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Studying the Effect of Montmorillonite Nanoclay on Mechanical Properties and the Amount of Nanoclay on Epoxy Siloxane Hybrid Coatings

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ABSTRACT

Organic modified polysiloxanes are generally recognized as the newest generic class of high performance protective coating and now widely used in new construction, heavy duty OEM, marine and industrial maintenance painting. A series of polymer–clay nanocomposite (PCN) materials that consist of siloxane-modified epoxy resin and inorganic nanolayers of montmorillonite (MMT) clay has been prepared through a thermal ring opening polymerization using 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane as a curing agent. Dispersion of nanoclay in these coatings was prepared by ultrasonication method. The mechanical properties of the nanocomposite coatings such as abrasion, hardness, adhesion and weathering resistance were increased by addition of nanoclay montmorillonite. Stability and morphology of the nanocomposite coatings was evaluated by TEM, XRD and optical microscope .The results showed a stable dispersion of clay layers in the matrix and higher dry and wet adhesion in comparison with pure epoxy –siloxane coating. Prog. Color Colorants Coat. 7(2014), 11-18. © Institute for Color Science and Technology.

1. Introduction

Coatings degrade by thermal and photoinduced oxidation and are subjected to chemical attacks. This results in deterioration of coating properties such as color and gloss retention, flexibility, adhesion and corrosion resistance, which in turn reduces overall coating durability and service life. Polysiloxane coatings are largely inorganic in nature [1]. Polysiloxane is one of the newest classes of coatings that are known. These coatings are based on pure inorganic siloxane resin and these are high solid and have low VOC. The hybrid coatings (epoxy and polyether siloxane) create a two-component coating which cures at room temperature. The siloxane bond has about 50% ionic character and is readily hydrolyzed, especially when catalyzed by an acid or base. Coating

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durability in weathering is thought to be due to the reversible nature of siloxane hydrolysis [2]. In addition, they have excellent compatibility with the most of the zinc epoxy primers and zinc silicate. [3-6].Sheet silicates are used for increasing the hardness and wear resistance and improving the adhesion of organic coatings. Because silicate atoms are inorganic, these cause the coatings to have high mechanical properties. In recent years, epoxy-siloxane hybrid coatings have been introduced to have the ultimate durability and weather resistance as a protective coating system [7]. Organic polysiloxane hybrid coatings vary from about 30 to 80% siloxane content to give optimum performance in terms of adhesion, mechanical properties and chemical, corrosion and weathering resistance[8].

To further improve the protective properties of the epoxy siloxane coatings, inorganic nanoclay of montmorillonite (MMT) clay has been used and it increases the barrier properties also decreases the permeability [9].

Montmorillonite (MMT) is a special type of polymer/clay nanocomposites because of its lamellar structure. The presence of this material improves some properties of the resulting nanocomposite such as stiffness and protective properties of the corrosive elements [10].

Epoxy-siloxane hybrid coatings exhibit the properties of organic resins and inorganic resins simultaneously and therefore can be used as an alternative coating for the traditional epoxy/polyurethane systems, providing the weathering resistance combined with the desirable mechanical properties. In this article, we used 1%, 3%, 5%, 7% nanoclay in epoxysiloxan and compare their mechanical properties with pure epoxysiloxan

2. Experimental

2.1. Materials

The epoxy-siloxane resin known as Silikopon EF, an Evonik product, was used as the polymeric matrix. The typical characteristics of the resin are shown in Table 1.

The resin was mixed with the correct ratio of aminosilane hardener known as DynasylanAmeo, an Evonik product, with the properties shown in Table 2.

The layered nanoclay used was Closite 30B, a product of Southern Clay Products (USA), which is a natural montmorillonite modified with quaternary ammonium salt.

Table 1: Silikopon EF properties.

Property	Value
EEW	420-480 g/equ
Solid content	96-100%
Viscosity at 25ºC	1000-2000 mPas
Density at 25ºC	1-1.2 g/ml

Table 2: Dynasylan Ameo characteristics.

Property	Value
Density	0.95 gr/cc
Refractive index	1.422
Boiling point	>68 ˚C
Flash point	93 ˚C
Viscosity	1,85 mPa.s

Figure 1 shows the chemical formula of the organic modifier. The technical data of Closite 30B are shown in Table 3.

