Characterization and corrosion performance of epoxy siloxane/organoclay coatings

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Abstract—The preparation of epoxy siloxane /clay nanocomposites (NCs) and their insertion into coatings are of great importance since the NCs could enhance the protective performances. In this study, epoxy siloxane NCs with 0, 1, 3 and 5 wt% of organo-montmorillonite (Cloisite 30B) were prepared under ultrasonic irradiation. The investigation was carried out using X-ray diffraction (XRD), salt spray exposures, adhesion and hardness measurements. All of the NC coatings protected the steel from corrosion. The hardness value of NC coatings increased with increasing nanoclay content.

Keywords—epoxy siloxane; clay; corrosion; salt spray; adhesion;

I. INTRODUCTION

A novel coating of high performance polymeric material is a need of today. These polymeric materials have superior mechanical, thermal and anticorrosive properties ideally suitable for adverse environmental conditions [1]. Inorganic-organic hybrid resins have become a creative polymer with unique combination of distinctive properties of both constituents for applications in various industries [2].

Among anticorrosive coatings, thermosetting epoxy resins are commonly used as organic coatings for corrosion protection due to their outstanding process ability, excellent chemical properties, good corrosion resistance and strong adhesion performance. However, the serious moisture absorption and volume shrinkage of traditional epoxy resins lead to the diffusion of absorbed water into the epoxy–steel interface and initiate corrosion of the metal substrate particular in wet conditions. Therefore, many researchers have devoted their efforts to develop advanced anticorrosive coatings by enhancing the interfacial adhesion between organic coatings and metallic surfaces, by modifying the formulation components of organic epoxy resins through the introduction of silane coupling agents [3], or by preparing the epoxy–siloxane hybrid binders [4].

Besides improving adhesion mentioned above, decrease in coating permeability of aggressive species (e.g., water, oxygen, and ions) also shows enhanced protective properties. The ability of a coating to prevent the corrosion reaction at a metal surface could be increased through the introduction of inhibitors [5,6] or anticorrosion fillers [5,7] into a coating, which could retard the diffusion of aggressive species (barrier effect), form a passive layer at the coating/metal interface, or act as an anode (cathodic protection), respectively.

Among inorganic additives, the nanoclays are useful in improving the anticorrosive and barrier properties of neat epoxy resins [8-11] and commercial epoxy coatings [12-14].

Layered silicates, consisting of stacked silicate platelets of 1 nm thickness and 200-500 nm in diameter, are usually rendered organophilic through an ion exchange within the clay galleries to enable swelling through the organic monomers or polymers [15]. Dispersion of the organically modified silicate platelets on a nanometer scale has shown improvement in various coating properties such as modulus and stiffness in some cases, barrier properties and flame retardency. The corrosion protection is directly related to the improvement in the coatings barrier properties, which are influenced by the filler dispersion in the polymer matrix [16,17].

In this study, organically modified montmorillonite was incorporated into resin solution under an ultrasonic homogenizer. The prepared polymer–clay nanocomposite (NC) materials are characterized by X-ray diffraction (XRD), adhesion and hardness tests, and salt spray method.

II. EXPERIMENTAL

A. Materials

Silicone-epoxy resin (SILIKOPON EF with epoxy equivalent weight of 450 g/mol, supplied by Evonik Industries, Germany) and aminosilane (Dynasylan 1124 with amine equivalent weight of 110 g/mol, supplied by Evonik Industries, Germany) were used as resin and curing agent, respectively. Organomontmorillonite (Cloisite 30B) was purchased from Southern Clay Products. Acetone (Merck) was used as a solvent.

B. Preparation

For the preparation of the samples, first, the silicone–epoxy hybrid resin / solvent solution (75/25, wt%/wt%) and organoclay were sonicated with a high-powered sonication
instrument (UP 400-A, TOP sonics Co., Iran) for 90 min, and then, the stoichiometric amount of the hardener (resin/hardener =100/20.3) was added to the resultant mixtures and mixed well. It should be noted that the solvent was evaporated before adding the hardener to the mixture. The organoclay content used was 1, 3 or 5 wt%. A coating without nanoclay was also prepared for comparison. The coatings were applied by air spray on blasted (Sa 2.5) carbon steel plates (15X10 cm²). The samples were dried in the room temperature for two weeks. The thickness of coatings was in the range of 60±5 μm uniformly. Table I illustrates the abbreviation of prepared coatings.

C. Characterization

X-ray diffraction (XRD) measurements were performed to investigate the characteristic peak of composites using a Philips PW 1730 X-ray diffractometer with CuKα radiation (λ = 1.5401 Å) operating at 40 kV and 30 mA. The data was obtained in the 2θ range of 1-10º at the rate of 1º/min and with the step size of 0.02.

The cross-cut adhesion test was accomplished according to ASTM D3359 by scratching parallel lines in both longitude and latitude directions on the coating using a scalpel. A standard adhesive tape was then applied to the surface and peeled off. The visual inspection of the tape is performed based on the amount of coating removed from the surface. Adhesion strength was rated according to a scale from 0B (the weakest) to 5B (the strongest). The pull-off adhesion of samples was measured using an Elcometer adhesion tester according to ASTM D4541.

Salt spray test was performed with ERICHSEN equipments in accordance with ASTM B117 and then anticorrosion performance of coatings was investigated according to ASTM D714.

The König pendulum hardness was measured with an Erichsen 299/300 Instrument. The coated plate was placed in hardness instrument and test was applied. Hardness of coating was measured from the number of oscillations of the pendulum swinging on the test panel. The test was carried out in accordance with the ISO 1522 standard.

