

Preparation and Characterization of Structure and Corrosion Resistivity of Polyurethane /Montmorillonite/Cerium Nitrate Nanocomposites

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Received: January 25, 2014; revised: June 29, 2014; accepted: September 15, 2014

Abstract

In this study, nanocomposite coatings based on polyurethane cerium nitrate montmorillonite (MMT) were prepared, applied on carbon steel substrates, and investigated. The nanocomposite coatings were successfully prepared by the effective dispersing of nanoparticles in polyurethane resin by mechanical and sonication processes. The state of dispersion, dissolution, and incorporation were characterized by optical microscopy, sedimentation tests, and transmission electron microscopy. The structure and properties of the nanocomposite coatings were investigated by X-ray diffraction and anticorrosive properties of the nanocomposites were studied by Tafel polarization measurements. The experimental results showed that the PU/MMT/Cerium nitrate nanocomposite coatings were superior to the neat PU in corrosion protection. In addition, it was observed that the corrosion protection of the nanocomposite coatings was improved as the clay and cerium nitrate loadings were increased to 4 wt.% to 2 wt.% respectively.

Keywords: Cerium Nitrate, Nanocomposite Coating, Montmorillonite, Polyurethane, Corrosion

1. Introduction

Polyurethane is one of the most interesting synthetic materials in industry, which is being extensively used for different applications such as coatings, adhesives, construction, fibers, and foam because of its high flexibility, good processability, excellent water resistance, good resistance to acids and solvents, better alkaline resistance than most of other polymers, good abrasion resistance, and good mechanical properties. Its synthesis, morphology, chemical, and mechanical properties have been the subject of a great deal of attention in recent studies (Wu et al., 2001; Jeong et al., 2000; Meincken et al., 2006).

Polyurethane (PU) is extensively used in protective coatings as a resin; however, this resin has some disadvantages such as low thermal stability and barrier properties (Rehab et al., 2005). These properties can be modified by adding fillers such as montmorillonite organoclay to the polymer matrix. The incorporated nanoparticles into PU matrix results in improving coating properties such as adhesion, pendulum hardness, barrier properties, thermal stability, and corrosion resistance (Ahmadi

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et al., 2007; Lv et al., 2008; Choi et al., 2004; Špírková et al., 2008; Chen-Yang et al., 2005; Chen-Yang et al., 2007).

Clay is nontoxic, cheap, available, and environmentally-friendly. It is a special type of layered silicate, which has been commonly used for the fabrication of nanocomposite coatings in recent years (Theng et al., 2012; Zhang et al., 1993; Pinnavaia et al., 2000; Zaarei et al., 2009). In the 1980's, the technology of clay nanocomposite was submitted by the Toyota Corporation (Liu et al., 2007). Researchers showed that the incorporation of a small amount of clay (1–4%) into the polymer matrix can improve anticorrosion, barrier, thermal, and mechanical properties, and it also decreases liquids and gases permeability in comparison to pure polymeric coatings (Zaarei et al., 2008).

Obtaining a stable dispersion in which the silicate nanolayers are completely exfoliated in the polymeric matrix is an important factor in attaining the best properties of polymer–clay nanocomposites; therefore, during nanocomposite preparation, the evaluation of the morphology of these nanocomposites is crucial (Giannelis et al., 1996; Fornes et al., 2001; Samyn et al., 2008; Ratna et al., 2006; Wagener et al., 2003).

For a long time, chromates have been widely applied as an effective corrosion inhibitor in coatings. Surface pretreatments are based on chromates because of their high protection efficiency. However, due to increased environmental concerns, these pretreatments will be prohibited because of the toxicity and carcinogenic of chromates. Therefore, new alternative is substituted. Rare earth salts have been used as the new corrosion inhibitors. Cerium is one of these alternatives, which can reduce the corrosion rate of metals by inhibiting cathodic reactions. The first studies on this field are those of Hinton, who found that cerium nitrate was effective in reducing the corrosion rate of aluminum alloys (Montemor et al., 2001).

Subsequent researches showed that cerium nitrate also has healing abilities and improves the corrosion resistance (Cabral et al., 2006).

