Progress in Organic Coatings 114 (2018) 40–46

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Single microcapsules containing epoxy healing agent used for development in the fabrication of cost efficient self-healing epoxy coating

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ARTICLE INFO

Keywords:
Self-healing
Encapsulation
in situ polymerization
Epoxy resin
Poly (urea-formaldehyde)
Polyaminoamide

ABSTRACT

In this study, to reduce the size significantly, a number of microcapsules were prepared to apply in situ encapsulation method with poly(urea-formaldehyde) (PUF) as the shell material and epoxy resin (EPL 1012^{R}) as the core substance. Upon that, a systematic investigation was done on the properties of microcapsules affected by the synthesis procedure. In their optimum state, the synthesis parameters were concluded to exhibit the following properties: viscosity of oil phase of 15–25 (mPa.s), initial pH = 4, emulsifier of sodium dodecyl benzene sulfonate (SDBS) and 0.5 (wt.%) content for the emulsifier. Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and Thermogravimetric Analysis (TGA) were applied to study morphology, chemical structure, mean size, size distribution and thermal properties of the resulting microcapsules. The morphological study showed the microcapsules prepared by SDBS (0.5 wt.%) are of spherical nature with few adhesions and the average diameter 2.13 (μm) for encapsulation of epoxy resin. The yield and core content for those microcapsules were determined 50 (wt.%) and 54 (wt.%), respectively. Investigating the microcapsules' chemical structure revealed successful encapsulation of the epoxy resin in PUF shell and the results were confirmed by thermal analysis. Self-healing performance of the coatings containing epoxy-microcapsule was evaluated by salt fog corrosion test by ASTM B117 and eventually showed excellent corrosion resistance in scratched coatings confirming self-healing properties. Furthermore, electrochemical tests were employed for quantitative investigations of self-healing performance of the coating which confirmed the salt fog corrosion results.

1. Introduction

The fast-paced subject of self-healing encompasses a variety of polymers namely; polymer coatings and polymer composites [1–3]. As of today, scientists have developed such life-long materials according to the patterns they discovered in nature to have a solution for unpredictable damages that are likely to happen during their utilization. It is the embedment of micro/nanocapsule based systems, as well as micro/nanofiber based systems containing healing agents, that helps self-healing materials exude the healing agent in composites and coatings to create this characteristic in them [4,5]. The equal distribution of micro/nanocapsules while trapping the healing agent in the matrix, helps to avoid unfavorable reaction between the matrix and the reactive elements may result in unpredictable leakage [6].

Epoxy resins have the potential to react with various hardeners and curing agents at a different temperature. Subsequently, they are categorized as one of the most important healing agents [7]. Consequently, a large number of studies have been conducted lately aiming to utilize epoxy resins to improve self-healing polymers [8–10]. As a result, the microencapsulation of epoxy resins has increasingly attracted researchers' interest because of superior compatibility between the healing agent and the epoxy based polymeric matrix [11,12].

The healing system efficiency highly depends on design and microcapsule synthesis. For materials to be self-healing, the encapsulated healing agents should have the right size, strength and maximum bonding to the host matrix. Moreover, encapsulation strategies affect shell thickness and the mean particle size which the capsules release properties depend on [13]. It is essential to precisely control the process of encapsulation to ensure the desirable performance by the creation of proper features in them. Invariably, choosing the most optimum experimental conditions is crucial [14,15].

Casco et al. [16] studied the elements affecting urea- formaldehyde/ epoxy resin microencapsulation process. The results indicated that reducing reaction temperatures and the stirring rate highly affected

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http://dx.doi.org/10.1016/j.porgcoat.2017.09.019
Received 12 February 2017; Received in revised form 2 September 2017; Accepted 29 September 2017

encapsulation yield. Yuan et al. [17], investigated the effect of shell wall thickness on microcapsules with epoxy and found out that any increase in shell wall thickness and surface smoothness would lead to thermal stability improvement. Additionally, Ting et al. [18] investigated the effect of emulsifying time of core materials, the content of emulsifier and solid content in the form of the final product and the microencapsulation process. Blaiszik et al. [19] succeeded in producing epoxy resin-solvent/urea-formaldehyde with 10–300 μm diameters by adjusting the rate of agitation. These capsules consisted of a thin shell wall (160 nm) and a rough outer shell wall, which adhered better and easier to an epoxy matrix in self-healing polymers.

Moreover, Nesterova et al., [20] attempted to define a robust method to form stable microcapsules through four in situ microencapsulation procedures of epoxy/urea-formaldehyde. Their findings indicated that microcapsule production was tremendously affected by experimental conditions considering the urea-formaldehyde as the shell material. What is more, the encapsulation of viscous liquids was challenging in all the approaches. The emulsification of the resin in the aqueous stage (timing of emulsification, mode and the rate of stirring) was investigated by Ollier et al. [21] to find out that these components determined the quality, form, and size of the resulting capsules and the yield of encapsulation. The results revealed that the encapsulation was possible merely for the diluted blends of epoxy resin with 20% of reactive dilution.

Nevertheless, standard emulsion encapsulation techniques could yield lower limit of almost 10 μm diameter of capsule [22]. Submicron and nano PUF capsules filled with DCPD were produced using a mixture of in situ encapsulation and ultra-sonication technique [23]. This technique was established to produce nanocapsules with smooth outer surface and thin shell walls. Zhao et al. [24] presented a universal technique to produce nanocapsules from polymers such as poly (vinyl acetate) (PVAc), poly (L-lactide) (PLLA), poly (vinyl formal) (PVF), poly (methyl methacrylate) (PMMA), and poly (vinyl cinnamate) (PVCi) using a combination of mini-emulsion and solvent evaporation techniques.

