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Investigation of surface morphology, anti-corrosive and abrasion resistance properties of nickel oxide epoxy nanocomposite (NiO-ENC) coating on mild steel substrate

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ABSTRACT

A series of epoxy (E) nickel oxide (NiO) nanocomposite materials has been successfully prepared by high speed dispersion of nickel oxide nanoparticles in diglycidyl ether of bisphenol A (DGEBA) type of epoxy resin. The nanocomposite materials were characterized by Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), atomic force microscopy (AFM) and scanning electron microscopy (SEM). In order to understand the effect of different concentrations of NiO nanoparticles on the corrosion inhibition performance of the epoxy coatings, nickel oxide epoxy nanocomposite (NiO-ENC) coatings were investigated by salt spray resistance as per ASTM B-117 test method. The results showed that NiO-ENC coatings with 0.5% NiO nanoparticles on surface prepared mild steel were much superior in corrosion protection, with respect to the other samples. Incorporation of NiO nanoparticles inside the epoxy matrix showed significant increase in the abrasion resistance of the coating at specific concentrations when tested under different abrader wheels. These phenomena can be attributed to specific morphology of the nanocomposite and interaction of the NiO nanoparticles with epoxy matrix.

1. Introduction

Corrosion of metals has serious economic impact and is an enormous problem throughout the world. Various methods have been used to protect metals from corrosion. Among them, polymeric coatings may be the most widely used methods. Mild steel is most widely used metal for infrastructure and machineries due to various engineering properties and economy but highly prone to corrosion. Therefore, protection of mild steel structures from corrosion is an important subject of research. To have a durable protection of structures, protective coating is expected to have excellent bond strength and high abrasion resistance along with anticorrosive property. Various research work including polymer modifications, pigment modifications [1] and use of specialized functional fillers and additives are going on in the field of polymeric coating to enhance coating properties.

Polymer nano composites (PNCs) are compounds in which metal or metal compound nanoparticles are distributed in a polymer matrix [2,3]. Montmorillonite (MMT) is the most frequently used clay in the preparation of PNCs. Recently many other polymer nanocomposites have been synthesized and studied for anticorrosion and abrasion resistance properties over various metallic substrates. PNCs have attracted interest in engineering plastics and coating material applications due to their excellent properties such as high-dimensional stability, heat deflection temperature (HDT), reduced gas permeability, optical properties [4,5], flame retardancy [6] and enhanced mechanical properties [7,8]. The elastic modulus of the nanocomposites was studied at various concentrations of nanoclay. It was found that there is increase in elastic modulus with increase in concentration of nano clay; however the rate of elastic modulus improvement found decreasing [8]. Various polymer nanocomposites have been evaluated for different functional properties including anticorrosion and abrasion resistance. Waterborne alkyd resin modified with nano alumina showed improvement in anticorrosion behaviour, studied by EIS [9]. Among various protective coating polymers, Epoxy is most widely used material for commercial applications due to its high adhesion on mild steel, good electrical properties, environmental

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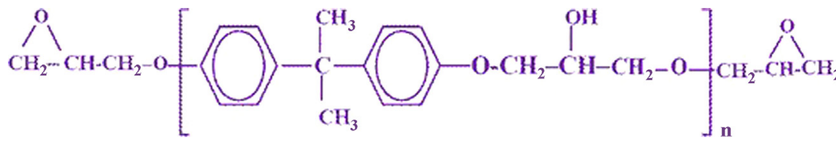

Fig. 1. Chemical structure of epoxy resin.

stability (other than chalking), good processability and relatively low cost. The barrier properties of epoxy coatings are increased by dispersing inorganic fillers of different chemical nature and morphology inside epoxy matrix. The barrier, adhesion, abrasion resistance and corrosion inhibiting features have very important role in service life of protective coatings. Recently many efforts have been taken to improve abrasion resistance, adhesion and anticorrosive properties of organic coatings by modifying with silane/siloxane-coupling agents, preparation of hybrid binders etc [10]. The chemical modifications of the clay cause a desired effect on its final properties, improving the performance of the nanocomposites in terms of thermal and water barrier properties in epoxy-clay nanocomposites [11,12]. Comparative study of epoxy-polyamide coating on hot-dip galvanized steel of micro ZnO versus nano ZnO showed nano zinc oxide advantageous in corrosion resistance and deterioration behavior [13,14]. The co-incorporation of nano Na-montmorillonite (Na-MMT) and MCM-41 (mesoporous silica) into the epoxy coating possessed the best corrosion resistance than incorporating either Na-MMT or MCM-41 nano particles separately due to different interfacial structures between the fillers and the matrix [15]. The incorporation of electro-active polyimide clay nanoparticles material [16] and sol gel coating containing zirconia nanoparticles improved barrier properties. Doping the hybrid nanostructured sol–gel coatings with cerium nitrate led to additional improvement of the corrosion protection [17]. Nanocrystallites of Ni co-deposited with Cr can act as crack bridging and crack bowing in protective coatings [18]. Enhancement in the barrier properties and corrosion protection by incorporation of SiO_2, Zn, Fe_2O_3, halloysite clay nanomaterials were observed in epoxy coating [19,20].