III. RESULTS AND DISCUSSION

A. X-ray diffraction

The XRD spectrums of the Cloisite 30B and the NC samples with different wt % of nanoclays are shown in Fig 1. By using the Bragg’s law (1) where λ is the wavelength of the X-ray radiation (1.54 Å)[16], d corresponds to the spacing between the (001) diffraction lattice plane and refers to measured diffraction angle, the interplanar distance between nanoclay platelets was 18.24 Å.

\[ 2dsin\theta = n\lambda \]  

From Fig.1, we can see that all the d-spacings of the NC materials are higher than that of organophilic clay, indicating that a significant degree of intercalation dispersion has occurred in epoxy matrix. The increment of d-spacing of the clay in all of the samples was about 43- 45Å revealing that the space between silicate layers has increased about 25-27Å by the epoxy siloxane chains. It suggests that the sonication has been effective in intercalation of clay stacks in the epoxy siloxane resin. It can also be seen that as the concentration of clay increased, more ordered structures are obtained as more intense peaks. Based on the above results, that the presence of the nanoclay in the NC shifted 2θ angle to lower values, and therefore the interplanar distance to higher ones.

B. Adhesion analysis

Table II shows the results of adhesion tests for prepared nanocomposite coatings and the sample with no clay content. Pull-off and cross-cut adhesion tests were used to determine the strength of the bond between the substrate and coating. In the pull-off test, adhesion is measured in terms of forces used to separate the test dollies glued to the coating film from the base metal. The results of the pull-off adhesion tests showed that all the samples adhered well to the substrate and the coating films did not detach from the substrate.

The results for the cross-cut adhesion test of all samples did not exhibit any removed areas (0% removing), thus achieving classification 5B in accordance with ASTM D3359-Method B15. It can be seen that the adhesion does not vary with increase in clay concentration and all of the samples show excellent adhesion. These results provide evidence of high mechanical resistance coatings regarding adhesion, which is an important factor in terms of the anticorrosive properties of the coatings.
According to the literature [18,19], the adhesion mechanism of epoxy resins on metallic substrates is quite complex and many theories have evolved, whereby the mechanical interlocking theory and the adsorption theory are the most acceptable in explaining epoxy/metal interface properties. The mechanical interlocking mechanism is based on the diffusion of adhesive into pores, holes, and crevices of an adherend and it is very effective on porous or rough substrates. The adsorption theory describes adhesion by the forces (e.g., hydrogen bonding) acting between the atoms in the interface region when the sufficiently intimate intermolecular contact is achieved at the interface. On the other hand, silicone-modified polymers generally have good adhesion to metals due to the presence of reactive silanol groups in the resin. The mechanism of adhesion is similar to that of silane coupling agents [20].

### C. Salt spray test

The anticorrosive properties of the coating systems were evaluated by the salt spray test according to ASTM D 714. The coating systems, artificially damaged with X shape scribe, were tested for 700 h. The appearance of blisters and corrosion products around the scribes on the surface of a coating is a sign that the electrolyte had penetrated under the coating, and that the corrosion process was in progress. Thus, the size of the blisters, blister density, rusting degree, and extent of coating delamination (adhesion loss) in the scribed area are used to compare the anticorrosion performances of the coatings [21].

In this study, the samples were placed in salt spray chamber for 700 hours. The appearance of samples after 700 h exposure in salt spray test is shown in Fig. 2. No visible corrosion products were seen on the surface of the unscratched area of the coated panels after 700 h of exposure to salt spray media. Corrosion products were seen mainly on scratched area of the coated panels. It might be expected that corrosion resistance of epoxy siloxane / organoclay NC coated panels to be higher than that of pure coating (EPS sample) for a longer time of salt spray test. The incorporation of Cloisite 30B into the resin leads to higher corrosion stability of the coating systems in a salt spray chamber, due to the barrier mechanism of protection by organoclay. The barrier effect is attributed to the increase of the difficulty of diffusion (tortuosity) of liquids or gases molecules throughout the polymer film.

In general, it can be said that all the coated panels show excellent corrosion resistance after exposure to salt spray for 700 hours. The superior corrosion resistance showed by coating systems may be due to the inherent water repelling nature of silicone.

Since the coatings showed high corrosion resistance, this test will be continued for a prolonged period that the corresponding results will be reported in future papers.

### D. Hardness test

The average hardness values of test panels are shown in the Fig.3. By adding nanoclays into epoxy siloxane resin, the hardness of NCs increased direct proportionally with the nanoclay contents. The enhancements of the hardness of NCs by adding more nanoclays were due to the increase of nanoclay clusters size. The intercalated nanoclay clusters in

![Fig. 2. Surface aspect of the samples after 700 h exposure to salt spray media: (a) EPS, (b) NC 1%, (c) NC 3%, and (d) NC 5%.](image-url)
the NCs form spherical nanoparticles and the sizes of the clusters are varying depending on the wt % of nanoclays [22]. Any further addition of nanoclays most probably will deteriorate the mechanical properties of the NCs. The existence of the optimum reinforcement in the NCs is owing to the distances between the clusters are close enough to construct a three dimensional network of the interphase material around them and that is the strongest reinforcement of the polymer matrix by nanoparticles as stated by Zhang et al [23].

IV. CONCLUSION

In this work we developed a series of NC coatings using epoxy siloxane resin and organoclay. The structural characteristic of the coatings was evaluated by X-ray diffraction measurement. It was observed that the clay layers were dispersed and intercalated into the resin. The effects of the organoclay particle loading on the hardness and adhesion properties of the resultant coatings were studied. The incorporation of Cloisite 30B into the polymer coatings increased the hardness compared with the neat resin. The results of both adhesion tests (pull-off & cross-cut) showed that all the samples adhered well to the substrate. Anti-corrosive properties of the coatings were investigated using salt spray test. The corrosion protection performance was satisfactory for all coatings submitted to the salt spray exposure for 700 hrs.

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REFERENCES


