SYNTHESIS AND CORROSION PROTECTION BEHAVIOR OF EPOXY-TiO_2-MICACEOUS IRON OXIDE NANO - COMPOSITE COATING ON St-37

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Abstract: *The micro layers micaceous iron oxide and nano-TiO_2 were incorporated into the epoxy resin by mechanical mixing and sonication process. Optical micrographs showed that the number and diameter size of nanoparticle agglomerates were decreased by sonication. The structure and composition of the nanocomposite was determined using transmission electron microscopy which showed the presence of dispersed nano-TiO_2 in the polymer matrix. The anticorrosive properties of the synthesized nano-composites coating were investigated using salt spray, electrochemical impedance spectroscopy and polarization measurement. The EIS results showed that coating resistance increased by addition of micaceous iron oxide micro layers and nano-TiO_2 particles to the epoxy coatings. It was observed that higher corrosion protection of nanocomposite coatings obtained by the addition of 3 %wt micaceous iron oxide and 4%wt nano-TiO_2 into epoxy resin.*

Keywords*: Corrosion, Nano-composite coatings, Impedance, Micaceous iron oxide.*

1. INTRODUCTION

Polymeric coatings have been developed due to their good barrier properties. However, pristine polymeric coatings are still permeable to corroding agents such as water, oxygen and destructive ions. In order to enhance the barrier properties of these polymeric coatings many researchers have used various kinds of additives such as extenders and inorganic pigments [1].

Nanocomposites are a combination of two or more phases containing different compositions or structures, where at least one of the phases is in the nanoscale regime. These materials exhibit different behavior from conventional composite with microscale structure, due to the small size of the structural unit and the high aspect ratio [2]. The final properties of the nanocomposites are determined by the component properties, composition, micro-structure and interfacial interactions. However it has been established that the properties of nanocomposites are strongly influenced by the dimensions and micro structure of filler phase [3]. Generally the anticorrosion, mechanical, barrier and other properties of nanocomposite is better than the composites which have been filled with micron size filler particles [4-7].

Epoxy coating have been widely used to protect steel from environmental attack. High corrosion resistance of epoxy coatings refer to the high cross-linking density and high adhesion strength [8]. Inorganic pigment can be added to the epoxy coating to deferment of corrosion or prolong the duration of protection [8-10]. Nano-TiO_2 particle was industrial pigment which was used to increasing corrosion resistance [11]. The size and shape of TiO_2 nanoparticle and its dispersion state influence on mechanical properties and corrosion resistance of nanocomposites [11-13].

Using lamellar and circular anticorrosive pigment such as MIO and nano-TiO_2 can be improved the corrosion resistance as the barrier properties against corrosion agent [8,14]. Micaceous iron oxide (MIO) is a nontoxic lamellar pigment which essentially is a type of hematite (Fe_2O_3). MIO is insoluble in water, organic solvents and is only slightly soluble in strong acids at elevated temperatures [15]. MIO lamellar align parallel to the substrate within the paint as a barrier against the seepage of corrosive solution [16]. Coatings containing lamellar pigments like MIO show a tortuous path of diffusion for the aggressive species [17].

The aim of this study was to prepare a

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nanocomposite epoxy coatings containing nano-titanium dioxide and micro layers of micaceous iron oxide with good dispersion properties. The dispersion morphology and degree of agglomeration were analyzed by sedimentation tests, optical microscopy, and transmission electron microscopy (TEM). As well as, the effect of nano-TiO_2 and micro layers of MIO against corrosive agents was investigated by electrochemical impedance spectroscopy (EIS), Tafel and salt spray test. Finally to investigate the adhesion of nanocomposite coating, pull-of tests were employed.

2. EXPERIMENTAL

2. 1. Materials

Epoxy resin was diglycidyl ether of bisphenol A (DGEBA) and epoxy hardener was epikure F-205 which was low viscosity modified cycloaliphatic amin curing agent and was used in the formulation in room temperature. TiO_2 nano-particle (Degussa p-25 anastase) with an average diameter of 25 nm was applied as an additional reinforcement. MIO micro layers, hematite (Fe_2O_3) and magnetite (Fe_3O_4), were identified to be the most abundant iron phases. Ethanol was used as a solvent from Merck, Germany.