2. Experimental

2.1. Material

The organoclay used in this study was modified MMT clay (Closite 20A; dimethyl, dehydrogenated tallow, quaternary ammonium–modified MMT) with a particle size of 2–13 μm , a layer thickness of 1 nm, and was received from Southern Clay Company (Gonzales, TX, USA). Cerium (III) nitrate was provided from Scharlab, Spain. Ethanol was supplied by Merck 100983 (Germany) as the solvent. Polyurethane resin, Methylene diphenylene diisocyanate was provided from Bajak Paint Company.

2.2. Nanocomposites preparation

For the preparation of the compositions, 1-3 grams of cerium nitrate was dissolved in 10 ml xylene at 27 °C and mixed for 15 min; MMT was then added to PU resin according to weight percent of the solid parts of the paints. PU, MMT, and cerium nitrate-modified xylene were mixed mechanically with a high-shear mixer at 1200 rpm for 2 hrs; these mixed compositions were then sonicated with a high-powered sonication instrument for 40 min with an external cooling bath to prevent increasing the temperature of the composition. The ultrasonication process was performed at a frequency of 20 kHz with an inlet ultrasound power of around 1 W/ml (UIP 1000hd ultrasonic processor, Hielscher ultrasound technology). The sonicated compositions, which include different percentages of clay and cerium nitrate, are shown in Table 1. For degassing, the samples were held in a vacuum oven for 30

min at 50-60 °C, and the compositions of tiny bubbles were removed. Finally, hardener was added to composite with the mass ratio of 1:4 with respect to PU and mechanically mixed again.

Table 1
Designation of formulations based on particles compositions.

| Nanocomposite coatings | Montmorillonite (MMT) pigments (wt.%) | Cerium nitrate (CN) pigments (wt.%) |
|------------------------|--|--|
| 0C0CN | 0 | 0 |
| 0C2CN | 0 | 2 |
| 2C2CN | 2 | 2 |
| 3C2CN | 3 | 2 |
| 4C0CN | 4 | 0 |
| 4C1CN | 4 | 1 |
| 4C2CN | 4 | 2 |
| 4C3CN | 4 | 3 |

2.3. Coating application

SAE 1010 carbon steel panels (15cm×8cm×0.2cm) were used as metallic substrates. The panels were subjected to a sequence of chemical cleaning and mechanical surface polishing with emery papers from #400 to #1000 to remove any trace of surface oxides and were kept in the desiccator. Prior to coating application, the panels were extensively cleaned with acetone and toluene. The coatings were applied by means of a film applicator. The thickness of dry coatings was measured with Elcometer FN 4653 digital coating thickness meter (Elcometer Co. Ltd.), and was chosen in the range 50-60 μm. The panels were kept in the laboratory atmosphere for two weeks before beginning the tests to ensure the complete curing of the coatings.

2.4. Nanocomposites structural characterization

The optical homogeneity of the nanocomposite dispersions and the effect of sonication process on de-agglomeration of clay aggregates were examined using an Olympus Bhzzuma optical microscope. The optical micrographs of the samples were obtained after 2 hrs mechanical mixing and 40 min sonication.

The suspensions stability was analyzed by a sedimentation method. The blends were placed at 128 °C for 2 hrs to observe the amounts of the clay precipitated.

XRD analysis was carried out with a Philips model X'PERT MPD X-ray diffractometer with Cu K α radiation ($\lambda=1.54\text{\AA}$) operating at 40 kV and 40 mA for the evaluation of the intercalation/exfoliation of nanoclay in the polymer matrix. The diffraction patterns were obtained in the 2θ range 0.5-10° at a rate of 0.5°/min.

Transmission electron micrographs (TEM) technique was used to analyze the morphology of the bulk samples and to evaluate the state of the dispersion. The TEM samples were prepared by cutting the cured nanocomposites by an ultra-microtome instrument (OMU3, Reichert, Austria) that was equipped with a diamond cutter. The thickness of the TEM samples was about 70–100 nm. Then, the samples were put on 300-mesh copper grids. The TEM images used is of bright field type and is taken with a Philips-EM208 at an acceleration voltage of 100 kV.