In recent years, NiO nanoparticles as a kind of functional material has attracted extensive interest due to its novel optical, electronic, magnetic, thermal, and mechanical properties which has potential application in catalyst, battery electrodes, gas sensors, electrochromic properties [21], photoelectronic devices, electrochemical [22] and so on. NiO coated with lithiated Co and Ni solid solution oxide showed more stable cathode in molten carbonate fuel cells [23]. NiO thin films were prepared with controlled structural and electrical properties [24]. NiO in micron size particles were evaluated for anticorrosion behaviour by magneton sputtering deposition method and study of EIS in H_2S Electrolyte [25]. A ferromagnetic-like behavior of ultrafine NiO nanocrystallites with grain size of 5 nm was reported [26,27].

Current work investigates the influence of nickel oxide nano particle in different concentration inside epoxy matrix on the abrasion resistance, glass transition (T_g), surface morphology and anticorrosion properties. The work provides further understanding of interaction of nanoparticles with epoxy matrix and help designing high performance epoxy coating for corrosion protection. Infrared spectroscopy study in the present work reveals a strong interaction of NiO nanoparticles with epoxy, probably with —OH group of the epoxy resin which at lower concentrations nullifies a peak at 421 cm^{-1} of neat epoxy (n-E) and appearance of a new peak due to nano NiO interaction at 456 cm^{-1} with increase in concentration. Differential scanning calorimetric study reveals reduction in T_g and enhancement in polymer stability at higher temperature with increase in NiO nanoparticles concentrations inside polymer matrix.

2. Experimental

2.1. Materials

Epoxies have been widely used for steel structure protection due to its excellent chemical resistance, good electrical insulation properties, strong adhesion over wide range of substrate and excellent barrier properties. The epoxy resin used in current study of NiO-ENC coating is based on unmodified diglycidyl ether of bisphenol A (DGEBA) having epoxide equivalent of 183–189 g/eq and a viscosity (η) of 11,000 centipoises, 25 °C, commercial name Araldite GY-250 procured from Huntsman corporation. A cycloaliphatic polyamine adduct used as curative is sourced from Air products. Epoxy resin is condensation product of epichlorohydrin and bisphenol A, having reactive oxirane ring terminated both sides which open in presence of amines. —OH group inside the molecule is responsible for better adhesion with metal substrates. A general structure of unmodified epoxy resin is given in Fig. 1.

The NiO nanoparticles used in this study is synthesized following similar preparation method described by Li et al. [28], well characterized by various characterization methods (DLS, XRD, FTIR, AFM, SEM), having mean particle size of 45 nm. Metallic substrate used during study is mild steel having following composition analyzed by spectroscopy method: Fe—99.392%, C—0.064%, Si—0.034%, Mn—0.368%, P—0.019%, S—0.012%, Cr—0.002%, Cu—0.060%, V—0.001%, Al 0.042%, Co—0.006%.

2.2. Preparation of NiO-ENC coating

Desired amount of Diglycidyl Ether of Bisphenol A (DGEBA) epoxy resin and NiO nanoparticles were mixed together under high speed disperser (HSD, Dispermill make Netherlands), for 1 h at 1500 RPM to disperse NiO nanoparticles inside epoxy resin. The dispersion process is performed in a steel vessel by saw tooth type blade disperser (having vessel diameter to blade diameter at the ratio of 2:1). Maximum material temperature gained during the dispersion is 65 °C. No solvents were added during the dispersion process. Dispersion of NiO nanoparticles was tested using Hegman gage (ASTM D1210). Also, coating dispersion was verified by visual transparency test by spreading the coating on glass plate and viewing for any agglomeration from opposite side of the plate in daylight. By this method, five samples containing different concentration of NiO viz. 0.12%, 0.25%, 0.5%, 0.75% and 1 wt.% were prepared for various studies. The stoichiometric amount of the curing agent was added to the mixture before coating process is conducted on cold rolled mild steel substrate.

2.3. Surface preparation, coating applications and test specimen

The mild steel test specimens were prepared by mechanical cleaning using 60 grit aluminum oxide sand paper (3M Co.), meeting surface preparation Swedish standard St-3. Epoxy containing nano NiO is mixed with cycloaliphatic polyamine curative in suitable mixing ratio before application. Coatings were applied at two different thicknesses viz. 100 μm and 18 $\pm$ 2 μm by brushing and spray application methods, respectively. Specimens for salt spray resistance test were applied by air assisted high volume low pressure (HVLP) spray gun of Anest IWATA W-400 make, 1.4 mm nozzle,