2. 2. Preparation of Nanocomposites

TiO_2 nano-particles were added to the epoxy resin and mechanically mixed for 90 min at 1200 rpm, and was subjected to sonication for 60 min. The high-power sonication instrument UIP1000hd (Hielscher, Germany) was used. Cool water was used for constant temperature during sonication process. Subsequently, MIO micro layers were dissolved in ethanol at 27 °C, mixed for 20 min, and then added to the TiO_2 epoxy resin nano-composites. The mixture was mechanically mixed for 120 min. Finally a hardener was added with the mass ratio of the hardener/epoxy resin at 50/100, and the mixture was subjected to high-shear mixing for 10 min. The nano-composite paint formulation was designated based on a weight percent of particles and are shown in table 1.

2. 3. Sample Preparation

The st-37 carbon steel panels were used as metallic substrates. Before coating application, substrates were cleaned by a sequence of a chemical cleaning and mechanical surface polishing with emery papers from #100 to #1000 to remove any trace of surface oxide and then degreased with toluene and acetone. The coating was applied over the cleaned carbon steel panel using a film applicator with thicknesses of 20±3 μm for all panels. To ensure the film curing, the panels were kept in the laboratory atmosphere for 8 days.

2. 4. Corrosion Tests

To investigate the optical homogeneity dispersion of nano-TiO_2 and epoxy resin, an Olympus BHZZ-UMA optical microscope was used. The suspensions stability was analyzed by a sedimentation method in order to study the stability in organic environment. The mixture was placed in a furnace at 135 ºC for 2 h [18].

Table 1. Designation of formulations based on particle composition.

Nanocomposite Coatings	Micaceous iron oxide (MIO) pigments wt%	Titanium dioxide (TiO_2) pigments wt%
0M 0T	0	0
3M 0T	3	0
0M 3T	0	3
3M 3T	3	3
3M 4T	3	4

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The Transmission electron microscopy (TEM) was done using Philips CM30. TEM allows a qualitative understanding of the internal structure [19].

Electrochemical impedance spectroscopy (EIS) is a useful non-destructive technique in studying coating durability [20, 21]. Conventional three electrode cell was employed with using 3.5 % wt. NaCl solution as electrolyte at room temperature. Coated panels were acted as working electrode with an exposed area of 1.930 cm^2. A Pt electrode as counter electrode and a saturated Ag/AgCl as reference electrode were employed. The EIS measurements were carried out with Autolab PGSTAT 302N Potentiosat /Galvanostat and FRA2 frequency response analyzer at open circuit potential (OCP) with AC amplitude of 10 mV over a frequency range of 100 kHz to 10 Hz. Interpretation of impedance data was performed using Autolab Frequency Response Analyzer (FRA) software.

Salt spray tests were carried out in CTS-114D salt spray fog chamber by B.AZMA co. according to ASTM B117 for a period 1000 h.

The coating initial adhesion and retained adhesion after removing from the salt spray chamber was measured by using a direct pull-off adhesion test. The pull-off test was done by a digital adhesion tester (Elcometer 108, Elcometer Co., England) according to ASTM D4541-02 at ambient temperature. For measuring the adhesion after exposure, the samples were removed from the salt spray chamber, rinsed with deionized water and allowed to dry for 48 h at ambient temperature.

3. RESULTS AND DISCUSSIONS

3. 1. Optical Microscopy Results

The distribution of nano-TiO_2 in the epoxy matrix can be determined by using the optical microscopy. Fig. 1a shows that the optical micrographs of 4 wt% nano-TiO_2 in epoxy resin after mechanical agitation and sonication process. As can be seen, in Fig. 1a, many agglomerates are observed in the sample that is mechanically mixed at 1200 rpm for 90 min. These agglomerates are due to the cohesive forces between nanoparticles. Fig. 1b shows that the number and diameter of agglomerates are greatly decreased by using sonication process for 60 min and the distribution of nanoparticles is improved. This shows that sonication process is an effective method for dispersion of the de-agglomerations.