The coating initial adhesion and the adhesion retained after exposure in a 5 wt.% aqueous NaCl solution were measured by using a direct pull-off adhesion test method in accordance with ASTM D4541 type III (self-aligning adhesion tester). The dollies with an area of 0.5 cm^2 were bonded to the coating using an appropriate adhesive (Cyanoacrylate MC1500). In the case of adhesion measurement after exposure, the samples were removed from the salt spray chamber at the end of 1000 hrs exposure, rinsed completely with deionized water, and allowed to dry for 48 hrs at ambient temperature. The glued dollies were then allowed to dry for 48 hrs at room temperature. A digital adhesion tester (Elcometer 108, Elcometer Co. Ltd.) was employed. To ensure reproducibility and to statistically characterize the test area, all the measurements were obtained from at least three experiments.

The Tafel plots were obtained after 20 days of immersion at a potential of 200 mV higher and lower of the open circuit potential (E_{ocp}) and at a scanning rate of 0.5 mVs^{-1} . The interpretation of impedance data was performed using Autolab Frequency Response Analyzer (FRA) software.

3. Results and discussion

3.1. Optical microscopy results

Figure 1 presents the optical micrographs of the suspensions having 4 wt.% clay and 2 wt.% cerium nitrate after mechanical agitation and sonication processes. The dispersion which was mechanically agitated for 2 hrs, contained a lot of MMT agglomerates (see Figure 1a). These agglomerates are formed during the wetting of MMT with polyurethane due to cohesive forces between clay stacks. When sonication process was applied to the suspension for 30 min, size and quantity of the agglomerates were greatly decreased and the distribution of clay was improved (see Figure 1b). These results show that sonication process is an effective method to de-agglomerate and disperse the nanocomposite mixture.

a)



**Figure 1**

Optical micrographs of 4c2cn: a) after 2 hrs of mechanical agitation and b) after 30 min of sonication.

3.2. Stability

Sedimentation was visually observed for the mixtures that were held at 50 °C for nearly 2 weeks. Sediments could be seen in the matrix with an insufficient dispersion and intercalation of the clay particles. An insufficient dispersion process caused sedimentation, but using ultrasonic mixing improved the distribution of particles and prevented the agglomeration of the clay particles. Table 2 shows the sedimentation results of the mechanical mixing and ultrasonic of particles within the matrix.

Table 2
Results of sedimentation test of different samples.

| Composition | Sedimentation after high shear mixing | Sedimentation after ultrasonication |
|-------------|---------------------------------------|-------------------------------------|
| 0C0CN | - | - |
| 0C2CN | - | - |
| 2C2CN | + | - |
| 3C2CN | + | - |
| 4C0CN | + | - |
| 4C1CN | + | - |
| 4C2CN | + | - |
| 4C3CN | + | - |

3.3. XRD

The state of intercalation or exfoliation of nanoclay structure in PU and the degree of cerium nitrate dissolution and clay sheets separation in the polymer film were analyzed using wide angle X-ray diffraction (WAXD) patterns as presented in Figure 2. The *d*-spacing can be obtained from Bragg's equation, as well as from the angle of maximum intensity. The neat MMT has a *d*-spacing of 2.42 nm

and cerium nitrate has a d -spacing of 4.204 nm. According to the XRD patterns, the neat cerium nitrate (CN) exhibits the reflection peak at 2.1° . On the other hand, the peak intensity of the sample 0C2CN is less remarkable. Thus it is concluded that cerium nitrate is dissolved in the matrix.

The increments of d -spacing for 4C0CN and 4C2CN clays caused by high-shear mixing and high-intensity ultrasound were 49.02 and 46.44 nm respectively. However, it can be seen from Figure 2 that the intensity of the peak is less remarkable because of the small amount of clay.