2.2. Sample preparation

Nanocomposite samples were prepared by dispersing different loadings of nanoclay in the epoxy-siloxane resin. The first step was mixing the clay/resin mixtures for 1 hour by means of a high-shear mixer. Dispersion was then continued by sonication for 45 minutes (cycle: 0.6, amplitude: 0.8).

The samples containing 0%, 1%, 3%, 5% and 7% nanoclay were referred to as EPS, NC1%, NC3%, NC5% and NC7%. The prepared samples were first mixed with the correct ratio of hardener and then were applied by a film applicator on Sa2 1/2 sand blasted steel panels

2.3. Characterization Tools

2.3.1. Turbidimetry

Turbidity of dispersions as a factor of stability was measured by HACH 2100 AV Turbidimeter according to ASTM D 5180-93.

2.3.2. X-Ray Diffractometry (XRD)

XRD measurements were performed to investigate the characteristic peak of composites using a Philips model X'PERT MPD X-ray diffractometer with CuK_{α} radiation (λ = 1.5401 Å) operating at 40 kV and 40 mA. The data was obtained in the 2θ range of 0.5-10º at the rate of 1º/min and with the step size of 0.02.

2.3.3. Transmission Electron Microscopy (TEM)

Transmission electron microscopy measurements were carried out on a PHILIPS-CM200 instrument operated at 200 KV acceleration voltage. The samples were prepared by cutting the cured bulk nanocomposites by ultra microtome instrument (OMU3, Reichert, Austria) which was equipped by a diamond cutter. The thickness of TEM samples was about 70-100 nm.

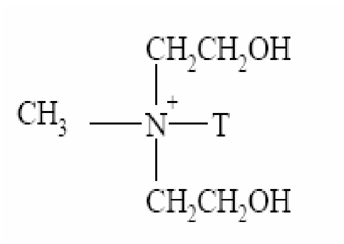

Figure1: Organic modifier.

Where T is Tallow (~65% C_{18},~30% C_{16},~5% C_{14})
Anion: Chloride
MT2EtOH: methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium

Table 3: Closite 30B properties.

Property/ Treatment	Value
Organic modifier	MT2EtOH
Modifier concentration	90 meq/100 gr clay
Dry particle size	90% less than 13µm
Density	1.98 g/cc
X-Ray results	d001: 18.5 Å

2.3.4. Salt Spray

Salt spray chamber was used to evaluate the performance of coatings in corrosive environment. The salt spray instrument used was S85 V400 (Pars HormCo., Iran). The samples were then evaluated according to ASTM B117 and ASTM D 714.
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3. Results and discussion

3.1. Turbidimetry Results

The stability of samples was evaluated by measuring the turbidity of samples in different time intervals using HACH 2100 AV Turbidimeter. Stable dispersions are expected to show negligible reduction in turbidity during the test time [10, 11].

According to the results obtained in Figure 2, there is no significant change in turbidity during 120 hours, therefore it can be concluded that all of the dispersions have been stable and no sedimentation has occurred during this period.

3.2. XRD Results

X-Ray Diffraction analysis was carried out for measuring the space between the silicate layers of clay particles. According to the XRD patterns depicted over the diffraction range of 0.5 to 10 for the "as received" Closite 30B nanoclay and based on the Bragg's law, the d (001) of the clay was 18.02 Å as shown in Figure 3 which indicates the spacing between the silicate sheets in terms of basal interplanar spacing of the clay.

Figure 3 also shows the XRD patterns of NC1%, NC3%, NC5% and NC7% samples. The increment of d-spacing of the clay in all of the samples was about 41-46Å revealing that the space between silicate layers has increased about 23-28Å by the epoxy siloxane chains.

It suggests that the sonication has been effective in intercalation of clay stacks in the epoxy siloxane resin. The sonication beside hydrophilic nature of the alkyl ammonium treated clays allows the epoxy siloxane molecules to migrate between the layers.