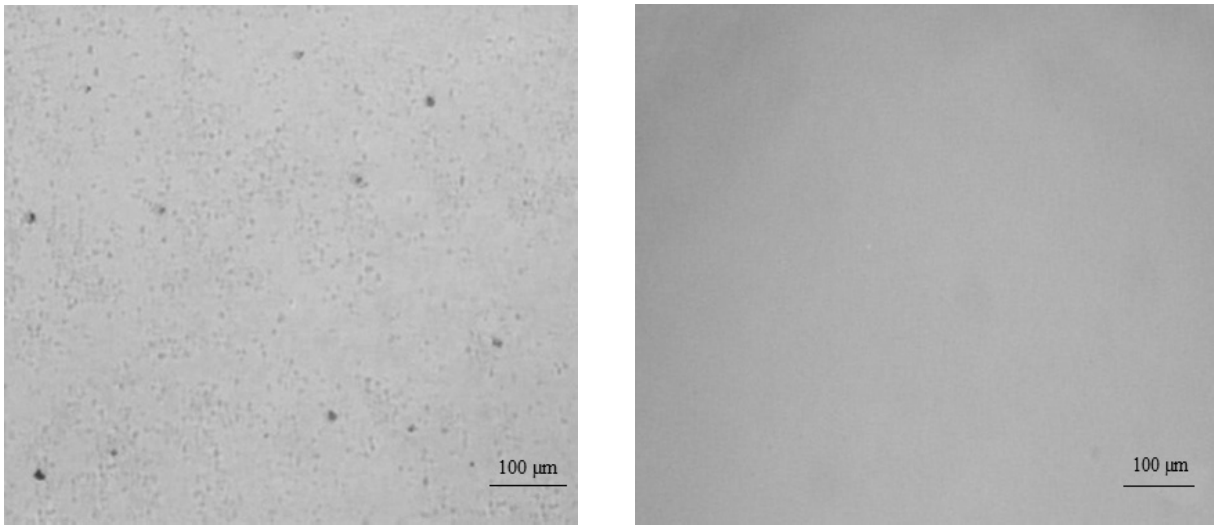

Fig. 1. Optical micrographs of 0M4T suspensions: (a) After 90 min mechanical agitation (b) after 60 min sonication.

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3. 2. Stability

To investigate the stability of nano-TiO_2 and micaceous iron oxide (MIO) in epoxy resin, mechanical mixing and sonication were used. The results in table 2 show that the dispersion of nano-TiO_2 in mechanically mixed sample is improved by using ultrasonic mixing due to the decrease in the nano-TiO_2 particles agglomeration. Also, table 3 shows that the deposition of MIO is observed after 45 min mechanical mixing and no deposition of MIO is seen after 120 min mechanical mixing of particle within the matrix.

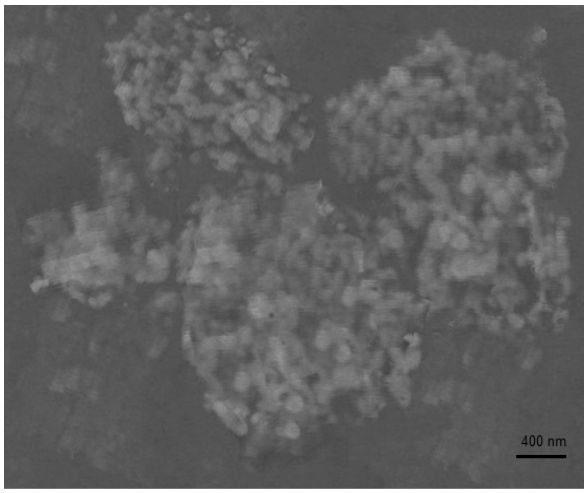

Fig. 2. TEM micrograph of nanocomposite 0M4T.