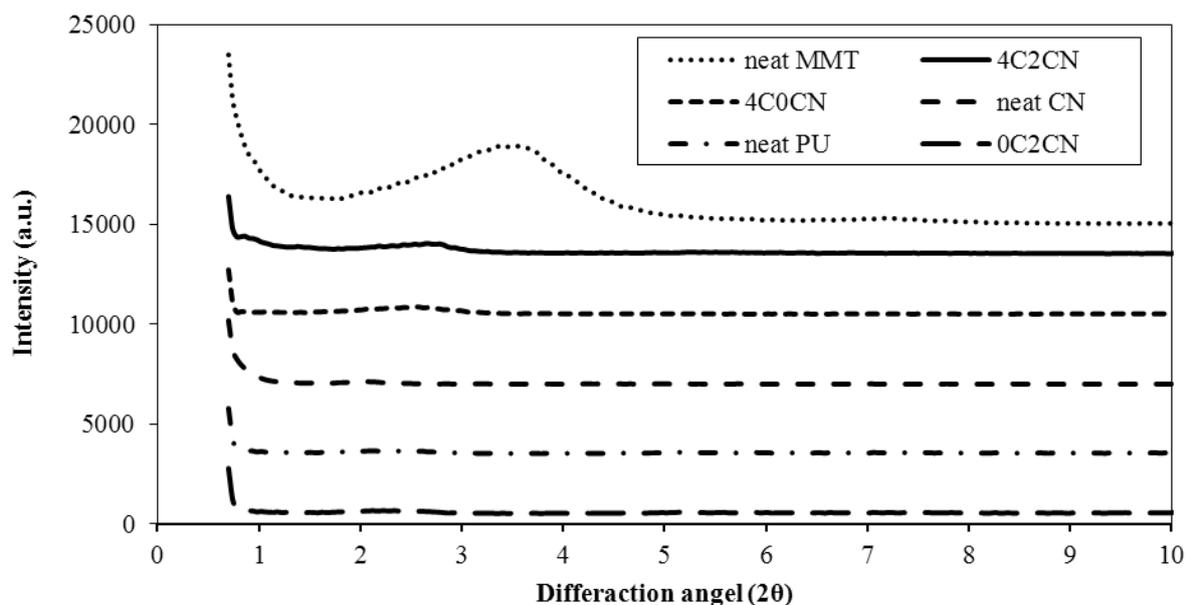


Figure 2

XRD patterns of the neat MMT, neat polyurethane, and polyurethane/cerium nitrate/MMT nanocomposites.

3.4. TEM

Figure 3 shows the TEM images of the 4C2CN sample, where the dark areas show clay platelets and the gray areas represent the polymeric matrix. The dominant morphology was intercalation. The main reason for this morphology was the method of nanocomposite preparation (Malucelli et al., 2009). The morphology plays an important role in the properties of the final nanocomposite (Giannelis et al., 1996; Fornes et al., 2001). According to the TEM results, it can be concluded that the method used for nanocomposite preparation was an acceptable method for stacks decrease. The separation of clay layers indicates the intercalation of clay layers. Platelet spacing indicated by TEM images shows that the trend was confirmed by the XRD results.

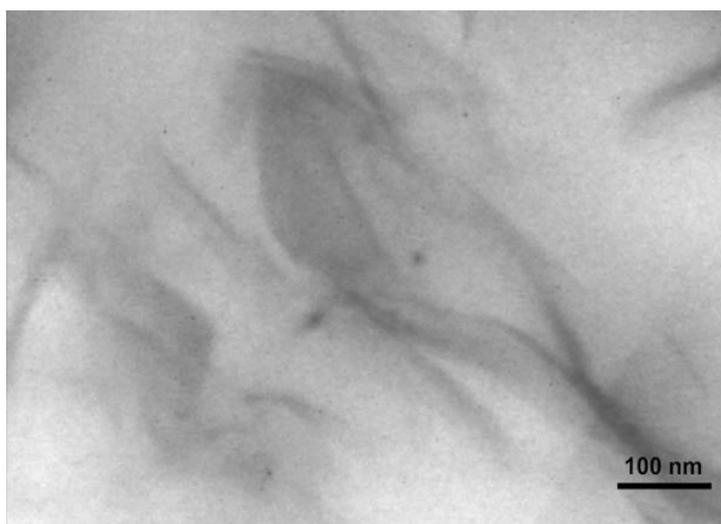


Figure 3
TEM micrographs of nanocomposite 4c2cn.

3.5. Tafel polarization study

The corrosion protection of the nanocomposite coatings on mild steel plates was evaluated by Tafel extrapolating method. This was carried out through the determination of polarization resistance (R_p) and corrosion current (I_{corr}) after the immersion of the coated samples in a 3.5 wt.% NaCl solution for 20 days. The Tafel diagrams of the different scratched coatings for 20 days are shown in Figure 4. Tafel calculations are listed in Table 3, where I_{corr} , CR , β_a , β_c , and R_p are the corrosion current, corrosion rate, anode Tafel constant, cathode Tafel constant, and polarization resistance respectively. It can be noticed from Figure 4 and the results presented in Table 3 that the coating with 4 wt.% nanoclay and 2 wt.% cerium nitrates has the lowest I_{corr} and thus the best corrosion resistance, which, as mentioned before, could be a result of the increase in the tortuosity of the diffusion pathways of water and oxygen molecules due to the presence of the clay and cerium nitrate; it appears that the action of particles as barrier to corrosive attacks can also be responsible for increasing the corrosion resistance of nanocomposite coatings.

