Development of steel coatings reinforced with nanoclay particles for corrosion and wear protection

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Abstract. During the last years, clay nanocomposites have attracted a lot of attention among research and industrial community. Recently, due to their great potential diverse fields, nanoclay reinforcements have been identified as interesting materials for a wide range of applications, such as additives in coatings, paints, inks and greases, as rheological modifiers, oil refining, catalyst, biocomposites, and thermal dissipators, among others. Montmorillonite (MMT) is a crystalline hydrous phyllosilicate (layer silicate), a clay fraction of soil which is one of the most important species of clays. MMT nanocomposite coating was fabricated by uniformly dispersing laminar nanoclay structures within enamel painting. In the present work, we evaluate the anti-corrosion and tribological performance of coatings reinforced with MMT nanoclay at various filler fractions, 0.1wt.%, 0.5wt.% and 1.0wt.% Samples were evaluated on a salt spray (fog) chamber according to ASTM B117. Nanocoatings evaluation was performed according to ASTM D714; nanoclay reinforcement at 0.5wt.% improved up to 290% the corrosion resistance without any painting detachment, also improving ~320% after displaying blistering on the surface, as compared to base painting, respectively. This is representative of the significant enhancement as a protective corrosion barrier of the nanopainting. Tribological evaluation was performed with a pin-on-disk tribotester, according to ASTM G99, to determine the anti-wear properties of the nanocoatings. Improvement in all nanocoatings concentrations was achieved, being the highest enhancement by the 0.10wt.% MMT nanocoating, which exceeded the conventional paint by ~150%. This work gives a broad scope of opportunities for nanoclays reinforcing coatings and paintings for improvements on anti-corrosion and anti-wear performance, being a natural and environmentally friendly material.

1.Introduction
Corrosion is a critical issue on metals, which leads to its deterioration, caused by the interaction with the environment. Nowadays, with aid of Nanotechnology, nanocoatings are one of the emerging developing areas growing towards the solutions for design and fabrication of diverse types of surface protections with superb performance and improved durability at lower cost. Furthermore, nanocoatings provide great insight for implementing diverse and novel functionalities, enabling the possibility to develop and obtain innovative properties and characteristics through engineering smart multifunctional coatings [1–5].
Anticorrosion coatings provide a barrier which interacts between the metal’s surfaces and protects it from the environment. Corrosion could be driven by diverse external factors, such as temperature, moisture and chemical agents in the ambient, among others. These factors promote the generation and development of defects, such as microvoids, grain boundaries and cracks, which deteriorate the protective barrier effect of the coatings. According to Abu-Thabi et al. [6] this deterioration effect is more marked with traditional organic coatings that are reinforced with macroscale structures, leading to a large phase segregation among the solid inorganic macrostructures and the organic liquid phase in the formulated coating dispersions.

Functional surface coatings (whether organic, inorganic or hybrid) are a class of materials that can be tailored for many applications in which they should be able to perform well-defined array of functions. Organic coatings for instance, are widely applied for protection due to their relatively low-cost and easy application [7]. These coatings act as a physical barrier layer that prevents the penetration of corroding material or particles. Additionally, they serve as a reservoir for corrosion inhibitors which aid the coating for a more effective protection [8]. However, due to problems with toxicity associated with reinforcement particles commonly used, several studies have been developed to achieve more environmentally accepted coatings [9–11].

Generally, in industry, oil-based paintings show good processability, excellent chemical resistance and strong adhesion. However, they have the disadvantage to be brittle and sensitive to fracture toughness [8]. Outstanding improvements on physical and mechanical properties can be achieved with the addition of nanoparticles [4,12–15]. Carbon nanotubes presented potential applications due to its typical structure with high aspect ratio and anisotropic structure. However, its applications dramatically decreased because of their high production cost and synthesis. Instead, clay nanocomposites have gained attention as a cheap and biodegradable alternative, showing considerable improvements on mechanical performances, thermal stability, and barrier protection. On which low filler fraction (< 5%) have reported significant improvements [9,16,17] Noticeable performance of nanoclays is highly related to their morphology. Montmorillonite (MMT) consists of nano-layers structure that work as barriers, enhancing water retardation [17]. In this project, the effects of MMT as reinforcing agent on oil-based paint were studied under extreme corrosion environments and tribological applications. Samples preparation, tests parameters and results evaluation were done according the ANSI A250.3-2007 standard [18].