3. 3. TEM Analysis

The Van Der Waals forces between the nano-TiO_2 particles prevent dispersion of nanoparticles in the epoxy resin. Also the viscosity of epoxy resin has an important role in dispersion of nanoparticles [12]. Fig. 2 shows the TEM image of 4wt% TiO_2 - epoxy resin nanocomposite coating. It shows that the nanoparticles have been dispersed in the epoxy resin. The nano-particles are mostly in circular shape. Fig. 3 shows the TEM image of 4wt% TiO_2 - 3wt% MIO - epoxy resin. It can be concluded that nano-TiO_2 dispersed between the micro layers of MIO in the epoxy resin. Also Fig. 3 represents that the nano-TiO_2 and MIO micro layers act as a barriers against permeation of the corrosive solution or agents.

3. 4. Electrochemical Impedance Spectroscopy

EIS is conducted to understand the anticorrosive behavior of coatings when expose to a corrosive environment. High frequency part

Table 2. Results of sedimentation test of different samples.

Composition Code	Sedimentation after high shear mixing	Sedimentation after ultrasonication
0T 0M	-	-
3T 0M	+	-
4T 0M	+	-

Table 3. Results of sedimentation test of different samples.

Composition Code	Sedimentation after 45 min high shear mixing	Sedimentation after 120 min high shear mixing
0T 0M	-	-
3T 3M	+	-
4T 3M	+	-

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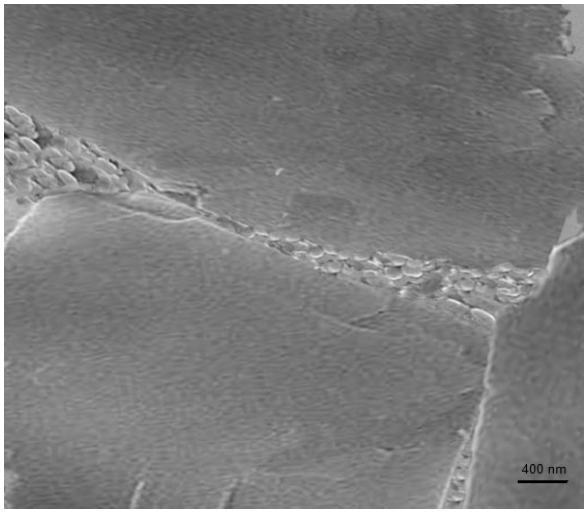
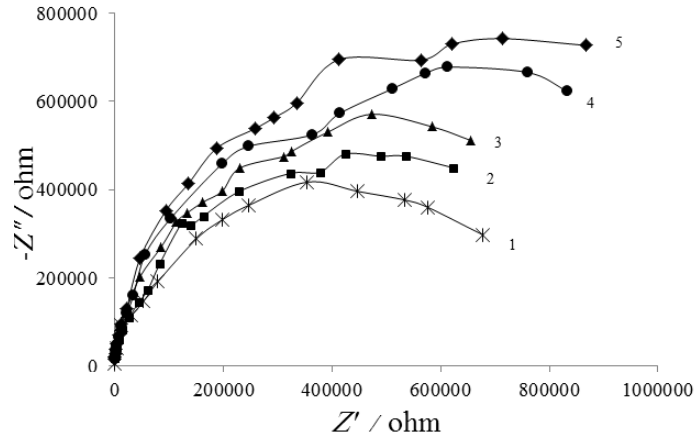


Fig. 3. TEM micrograph of nanocomposite 3M4T.

of electrochemical impedance spectroscopies of the different coated steel specimens were obtained during immersion to 3.5 wt% NaCl solutions in different immersion times (Fig. 4). The plots show a depressed capacitive loop for all coatings in different immersion times which arises from the time constant of the resistance and capacitance of the coatings. These results indicate that the coating resistance increases in the presence of the MIO micro layers and nano-TiO_2 due to the barrier properties which can prevent the penetration of corrosive ions through the coating [22, 23]. The results show that the presence of MIO micro layers and nano-TiO_2 containing epoxy resin, force the corrosive agents to travel a longer tortuous path to reach the substrate [8].

