



Nanoferrite dispersed waterborne epoxy-acrylate: Anticorrosive nanocomposite coatings



Obaid ur Rahman, Mohd Kashif, Sharif Ahmad*

Materials Research Laboratory, Department of Chemistry, Jamia Millia Islamia, New Delhi 110025, India

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ABSTRACT

Waterborne epoxy acrylate-butylated melamine formaldehyde (EpAc-BMF) coatings and ferrite (Fe_3O_4) dispersed nanocomposite (EpAc-BMF- Fe_3O_4) coatings have been developed with a view to effectively replace the hazardous solvent borne polymeric coatings. The physico-mechanical properties of these coatings were studied using standard protocols. Electrochemical measurements were made in 3.5 wt% solutions of NaOH, NaCl and HCl as well as in tap water (Cl^- ion 63 mg/L; Conductivity 0.953 mS/m). The salt spray test on coated and uncoated MS was carried out in 5 wt% NaCl solution for 600 h. Fe_3O_4 nanoparticles in matrix act as filler, which fill the pinhole, interstitial crosslinked spaces and other coating artifacts (micro cracks and voids) regions besides provide strength to the coating material. Electrochemical studies revealed that EpAc-BMF- Fe_3O_4 coatings were found to be effective in restricting the penetration of aggressive ions by forming a strong barrier layer at coating metal interface. Among various compositions of EpAc-BMF- Fe_3O_4 coatings, EpAc-BMF- Fe_3O_4 -2.5 coatings have shown highest corrosion protection efficiency in different corrosive media.

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1. Introduction

Corrosion is a phenomenon, occurring through the interaction of materials with their surroundings *via* electrochemical reactions, responsible for the catastrophic damages of infrastructures of oil industries, devices and other establishments [1]. It is considered as a major cause for the huge loss of energy and economy at national and international level [2]. The application of paints and coatings is one of the most convenient and promising methods used to combat corrosion. Volatile organic compounds (VOCs) in polymeric coatings cause health hazards and toxicity problems [3]. To overcome such problems many acts and regulations have been imposed on paints and coatings industries [4,5], ensuring the use of eco-friendly materials, like vegetable oil based polymeric coatings [6], waterborne polymer coatings [7] and UV curable coatings [8]. Waterborne polymer coatings can be applied as a potential alternative for VOC producing solvent borne polymer coatings [9]. Waterborne polymers show other useful characteristics over conventional solvent borne polymers like eco-friendliness, low viscosity, easy cleaning, non-toxicity and good applicability [10,11].

Among various polymers, epoxies show excellent chemical resistance, good electrochemical insulation and strong adhesion under stringent corrosive environments [12]. The epoxy coatings provide protection by acting as a physical barrier layer to control the ingress of deleterious species as well as a reservoir for the corrosion protection against the surface of metals and alloys by resisting the attack of aggressive species [13,14]. In spite of these advantages, epoxies are associated with some drawbacks too. It includes reduction in overall resin modulus [12], poor inherent brittleness responsible for low impact resistance, poor UV resistance and *palling* effect [15], all these drawbacks limit their applications in coating industries. During the last few decades, butylated melamine formaldehyde (BMF) has gained considerable attention as it acts as a good cross-linker for polymers having hydroxyl, carboxyl and amide groups. It provides excellent stability, wide compatibility and good hardness along with flexibility to the coatings. In addition, BMF can also be used as cross linker in organic as well as in aqueous media [16–18].