2. Materials and methods
An oil-based paint was used as matrix (see table 1). It was reinforced with nano-MMT on three different filler concentrations: 0.1wt.%, 0.5wt.% and 1.0wt.%, supplied by Sigma-Aldrich. Nanostructures were homogenously dispersed for 3–4 hours via water bath sonication [19]. Xylene was used as reducer between 10-15% for proper viscosity and drying time. Drying time was 25-30 minutes. Steel substrates (plates) were prepared according to ASTM-D1654 standard [20] for extreme corrosion environment evaluations and according to ASTM-G99 [21] for tribological evaluations, as well. Specimens were painted by air spray method. Coatings thicknesses were between 305 – 350 microns.

Salt-fog spray chamber complying with ASTM-B117 standard [22] was used for environment evaluations. Samples were exposed to 5% sodium chloride vapor (NaCl) concentrated fog at 30°C for 500 hours and revised periodically for further evaluations. ASTM-D610 [23] and ASTM-D714 [24] standards were followed for corroded area percentage and blister impact evaluation, respectively.
For tribological performance, pin-on-disk tribometer [16] was used to evaluate samples accordingly to ASTM-G99 wear procedures and further evaluations of coating behavior and wear velocity were obtained.

Table 1. Material properties.

| Materials          | Properties                     |
|--------------------|-------------------------------|
| **Coating**        |                               |
| Oil-based paint    | Density (25°C)                |
|                    | 1.07 g/cm³                    |
| **Substrates**     | Chemistry (mass, %)           |
| Steel plates       | C  max                         |
| Complex Phase      | Si  max                       |
|                    | Mn  max                       |
|                    | P  max                        |
|                    | S  max                        |
|                    | Cr  max                       |
|                    | Al  min                       |
| Montmorillonite    | Morphology: Laminar,          |
| (MMT)              | Aspect Ratio: 10 - 2000       |
|                    | Size: 1 – 200nm wide,        |
|                    | 2 μm length,                 |
|                    | Hardness: 1.5 - 2 Mohs        |

3. Experimental details

3.1. Specimen preparation

Steel substrates were prepared according to ANSI A250.3-2007. For corrosion evaluations, steel plates were cut from commercially purchased high quality complex phase steel at 6in by 4in (15cm by 10cm). The pretreatment of the surfaces of the specimen is also considered as an important step before the painting deposition in order to obtain a uniform coating. The substrates were sanded with 200-grit, 500-grit, 800-grit and 1200-grit sandpaper, removing remaining oxides and to obtain a smooth surface for better painting adhesion. The samples were then kept in a desiccator to avoid rusting or contamination. Similarly, specimens for tribological evaluations were prepared. A 1in (2.54cm) diameter disk-type samples were machined, and the same protocol as for steel plates was followed.

3.2. Spray coating

The spray material was prepared by stirring the paint for 30 min. MMT nanoparticles were added to the oil-based paint at various filler fractions (0.10wt.%, 0.5wt.% and 1.0wt.%) in 250ml containers. Subsequently, extensive water bath sonication (3-4 h) was used to homogeneously disperse the MMT nanostructures within the oil-based paint. Afterwards, xylene solvent was applied on the steel substrates to eliminate any contaminants or residue on the surfaces. Supplier recommended using 10-15% of the solvent to dilute the paint and obtain a proper viscosity to apply an optimum spray-coating process. A regular fan-type nozzle spray gun was used to paint the steel substrates. In order to obtain a proper thickness, testings applying diverse coating layers to be performed to measure the optimum variables for coating process. After these preliminary evaluations, painting variables were obtained: compressor pressure: 300kPa, distance from the nozzle to the steel substrate: 12in. (30.5cm), 4 layers per surface for 3 seconds, each. Lastly, a drying time of 24h is required, as minimum. It is highly recommended for specimens to be held for 72h before running evaluations.

3.3. Thickness measurement
The thickness of the nanocoatings was measured with a dry film thickness gauge (Elektro Physik MiniTest 600). The prepared thin films were uniform, smooth and had good adhesion to the steel substrate surfaces.

3.4. Salt spray evaluations
The salt spray fog corrosion test (ASTM-B117) was carried out in a chamber (Harshaw Filtrol, model GS-SCH#22) to evaluate the coating performance in a saline environment. Samples were subjected to 1000h of exposure to salt spray at 5% sodium chloride vapor (NaCl) concentrated fog at 30°C and revised periodically for further evaluations. ASTM-D610 [23] and ASTM-D714 [24] standards were followed for corroded area percentage and blister impact evaluation, respectively.

3.5. Tribological evaluations
For tribological performance, pin-on-disk tribotester [16] was used to evaluate specimens accordingly to ASTM-G99 wear procedures (table 2). Coating behavior and wear velocity were obtained. Wear scars were characterized with an Alicona IF-EdgeMaster optical 3D surface measurement system. Surface roughness profiles and 3D images of the blocks for each nanocoating are shown. Five replicas were evaluated by each set of testings.

