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Corrosion and wear resistance behavior of nano-silica epoxy composite coatings

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ABSTRACT

Recent developments made in the synthesis of nano-materials have demonstrated their contribution in the field of protective coatings. Sol–gel method is the simple and elegant technique for the preparation of nanosilica particles. The nano-silica composites were prepared by mixing the epoxy compounds and polyamide hardener and characterized by using X-ray powder diffraction (XRD), thermal analysis (TGA and DTA), FT-IR spectroscopic technique and SEM analysis. The size of the nano particles was confirmed by transmission electron microscopy (TEM). Mechanical properties of the nano-silica epoxy composites were determined by ASTM method. The wear index data of the nano-silica incorporated epoxy composite were found to be 32 mg/1000 cycles. Corrosion performance was evaluated by salt spray test and electrochemical impedance measurements. The nano-silica epoxy composite coatings withstood 720 h in salt spray test, whereas the micro silica coatings withstood up to 650 h. Electrochemical impedance spectroscopy results of the nano-silica epoxy composite coatings showed a resistance of $2.36 \times 10^6\ \Omega\,cm^2$ after 30 days of immersion in 3% NaCl solution, whereas micro silica incorporated coatings showed a resistance of $5.41 \times 10^4\ \Omega\,cm^2$ under similar conditions.

1. Introduction

Currently, nano-phase materials are extensively used because of their unique mechanical, electrical, optical and magnetic properties [1]. Inorganic particulate fillers in epoxy matrix composites have been extensively studied during the last two decades due to their increasing applications in coatings, electronic packaging and dental restorations [2,3]. Use of an additional phase-inorganic filler to strengthen the properties of the resin has been a common practice. Nano-particles can fill up the weak micro regions of resins to boost interactive forces at the polymer filler interfaces. Well-dispersed nanoparticles can effectively enhance the comprehensive properties of nano-composites, which are unique and different from any other composites with less than 5% of fillers [4,5]. Epoxy nano-silica composites have the advantages of low cost, good adhesion to most substrates, good corrosion and abrasion resistance and have many potential applications as sealants, paints, adhesives, etc. [6–9]. Zhou et al. [10,11] have found that nano-silica could obviously improve the UV absorbance and micro hardness of polyurethane coats, while micro-silica has no influence on these properties. Kinloch et al. [12] compared the mechanical and fractal properties of epoxy/inorganic micro and nano composites. Ng et al. [13] showed that most of the thermal and mechanical properties of the nano-particle filled epoxy composites are superior to those of the micro-particle filled epoxy composites at the same loading. It is well known that the load applied on the composites is mainly transferred to the fillers via an interface. It has been reported that the increase of specific surface area and contents of fillers enhance the mechanical and impact properties of the composites [14].

In the present research paper, preparation of nano SiO_2 particles, epoxy nano-silica composites, their characterization and the development of coatings based on both micro and nano silica particles are reported. In this composite, epoxy–polyamide resin is incorporated with titanium dioxide as main pigment and micro as well as nano-silica as extender pigments. Mechanical and corrosion resistance properties of these coatings were evaluated.

2. Materials and methods

Silicon tetra ethoxide and absolute ethanol were supplied by Merck. Epoxy 6071 and polyamide hardener (Synpol 125) was supplied by (CIBA-GEIGY), India, Ltd. Anatase Titanium dioxide, talc

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and silica were supplied by Jain Industries and Chemicals, Chennai, India.

3. Experimental

3.1. Preparation of nano SiO_2

The preparation procedure of silica particles from silicon alkoxides in alcoholic solutions was developed by Stober et al. and the resultant particles were excellent and uniform in dispersion [15]. In our study, nano SiO_2 particles were prepared by similar method. Solution A was prepared by mixing 10 g of silicon tetra ethoxide with 100 ml of ethanol. Solution B was prepared by mixing 400 ml of water with a few drops of concentrated HNO_3 solution. Solution A was added drop wise to solution B until a molar ratio of silicon tetra ethoxide:ethanol:water:nitric acid was 10:100:400:5. This mixture was heated to 348 K with continuous stirring at 900 rpm for 2 h. Then the content was cooled to 281 K in an ice bath, followed by vigorous stirring for 2 h and kept for 12 h. The product was washed with ethanol to remove residual water and dried at room temperature for 24 h. The resultant product was calcined for 4 h at 973 K and ground to fine powder.

3.2. Preparation of nano SiO_2–epoxy coatings

Epoxy polyamide based (50% volume solid) composite coating was prepared by using TiO_2, SiO_2 and talc as pigments. The Pigment Volume Concentration (PVC) of the formulation was 25%. The composition of the pigment formulation was 17.5 PVC of TiO_2, 2.5 PVC of SiO_2 and 2.5 PVC of talc. The size of the pigment used in the formulation was 37–40 μm. The solvent used in this formulation was, 1:1:1 mixture of xylene, methyl isobutyl ketone and butyl cellosolve. Similarly, another formulation was prepared by replacing the microsilica particles with nanosilica pigments.