Table 3

Polarization plots obtained after different times of immersion in a 3.5% NaCl solution after 20 days.

| Sample | $I_{corrosion}$ | β_c | β_a | R_p | CR |
|--------|------------------------|-----------|-----------|---------------------|------------------------|
| 0C0CN | 9.749×10^{-7} | 0.066 | 0.202 | 2.956×10^3 | 1.145×10^{-2} |
| 2C2CN | 7.978×10^{-7} | 0.076 | 0.275 | 5.696×10^3 | 9.370×10^{-3} |
| 3C2CN | 5.745×10^{-7} | 0.086 | 0.286 | 9.289×10^3 | 9.748×10^{-3} |
| 4C0CN | 1.020×10^{-6} | 0.087 | 0.289 | 5.353×10^3 | 1.198×10^{-2} |
| 4C1CN | 4.722×10^{-7} | 0.093 | 0.325 | 1.397×10^4 | 5.547×10^{-3} |
| 4C2CN | 1.243×10^{-7} | 0.088 | 0.216 | 3.319×10^4 | 1.460×10^{-3} |
| 4C3CN | 3.935×10^{-7} | 0.074 | 0.209 | 8.518×10^3 | 4.622×10^{-3} |

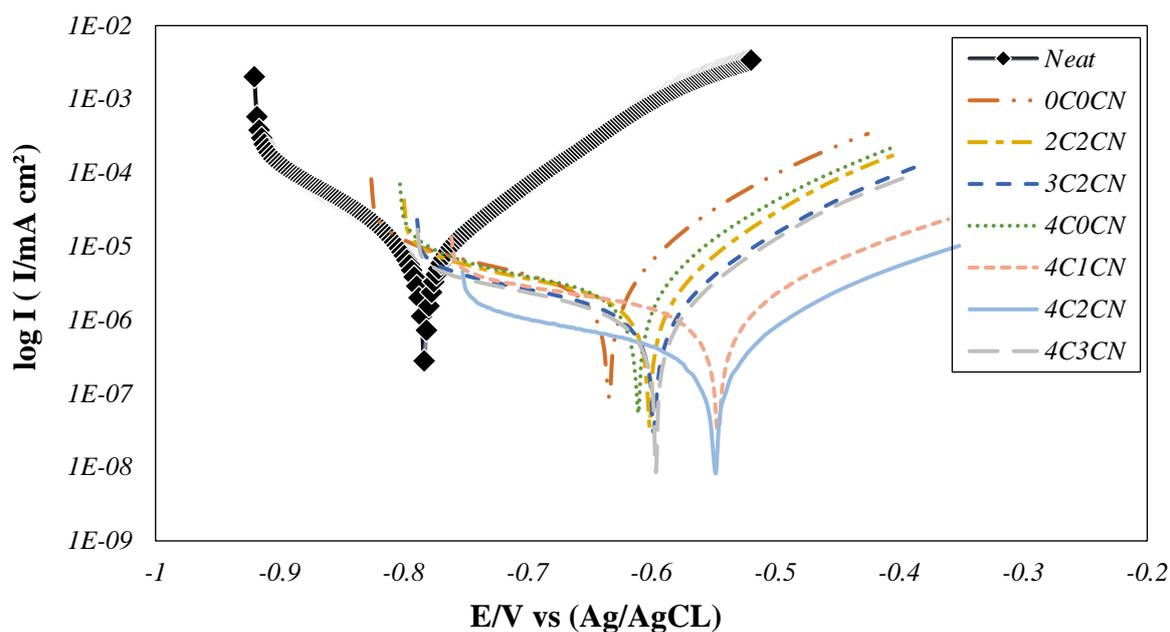


Figure 4

Tafel polarization curves measured after 20 days immersion in a 3.5 wt.% NaCl solution.