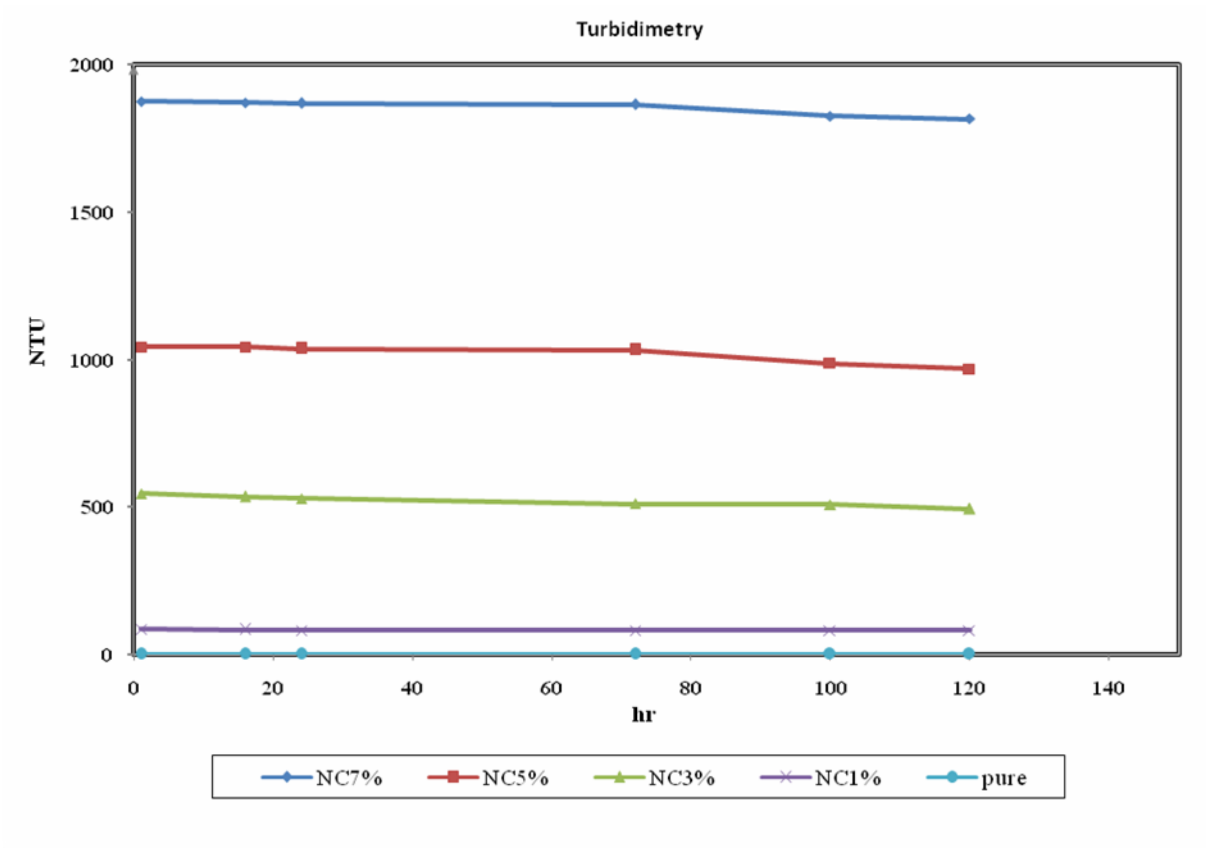

Figure 2: Turbidimetry results.

The alkyl ammonium ions have been suggested to reorient from their lateral bilayer structure in the dry state to a perpendicular orientation in order to accommodate the polymer [12]. During this mechanism, molecules driven between the layers intercalate the clay in the polymeric matrix.

3.3. TEM Results

Figure 4 shows TEM image of NC5% sample with 150k magnifications, where the dark areas show clay platelets and the gray areas represent the polymeric matrix. It can be seen that in some areas exfoliation dispersion and in major areas intercalation dispersion has acquired. The nanocomposite preparation method is the key to this morphology [13].

It must be noted that the morphology has a significant effect on the properties of the final nanocomposite [12,13]. Based on the TEM results, it can be concluded that sonication is an acceptable method for dispersing the nanoclay in the epoxy-siloxane resin. Regarding the fact that the results of turbidimetry, XRD and TEM analyses confirm each other, it can be recognized that the dispersion of silicate layers in the polymeric matrix has occurred.