It is not possible for large scale microcapsules to exist all over the matrix and in coatings; they are larger than coatings' thickness. Also, nano scale capsules do not have enough core materials [23]. As a consequence, in the present study, sub-microcapsules with epoxy resin were produced with significantly size reduction through a combination of ultra-sonication and in situ encapsulation techniques.

So far, two different epoxy-based methodologies are investigated both of which use epoxy resin as the only reactive healing agent. In some cases, catalysts, solvents, and heating are required to increase the efficiency of the self-healing system. The results obtained from both systems were favorable. The non-autonomous self-healing system functioned by melting particles of epoxy [25,26] or thermoplastic additives [27–31]. For an efficient self-healing, a single-part UV-curing epoxy was used in a flexible sensor skin [32]. Nonetheless, in the current study, the self-healing process was carried out at room temperature without adding any catalysts or solvents, while the healing process happened simultaneously between the polyaminoamide as a matrix's hardener and the epoxy-based healing agent. Fig. 1 schematically shows the reaction between the released epoxy resin (from ruptures capsules) and unreacted aminoaimdes group present in the coatings. Furthermore, using single microcapsules containing low viscosity epoxy resin, led to fabricating a cost efficient self-healing coating which would be desirable for industrial applications.

2. Experimental

2.1. Materials

Low viscosity epoxy resin (EPL 1012^{R}) was employed as the healing agent. Diglycidyl ether of 1.6-hexanediol (Inchem ed 180^{R}) with a viscosity of 15–25 (mPa.s) was obtained from Hexion and used as a reactive dilute (RDL) to decrease the viscosity of core material. The three components of the epoxy system, ED180^{R} from Inchem ltd and EPON 828^{R} from Hexion and its polyaminoamide based curing agent, Merginamide A280^{R} from Hobum oleochemicals, were employed as matrix substances and used without further purification. Urea and formaldehyde (37 wt.%) were obtained from Kimia Parse Chemical, Iran and were used as shell material of capsules. Resorcinol as a cross linking agent was provided from Merck Co. Also, Sodium dodecyl sulfate (SDS) and Sodium dodecyl benzene sulfate (SDBS), as the anionic surfactants, were purchased from Dae-Jung Co. Approximately 10 wt.% hydrochloric solution was prepared to control the pH value of emulsion. To optimize and evaluate the effect of the preparing conditions on the yield, core content, and average diameter of microcapsules, four syntheses' parameters (i.e., the viscosity of oil phase (with or without reactive dilute), initial pH, type and content of emulsifier) were investigated which summarized in Table 1.

2.2. Preparation of epoxy-containing microcapsules

Core-shell microcapsules containing healing agent were prepared via in situ encapsulation process of Blaiszik et al. [23] in oil in water emulsion. Urea, Resorcinol, and emulsifier were dissolved in water to make a continuous phase. At that point, the oil phase comprising of reactive dilute and epoxy resin was added to the reactor. After adjusting the aqueous phase pH value to 3–4 with HCl aqueous solution, an emulsion was made using a mechanical stirrer at the stirring speed of 300 rpm. After that, a tapered 3.2 mm tip sonication horn of a 750 W ultrasonic homogenizer (Cole–Parmer) was applied in the solution for 3 min at 40% intensity (3.0 kJ of input energy) with continuous mixing at 300 rpm. The emulsion changed from almost cloudy to opaque white. The addition of formaldehyde (37 wt.%) (Keeping the molar ratio between urea and formaldehyde at 2:1) started the polycondensation reaction. Along with that, the reaction continued for 4 h while the temperature was increased to 55° C. In the end, the suspension was cooled to room temperature and washed with deionized water for several times, and ultimately it was air-dried and filtered for 24 h.

2.3. Preparation of self-healing anti-corrosion coating

The prepared microcapsules were initially mixed into the diluted epoxy resin (EPON 828^{R} mixed with ED180^{R} in 3:1 ratio) to 10 wt.% at ambient temperature, followed by addition of modified polyaminoamide adduct (Merginamide A280^{R}) as hardener at mixing ratio of 100:58 wt.%. Several pieces of steel panel (150 × 100 × 1 mm^{3}) were polished with sand paper and, then degreased with acetone, and finally washed with distilled water. Afterwards, each dried panel was coated with the self-healing coating to a final thickness of 300 μm with a universal film applicator (ZEHTNER ZAU 2000.80). The coating was cured at room temperature for 7 days. After 7days, scratched was applied manually on the coating by an Elcometer DIN 1538 scratching tool with 0.5 mm cutter for salt spray tests. It should be mentioned, the capsule incorporated coating sample was kept in the air (~25° C) for 24 h, after cross-cutting. In fact, the sample was allowed to do its probable healing process. Control coating with pure epoxy was prepared with the same procedure. Both the self-healing and control samples were placed in salt spray chamber (Pars Horm Co-ASTM B117) for 48 h to evaluate their corrosion performance.

To investigate quantitatively self-healing ability of the coatings, electrochemical tests were employed for both control coating and the coating containing 10 wt.% of the capsules. In the electrochemical tests, the coated steel panels were used as one electrode in the electrochemical cell. The steady-state conductions between the coated steel panels and a platinum electrode were determined meanwhile the electrical potential, between the electrodes, held at 7 V through in the 1 M NaCl aqueous electrolyte. It should be mentioned that the panels were maintained in 1 M NaCl aqueous electrolyte for 1 week before