4a



4b

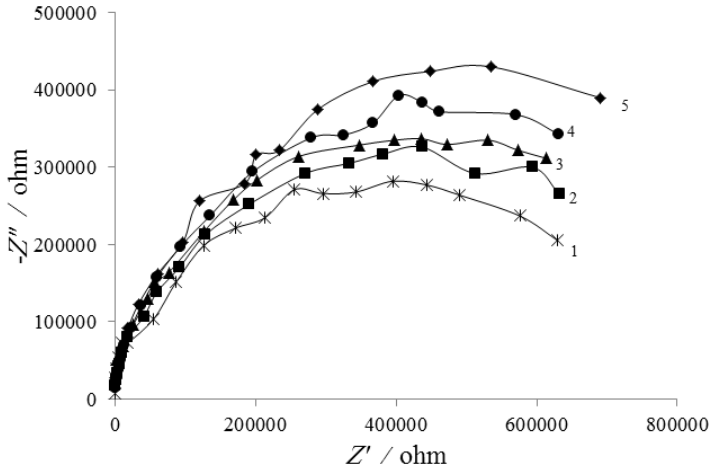


Fig. 4. Nyquist diagrams for different coated samples obtained at OCP after a) 1 day, b) 30 days and c) 60 days immersion in 3.5 wt.% NaCl solution: (1) neat resin, (2) 3M, (3) 3T, (4) 3M3T, (5) 3M4T.

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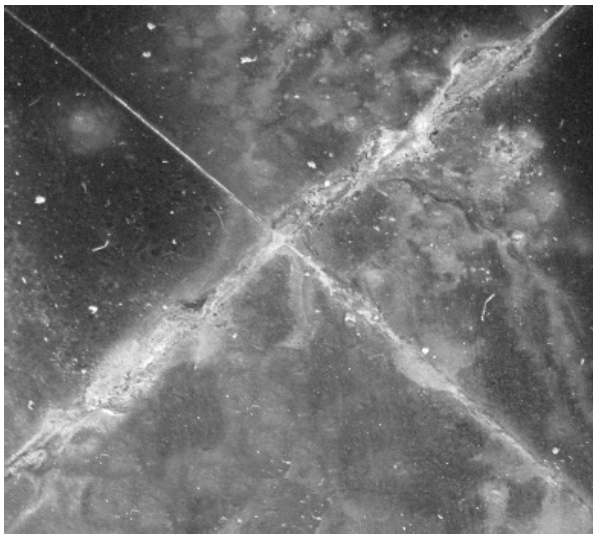
Nano-TiO_2 particles show higher corrosion resistance than the micro layers of MIO. It is found that TiO_2 fill the cervices and pinholes of polymer and their nano-size feature increase the tortuosity of the penetration path of corrosive ions. Also, epoxy resin containing both the micro layers of MIO and nano-TiO_2 pigments, 3M4T, has the best corrosion protection with respect to the other coating which is due to the cooperation of lamellar and circular anticorrosive pigment. In addition, with increasing immersion time, the coating resistance decreases due to the increase of water penetration to the coating [10, 24].

3. 5. Salt Spray Test

The salt spray test was performed as an accelerated corrosion testing method. To investigate the corrosion resistance of samples, after 1000 h exposure to corrosive environment, the rusts and blistering that formed along the X shape scribe of coating were checked. With increasing the blisters and rusts, the corrosion resistance decreases. Fig. 5 shows the micrographs of scratched coating samples after exposure. In all samples, corrosion begins from the scratch zone but shows different behavior in different samples.