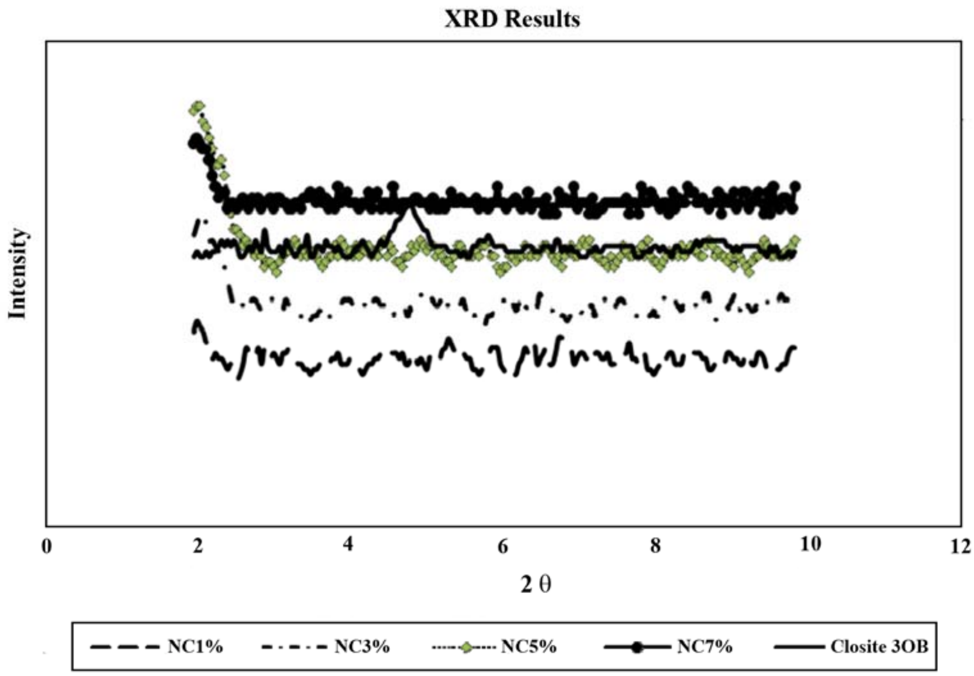

Figure 3: XRD results.

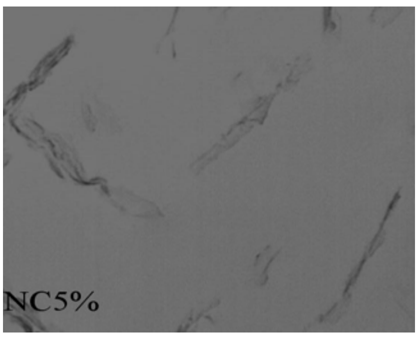

Figure 4: TEM image for NC5%.

3.4. Salt spray results

Samples were placed in salt spray chamber for 2000 hours and were evaluated according to ASTM B117, ASTM D714 and ASTM D1654.

Table 4 shows the salt spray results for the nanocomposites as well as the neat resin sample. According to the results after 2000 hours of testing, no failure was recognized in nanocomposite samples containing 3% nanoclay and more. Also no blistering or rusting occurred in NC1% and EPS samples; however the scribe creep in EPS sample was more than NC1%.

This happens because of the layered structure of nanoclay which increases the penetration path to the metallic substrate and acts as a barrier to the aggressive ions [14,15].

3.5. Hardness Test

Hardness of the samples was measured by the König pendulum hardness tester, 299/300 model of Erichsen co. from Germany (ASTM D4366). The results are shown in Table 5. It can be observed that when nanoclay increases in the coating, its hardness increases. Silicon atoms disperse in the mineral nanoclay particles which have high hardness, hence increasing the hardness of the coatings [16].

3.6. Adhesion Test

Adhesion of the samples was measured by pull off tester of Defelsko co. instrument from U.S.A (ASTM D4541). The dry adhesion of films measured, the wet adhesion test was done by immersing the coating sample into 3.5% wt sodium chloride solution for 50 days [6]. The dry adhesion of nanocomposite coatings and nanoclay-free coatings have not more differences. Wet and dry adhesion results are shown in Figure 5.

3.7. Abrasion Test

Abrasion tests were done on the nanocomposite coatings and pure epoxy –siloxane coating (ASTM D 4060-95) using Elcometer Taber Abraser 5131. CS10 abrasive was used and the weight of the samples for this test was 500 g.

Table 4: Salt spray results.

Samples	Blistering ASTM D174	Rusting ASTM D1654	Scribe creep
EPS	No blister	10	8
NC1%	No blister	10	9
NC3%	No blister	10	10
NC5%	No blister	10	10
NC7%	No blister	10	10

Table 5: König pendulum hardness result.

Sample	Hardness(cycle)
EPS	102
NC1%	136
NC3%	150
NC5%	158
NC7%	161
EP/PU	98

Test results based on the weight loss of the samples is shown in Figure 6. Increasing the nanoclay content, the interface between the polymer and the nanosheet also increases, because mineral nanoclay particles increase the hardness of the coatings.