Nanoparticles in anticorrosive polymeric coatings, remarkably improve the protection ability of polymer coatings. The inorganic and organic (polymer) hybrid nanocomposite coatings possess synergistic properties, *i.e.*, the plasticity, adhesion, water and chemical resistance properties contributed by organic (polymer) constituents, while good scratch hardness, impermeability, impact and bend resistance properties are induced by inorganic materials [19]. Nanocomposite coatings such as polymer-clay, polymer-silica,

* Corresponding author. Tel.: +91 11 26827508; fax: +91 11 26840229.
E-mail addresses: obb16@gmail.com (O.u. Rahman), kashmohd@gmail.com (M. Kashif), sharifahmad_jmi@yahoo.co.in (S. Ahmad).

polymer-graphene, etc. have potentially been used to combat corrosion [20–22]. Alumina (Al_2O_3), silicon oxide (SiO_2), zinc oxide (ZnO), iron oxide (Fe_2O_3) and clay nanoparticles are being used as fillers, extenders and pigments in polymeric coatings [23–27]. The presence of nanoparticles enhances adhesion [28] UV resistance and healing properties of coatings [14,29]. The incorporation of nanofillers or nanopigments in polymeric coatings led to the development of a new generation coating materials with enhanced properties.

The dark colored nano Fe_3O_4 with spinel structure act as an excellent inorganic pigment. And potential alternative for carcinogenic chromate pigment, by inducing promising adhesion and enhanced protection ability to polymeric coatings [30]. The literature survey reveals that the formulation of EpAc-BMF- Fe_3O_4 coatings has not been reported till date. Furthermore, it has also been observed that EpAc-BMF- Fe_3O_4 nanocomposite has superior anticorrosive properties as compared to our earlier reported work and to other reported waterborne polymer coatings and comparable to that of solvent borne epoxy coatings [7,31,32].

2. Materials and methods

2.1. Materials

Diglycidyl ether of bisphenol A, LY 556 (epoxy equiv. 180–185, Sp. gr. 1.23, refractive index 1.57, viscosity 10,000 CP) was procured from Ciba Specialty Chemicals, New Delhi India. Acrylic acid (72.06 g mol^{-1}) and ferrous sulphate heptahydrate ($278.05 \text{ g mol}^{-1}$) were obtained from Merck, India. Ammonium persulfate ($228.18 \text{ g mol}^{-1}$), ethylene glycol (62.07 g mol^{-1}), sodium lauryl sulfate ($288.38 \text{ g mol}^{-1}$) ammonium hydroxide (35.04 g mol^{-1}) from SD fine chemicals Pvt. Ltd., Mumbai, India and H_2O_2 (50 wt%; 34.01 g mol^{-1}) from Fischer Scientific, Mumbai, India. All chemicals were of analytical grade and used without any further purification.

2.2. Synthesis of waterborne epoxy acrylate (EpAc)

The synthesis of waterborne EpAc was carried out as per our earlier reported method [7]. Briefly, epoxy (0.01 mol) was dissolved in the solvent blend of ethylene glycol and distilled water (DW) (1:1 v/v) along with sodium lauryl sulfate (0.3 g; 0.001 mol) and was then placed in a four-necked round bottom flask, equipped with a condenser, nitrogen inlet tube and thermometer. The solution was stirred on magnetic stirrer with constant heating at 100°C for 15 min. Ammonium persulfate (1.38 g; 0.02 mol) and acrylic acid (0.1 g; 0.001 mol) were gradually added to the epoxy solution over a period of 1 h at 85°C and then refluxed for 3 h. The progress of the reaction was monitored by determining the acid values, epoxy equivalent at regular intervals. The reaction was terminated on achieving the desired acid value and epoxy equivalent.

2.3. Synthesis of Fe_3O_4 nanoparticles

Fe_3O_4 nanoparticles were prepared as per our earlier reported method [33]. Ferrous sulphate heptahydrate (3.00 g, 0.1008 mol) and ethylene glycol (50 ml) were taken in a 250 ml three necked flask, and the solution was stirred under a nitrogen atmosphere for 30 min. followed by drop wise addition of 20 ml of 0.5% aqueous solution of 50% H_2O_2 . The reaction was continued at 50°C for 4 h under continuous stirring. The reaction mixture was maintained in a highly basic environment (pH 13.0) by the addition of 25% aqueous ammonia solution. The synthesized nanoparticles were dialyzed for 24 h and purified by magnetic field separation, decantation and re-dispersion. Finally, the ultra-fine precipitate of

Fe_3O_4 nanoparticles were filtered and washed several times with water and methanol until the pH of filtrate reached to 7.0.