5a

5b



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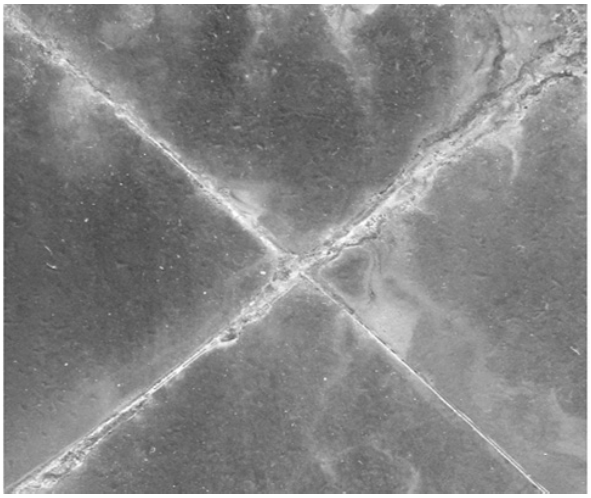
5c

5d



5e

Fig. 5. Surface images of scribed coatings after 1000 hours salt spray test: a) Neat resin b) 3M0T, c) 0M3T, d) 3M3T and e) 3M4T.

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As seen in Fig. 5a, the neat sample shows attendance of pin-holes, blisters and rusts that underwent drastic changes all over the scratches. By adding micro layers of MIO to epoxy (Fig. 5b) and nano-TiO_2 to epoxy resin, (Fig. 5c) the size of blisters and rusts decrease. This fact prove that the MIO and nano-TiO_2 has significant effect on corrosion resistance. In addition, in 3M4T sample (Fig. 5e), the size of blister, rusts and the change in dimension of scratch decrease to its minimum amount. The 3M4T sample represents that the cooperation of MIO and nano-TiO_2 and also the increase of the nano-TiO_2 are more effective in corrosion protection behavior. The nature, size and shape of nanoparticles which fill the cervices and pinholes of polymer are important to improve the corrosion resistance of nanocomposite. Therefore, the presence of MIO micro layers and nano-TiO_2 create longer barrier spots against corroding agents which cause a further increase in corrosion resistance of the coating.

3. 6. Pull-off Adhesion Test

Adhesion tests were performed on the epoxy resin in the presence of MIO and different loadings of nano-TiO_2. The dollies' with an area of 0.5 cm^2 were attached to the coating, using an appropriate adhesive material. The adhesion tests prior to exposure and after 35 days exposure in corrosive environment are shown in table 4. Exact determining of adhesion strength prior to exposure to 3.5 wt% NaCl is not possible since the coatings are always cohesive. After 35 days exposure to corrosive environment, the wet adhesion of coating to substrate decreases due to the penetration of corrosive agents and under coating corrosion of steel. It is observed that, higher wet adhesion of coating to substrate obtain in the presence of MIO micro layers and nano-TiO_2 and therefore the penetration of corrosive agents decreases. The 3M4T sample shows that by increasing nano-TiO_2, the wet adhesion of coating to substrate improves.

4. CONCLUSION

In the present study, MIO and TiO_2 nanoparticles were successfully dispersed into the epoxy resin matrix at various concentrations using mechanical agitation and sonication process through in-situ polymerization method. The results of optical microscopy and sedimentation test indicated that sonication process was an effective method to separate titanium dioxide stack and prevented from agglomeration to form a stable suspension. The optical observations revealed that the mechanical agitation was effective on MIO micro layers dispersion in epoxy resin. The TEM results showed that the nano-TiO_2 circulars dispersed and separated completely in epoxy resin. Electrochemical impedance measurements of the coated samples after various exposure times indicated the effect of MIO micro layers and nano-TiO_2 on the corrosion protection of coatings and showed an enhancement barrier properties and corrosion performance compared to neat coatings. Also the results revealed that 3 %wt MIO and 4 %wt TiO_2 nano-composite coating had higher corrosion resistance compared to the other samples. The results of salt spray test indicated that the corrosion products and depth of

Table 4. Pull-off adhesion test results after exposure in NaCl environment.

Sample characteristic	Adhesive strength before exposure (MPa)	Adhesive strength after exposure (MPa)
Neat epoxy	14	8.32
3M 0T	14	9.17
0M 3T	14	9.83
3M 3T	14	10.73
3M 4T	14	11.21

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penetration in scratched zone decreased for 3M4T sample. Also the results of pull off test showed that the 3M4T sample had higher adhesion to steel substrate after exposure to corrosive solution.

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