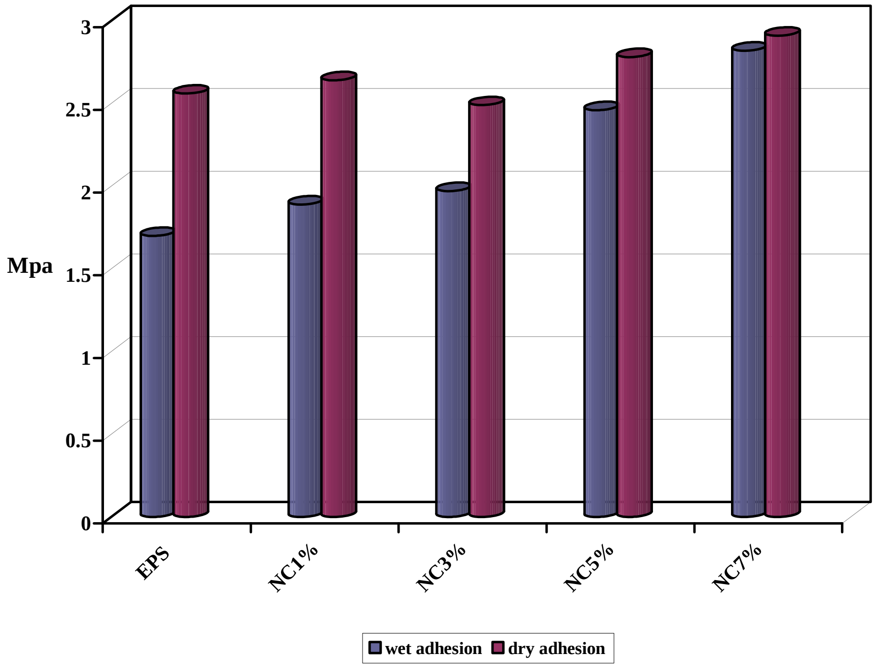

Figure 5: dry & wet adhesion (pull-off).

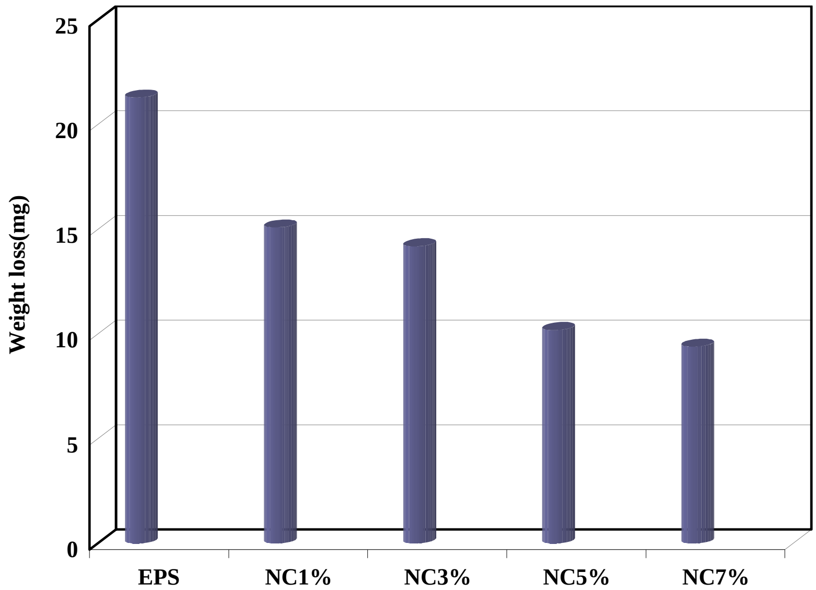

Figure 6: Abrasion results.

4. Conclusions

Epoxy-siloxane nanocomposite samples with different loadings of nanoclay were prepared via sonication. The dispersion of the clay into the matrix was investigated using turbidimetry, XRD and TEM analyses. It was observed that the clay layers were dispersed and intercalated into the resin. According to the results, the samples containing higher loadings of layered silicate showed higher adhesion, hardness and abrasion resistance due to the properties of the silicate layers. since the difference between the adhesion and hardness properties of NC5% and NC7% was negligible, and considering the application ease and economic issues, it can be concluded that NC5% is preferred for using as a hardness coating which has good adhesion to the steel surface

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