Mild steel panels of 10 cm × 15 cm size were sand blasted to get a white surface profile as per Swedish specification SA 2.5 [16]. The epoxy nano composite was applied over sand blasted steel surfaces by brush and cured for 7 days at room temperature. The coating thickness was measured and was found to be 40 ± 5 μm. This coating was used for mechanical and corrosion studies. Similarly, another set of panels was coated with the epoxy–micro SiO_2 composites for comparison.

3.3. Characterization of nano SiO_2

The powder X-ray diffraction (XRD) patterns of the SiO_2 particles were recorded using X'pert Pro PANaytical diffractometer (Syn Master793s). TEM images were taken with Technai 20 G^2 FEI, Netherlands. Fourier Transform Infrared spectroscopy studies (FTIR) were carried out by using Paragon 500 FTIR spectrometer. TGA and DTA studies were carried out using STA 1500 (Thermal Science Limited) under a nitrogen atmosphere. The thickness of the coating was measured using a thickness meter (model Exacto Electrophysik minutes 600 FN, range 0–2000 μm>).

3.4. Mechanical properties of coatings

Abrasion resistance was evaluated using Taber Abraser (model 5135) for 1000 cycles as per ASTM D 4060. The adhesive strength was measured as per ASTM D 4541 using Elcometer106. The impact resistance of the coating system was measured using the Universal Impact Tester 172 as per ASTM D 6905–03. The scratch hardness was measured as per ASTM D 3359 using Erichsen scratch tester 245/11.

3.5. Corrosion studies on coatings

The corrosion resistance properties of epoxy–nano SiO_2 composite coatings over the steel surface were evaluated by AC impedance measurements. The impedance measurements were carried out with PAR electrochemical impedance analyzer (PARSTAT 2273) over a frequency range of 10 kHz–10 mHz with applied signal amplitude of 20 mV. The electrochemical cell used for this study consists of an epoxy–nano SiO_2 composite coated steelas working electrode, a platinum foil as counter electrode, a saturated calomel electrode (SCE) as reference electrode and 0.5 M NaCl as electrolyte.

Similarly epoxy micro silica composite coated steel was used as the working electrode in another experiment. The corrosion resistance properties of both the nano and micro silica composites were compared using the above technique. The impedance measurements were carried out periodically for different durations (initial, 1 day, 7 days, 15 days and 30 days) of time.

Both types of coated panels in duplicate were scratched at the center and exposed in salt spray chamber, where 5% sodium chloride solution was atomized by compressed air to create a fog. This test was conducted in accordance with ASTM standard B 117.

4. Results and discussion

4.1. XRD analysis

The XRD pattern of silicon dioxide particles after calcination at 973 K for 4 h is shown in Fig. 1. It was observed that the broad peak obtained at an angle, $2\theta = 20.6$ with d spacing of 4.3 (JCPDS No. 47-1144) corresponds to the presence of SiO_2 crystallites. This confirmed that the particles were mostly amorphous in nature. The results are in accordance with Agger et al. [17]. The particle size of the prepared silica was calculated using the Debye-Scherer formula,

$$D = \frac{0.9\,\lambda}{\beta \cos\theta}$$

where D = particle size, λ = wave length in Å, β = full width at half medium and θ = diffraction angle.

Fig. 2 shows the XRD pattern of epoxy silica nanocomposites. The peak at $2\theta = 23.4$ represents nano silica particles in the epoxy composite coatings [18]. The XRD peaks in the wide angle 2θ range ascertained that the peaks at 25.6 and 48.3 are crystalline single phase of anatase TiO_2 (JCPDS No. 84-1286) [19].

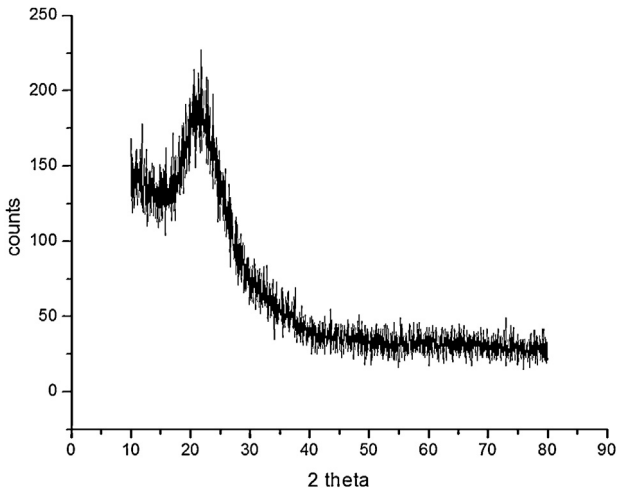

Fig. 1. XRD pattern of nano silicon dioxide powder.