7 M) was then added to the emulsion while heating the solution at a rate of 1 °C min^{-1} to the target temperature of 50–55 °C. The reaction was completed after 3 h. The synthesized microcapsule suspension was cooled down to ambient temperature, rinsed with deionized water, filtered and air dried for 24 h. For characterization purposes, the UF linear polymer was synthesized as per the procedure reported above since the hollow UF capsules cannot be synthesized without the core content.

2.3. Determination of core content by using Soxhlet method

The core content within the microcapsules was determined by acetone extraction. The microcapsules were dried at room temperature. Pre-weighed quantity (W_0) of dried microcapsules were sealed in a filter paper bag. The sample bag was placed in a Soxhlet apparatus after taking weight (W_1), extracted with acetone for 9 h, and finally dried in a vacuum oven at 70 °C. After cooling in a vacuum desiccator, the sample bag was weighed again (W_2). Eventually, the core content (A) of the microcapsules was calculated by following equation [37,38].

$$A\ (\%) = \frac{W_1 - W_2}{W_0} \times 100 \quad (1)$$

2.4. Characterization of active components loaded urea formaldehyde microcapsules

2.4.1. FTIR spectroscopy

The FTIR spectra of LO/MBT loaded UF microcapsules and UF microcapsules containing epoxy coating was recorded using Nicolet 380 (Thermo, USA) FTIR instrument having ATR attachment. The self healing process by the release of core materials was confirmed by recording the FTIR at the scratched area using a Nicolet Centraurus FTIR Microscope.

2.4.2. Particle size analysis

Particle size measurements were carried out using a Nanotrac photon correlation spectrophotometer by a dynamic light scattering method. Pure deionized water was taken in a square cuvette at the center of the goniometer. It was immersed in a vat counting refractive index matching fluid to minimize the flare at the cell wall; the fluid also acts as a thermostat. The data plotted as distribution number vs. the size was automatically measured by the software to calculate the mean size and size distributions of the microcapsules.

2.4.3. TG analysis

The Thermal gravimetric analysis of UF microcapsules was carried out using the Thermal Analyzer STA (Polymer Laboratory, Thermal Science Ltd.).

2.4.4. Morphology studies

The morphology of urea formaldehyde microcapsule was analyzed using Tescan (model vega3 SB-Easyprobe) scanning electron microscope.

2.5. Formulation and application of UF microcapsules containing paint

The epoxy resin (6071; Ciba Geigy) solution was prepared by dissolving solid epoxy having epoxy equivalent weight 450–500 in xylene. The UF microcapsules (3.54 g) were completely dispersed in the resin using attritor at 45 °C. The UF microcapsules containing epoxy resin solution was cured by polyamide (Sympol 115) having amine value 210–230 mg KOH/g (by $HClO_4$ method). The ratio of resin to hardner is 3:1. The paint was prepared in such a way that it had 30% volume solids and 10% UFLO/MBT microcapsules volume concentration. The UF microcapsules containing paint was applied by brush on mild steel. Before application of this coating, the steel surfaces (150 mm × 100 mm × 2 mm) were sand blasted to Sa 2.5. The coatings were evaluated after 10 days of curing at room temperature. The thickness of the coating was measured using a coating