Table 2. ASTM G99 tribology test parameters.

| Parameter                  | Unit  |
|----------------------------|-------|
| Load                       | 25 N  |
| Distance traveled          | 100 m |
| Testing time               | 1000 sec. |
| Angular Velocity           | 238 RPM |

4. Results and discussion
4.1. Corrosion evaluation: Blisters
During corrosion evaluation, coatings on steel substrates were analysed according to ASTM D714 standard. With this quantitative method, blisters size and density were observed and compared among the diverse nanocoatings and the oil-based paint. Furthermore, an important aspect of this analysis is the blister appearance and coating detachment from the steel substrate (figure 1).

[Figure 1. Blisters appearance and coating detachment under salt-fog spray evaluation.]

On this analysis it is observed that bare oil-based paint by 68h blisters appear and by 116h detachment of the coating was shown. For the 0.1wt.% MMT nanocoating, blisters also begin to appear at 68h exposure, however, coating damage was presented after 332h. Meanwhile, the highest performance was for the 0.5wt.% MMT nanocoating. In this case, blisters appear in the vicinity of 284h, and withstands up to 452h until coating initiates to detach, which represents a 290%
improvement, compared to bare paint. As seen on figure 1, for the 1.0wt.% MMT nanocoating blisters begin to appear at 236h, and coating detachment appear at 404h (248%, compared to bare paint).

4.2. Corroded Area
Degree of rusting was evaluated according to ASTM D610. Figure 2 shows representative surfaces of the steel substrates (coupons) that were evaluated up to 1000h.

![Figure 2](image)

**Figure 2.** Representative Steel plates substrates a) before starting corrosion evaluations, b) starting of blisters appearance and c) painting detachment.

On figure 3 it is shown that the base painting steel plates totally corroded in 500h. Furthermore, all the MMT-reinforced paintings withstand +400h until corrosion was present on the surfaces. Even though, the evaluations were taken up to 1000h (See inset on figure 3), the best performance was observed for the 0.5wt.% MMT nanopainting, which after 836h, presented a ~40% of corroded area on the steel coupons. This is reflected as ~250% improvement, compared to the bare paint at the same corroded level.
Figure 3. Time lapse ad corroded area of nanocoatings; inset shows a more detail performance of nano-MMT reinforcement on oil-based coating.

4.3. Tribological evaluation

Coatings wear resistance is another essential property for optimum performance of these systems. On this evaluation, all MMT nanocoatings showed excellent results, compared to oil-based paint. As previously mentioned (table 1), the testing time is set to 1000s., each evaluation is finished once the pin damage or breaks the coating and metal to metal start to interreact. Figure 4 shows the wear scar on the evaluated steel substrates (left side) as well as the 3D surface roughness measurements (right side).

Figure 5 shows the results on duration time of the wear behavior of MMT nanopaint. Here, the 0.1wt.% MMT nanopaint withstand longer of the nanopaints, improving ~170%, compared to base painting. It has to be noted that the evaluation time was stopped once the coating was damage or cracked, and metal to metal start to interreact.

Wear velocity is another critical aspect on the coating resistance to be scratched or damaged. It allows us to know the wear rate upon exposed movement of contact pairs. As lower wear velocity, highest would be the functional coating performance. From figure 6, it is observed that all MMT nanopaintings showed better behavior as compared to bare painting.
Figure 4. Top view of wear scars and 3D images of blocks and surface roughness of steel substrates: a) bare oil-base coating, b) at 0.1wt.%MMT, c) at 0.5wt.%MMT and d) at 1.0wt.%MMT.
5. Conclusions
Monmorillonite nanoreinforcements were incorporated to conventional oil-based paint for automotive components. On corrosion evaluation, even though 0.1wt.% MMT nanocoating presented blisters at the same level (hours) of saline environment exposure, it withstands up to 332h until damage was presented, representing ~180% increase, compared to bare oil-paint. The best performance was for the 1.0wt.% MMT nanocoating, which presented a ~250% improvement, compared to bare paint as well. On the corroded area analysis, oil-based paint totally decompose at 500h, meanwhile, all MMT nanocoatings withstand that mark without significant damage. The 0.5wt.% MMT performed better, for instance, after 836h, it presented a ~40% of corroded area, which means a ~250% improvement, compared to bare paint at the same corroded level.

On the tribological evaluation, it was clear that MMT reinforcement enables the wear characteristics of the oil-based paint. For instance, 0.1wt.% MMT nanopaint showed an enhancement of ~170%, compared to base paint, on the duration time of the coating. Here, wear velocity also plays a critical role, where all MMT nanopaintings showed significant improvements as well.
In summary, MMT nanoclay which is inexpensive, easy to handle, and environmentally friendly material, is suitable as reinforcement of coatings for wear and corrosion properties.

6. References

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