2.4. Preparation of butylated melamine formaldehyde cured EpAc (EpAc-BMF) resin

BMF cured waterborne EpAc was synthesized using a reaction mixture of EpAc and different amounts of BMF in the presence of ethanol. The reaction mixture was vigorously stirred at 120°C for 1 h. The resulting resins were designated as EpAc-BMF-70, EpAc-BMF-80, and EpAc-BMF-90, where suffix indicates the percentage of BMF (w/w). Among different compositions, resin with 80 wt% BMF exhibited good properties while BMF-90 resin was found to be brittle in nature, which might be due to the excessive cross linking between EpAc and BMF. EpAc-BMF-70 coatings took longer time to cure. Hence, EpAc-BMF-80 was used for the preparation of the nano Fe_3O_4 dispersed waterborne EpAc-BMF nanocomposite coatings [32].

2.5. Preparation of Fe_3O_4 dispersed waterborne EpAc-BMF nanocomposite (EpAc-BMF- Fe_3O_4) coatings

EpAc-BMF- Fe_3O_4 nanocomposite coatings were prepared by the dispersion of varying weight percent of Fe_3O_4 nanoparticles (0.5–2.5 wt%) in the 70 wt% solution of EpAc-BMF-80 in ethanol through sonication [34]. A homogeneous Fe_3O_4 suspended colloidal solution of EpAc-BMF-80 containing 0.5, 1.5 and 2.5 wt% of Fe_3O_4 nanoparticles, respectively was obtained as shown in Scheme 1. Finally, these homogeneous Fe_3O_4 suspended (colloidal) solutions were marked as EpAc-BMF- Fe_3O_4 -0.5, EpAc-BMF- Fe_3O_4 -1.5, and EpAc-BMF- Fe_3O_4 -2.5 where suffix indicates the weight percentage of Fe_3O_4 nanoparticles in waterborne EpAc-BMF-80 resin. Beyond 2.5 wt% loading of Fe_3O_4 in EpAc was not carried out as nanoparticles were found to undergo agglomeration and phase separation after 24 h. Hence, the solution only up to 2.5 wt% Fe_3O_4 dispersed EpAc-BMF-80 was used for the preparation of nanocomposite coatings. The EpAc-BMF- Fe_3O_4 coatings with various compositions were found to be cured at ambient temperature and formed well adhered homogeneous nanocomposite coatings on mild steel (MS).

2.6. Preparation and testing of coatings

EpAc-BMF-80 and EpAc-BMF- Fe_3O_4 nanocomposite coatings were applied by brush technique (using the solutions of 70 wt% of EpAc-BMF-80 and EpAc-BMF- Fe_3O_4 resin in ethanol) on commercially available mild steel strips (MS) of different standard sizes i.e. ($70 \times 25 \times 1 \text{ mm}^3$) for physico-mechanical test, ($25 \times 25 \times 1 \text{ mm}^3$) for electrochemical corrosion test and ($12 \times 12 \times 1 \text{ mm}^3$) for salt spray test as well as for morphological studies. These MS were first polished with different grades of silicon carbide papers (180, 320 and 500), followed by thorough rinsing with water, alcohol and acetone, dried in the air, then coated with 70 wt% EpAc-BMF-80 and EpAc-BMF- Fe_3O_4 solution. The coatings were dried and cured at room temperature.

3. Characterization methods

The structural elucidation of EpAc-BMF-80 and EpAc-BMF- Fe_3O_4 was carried out by FTIR spectroscopy on IRAffinity-1 Shimadzu, spectrophotometer, using ZnSe cell (in the range of $4000\text{--}400 \text{ cm}^{-1}$). The physico-mechanical characterizations of EpAc-BMF-80 and EpAc-BMF- Fe_3O_4 coatings were performed by standard methods. The specific gravity and refractive index of the coating materials were also measured by standard laboratory methods [35]. The specular gloss of coatings was determined at 45°

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