3.6. Pull-off test measurements

Pull-off adhesion test method was employed to determine the adhesive strength of the coating. In this way, adhesion is quantified in terms of the forces employed to detach the test dollies glued to paint film from the underlying metal. Table 4 shows the results of the adhesion tests for the coated samples prior to exposure and those removed at the end of 1000 hours of exposure. In the case of pull-off adhesion test, before the exposure of the coated sample to a corrosive environment, it was observed that almost all of the nanocomposite coatings had good adhesion to carbon steel, and amongst them, 4C2CN had the best performance. Table 4 shows that as nanoclay and cerium nitrate increase, adhesion in the nanocomposite increases. This improvement in adhesion may be due to the fact that nanoclay fills the voids and crevices in the steel substrates and the polymeric matrix, and thereby improving the adhesion between the coating and the substrate (Allie et al., 2008).

Generally, the forces needed to detach the film from the samples exposed to a 5 wt.% NaCl aqueous solution was smaller than those measured for the non-exposed samples, as shown in Table 4. Such a decrease is quite significant for the pure PU, whereas it is very small in the case of the PU/MMT/cerium nitrate nanocomposite coatings. Moreover, the reduction percentage in the nanocomposite coatings adhesion is decreased as the clay concentration is increased. As it was concluded from the previous results, the penetration of water molecules and aggressive ions are decreased by the incorporation of clay layers into the PU matrix. Hence a high reduction in neat PU adhesion to substrate may be due to the penetration of molecules into the coating, which can loosen the adhesion of the coating to the substrate and deteriorate other mechanical properties of the coating. Furthermore, the release of Ce (III) and the prevention of electrolyte from touching the uncoated area of the substrate is the other factor affecting the adhesion improvement (Nematollahi et al., 2010). This effect is decreased by increasing the cerium nitrate loading up to 2 wt.% in the PU matrix. Table 4 also shows that the wet adhesion of the coating containing 3 wt.% cerium nitrate is lower than that of the coating containing 2 wt.% cerium nitrate. This indicates that an excess of cerium nitrate in the film

leads to a negative effect on the interfacial adhesion, and a premature film delamination from the substrate happens (Turner et al., 2002).

Table 4

Pull-off adhesion test results (the data are expressed as the stress required to detach the film from the metallic substrate in MPa).

| Sample characteristic | Before exposure | After 1000 hours | Decrease in Adhesion (%) |
|-----------------------|-----------------|------------------|--------------------------|
| 0C0CN | 10.9 | 7.45 | 31.65 |
| 0C2CN | 11.73 | 10.61 | 9.54 |
| 2C2CN | 11.65 | 10.44 | 10.38 |
| 3C2CN | 12.02 | 11.21 | 6.73 |
| 4C0CN | 11.23 | 10.12 | 9.88 |
| 4C1CN | 12.16 | 11.19 | 7.97 |
| 4C2CN | 12.67 | 12.06 | 4.81 |
| 4C3CN | 11.98 | 11.22 | 6.34 |

4. Conclusions

1. The results of the optical microscopy and sedimentation test indicated that the sonication process was an effective method to separate nanoparticle stacks and prevent agglomeration, and thereby forming a stable suspension.
2. The results of the XRD and TEM indicated that the clay particles were dispersed and intercalated but not fully exfoliated into the PU matrix.
3. The results of a series of Tafel tests showed a superior corrosion protection on carbon steel panels compared to that of neat PU. Also, the addition of cerium nitrate into the polyurethane demonstrated good corrosion inhibition on carbon steel substrates and improved the resistance of scratched areas against corrosion.
4. The presence of nanoclay and cerium nitrate decreased the penetration of corrosive agents and corrosive solution, and it enhanced the wet adhesion of the coating to substrate (7.45 MPa in the neat polyurethane compared to 12.06 MPa in the 4C2CN sample nanocomposite).
5. The steel panels coated by the nanocomposites containing 4 wt.% MMT and 2 wt.% CN showed the highest corrosion resistance among the coating formulations.

Nomenclature

| | |
|-----------------|------------------------------------|
| β_a | : Cathodic Tafel constant |
| β_c | : Cathodic Tafel constant |
| CN | : Cerium nitrate |
| CR | : Corrosion rate |
| $I_{corrosion}$ | : Corrosion current |
| MMT | : Montmorillonite |
| PU | : Polyurethane |
| R_p | : Polarization resistance |
| TEM | : Transmission electron microscopy |
| XRD | : X-Ray diffraction |

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