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Polymer-Clay Nanocomposites for Corrosion Protection

Abdullah Al-Shahrani, Ihsan Taie, Aziz Fihri and
Gasan Alabedi

Additional information is available at the end of the chapter

Abstract

Nanoclays have evoked a great deal of attention lately for the preparation of novel nano-composite materials for several applications. This is attributed to their lamellar structures, which are distinguished by having high in-plane strength and stiffness, as well as a high aspect ratio. Nanocomposites have exhibited an advanced gas and water barrier properties compared to the pristine polymers. Such advancement plays a major role in enhancing the coating industry, specifically for corrosion protection. One main factor attributing to coating failure is its inability to maintain low water and oxygen permeability thought its service life. The penetration of these elements through the coating leads to corrosion initiation under the coating. The addition of clay to polymeric coatings has great potential to improve the corrosion protection performance of the coatings. This chapter will present the recent advancement in the preparation and utilization of clay nanocomposites as enhanced coatings for corrosion protection.

Keywords: clay, nanocomposite, organic coating, corrosion protection

1. Introduction

The function of a good coating on the metallic surface is to provide a physical barrier, preventing the metal to be in direct contact with the environment. Generally, the main principle to prevent corrosion is to eliminate one of the four main components causing the corrosion process (anodic reaction, cathodic reaction, electrolyte, and electrical connection between the cathode and the anode) [1]. Until about 1950, coatings were believed to act as a barrier, preventing water and oxygen to reach the metal. These two species are needed to drive the

oxygen reduction reaction (cathodic reaction) that initiates the corrosion process. In 1952, Mayne found that the diffusion rate of water and oxygen in an unpigmented coating is too high. Consequently, he suggested that the amount of water and oxygen arriving at the metal/coating interface is greater than the one required for corrosion to precede [2–4]. His hypothesis was based on the fact that the barrier action could not explain the effectiveness of the coating, while the conductivity of the coating is the main factor controlling the corrosion protection degree offered by the coating [2, 5, 6]. Mayne also reported that when the coating is immersed in a solution, it will gain a certain charge, negative or positive, depending on the nature of the coating. In this case, the coating will allow the opposite charge species to pass through. He believed that the permeation of these species will be through the bulk of the matrix. Corti attributed that the permeation of such species is affected by the presence of pores or imperfections in the coating. Based on that, he concluded the permeation to be through the pores and voids in the coating [2, 3]. Funke has a different understanding to the way the coating works to protect the steel. He believed that the protection degree that the coating offers depends on the degree of adhesion. The permeation of water through the coating will result in a water accumulation between the substrate and the coating, leading to coating blistering or coating delamination as a result of generating hydroxyl ions as products of the corrosion process. Such ions are believed to break the bond between the coating and the metal surface, and consequently, the coating adhesion will be significantly degraded [2, 7, 8]. Considering all the above approaches, loss of adhesion, the diffusion of water and oxygen, and the transport of the charged species can potentially result in poor corrosion protection performance. In general, mass transfer (diffusion) of a material in a specific environment is a result of a natural process tending to reach equality in concentration between two points. In the case of gases, the diffusion process will be mainly based on the difference in partial pressure, which is the driving force pushing the gasses from one side to another.

In case of polymeric coatings, the diffusion process will mainly depend on three factors: the nature of the polymeric coating, the magnitude of the driving force, and the nature of the diffusing species. The general mechanism of the permeability through the coating will follow three main steps: solution of small molecules in polymer, migrating through the polymer, and emergence of that molecule at the outer surface. Accordingly, the permeability can be presented mathematically as the product of solubility and diffusion as shown in Eq. (1) [9, 10]:

$$\text{Permeability} = \text{Solubility} \times \text{Diffusion (Henry's Law)} \qquad (1)$$

When a coating is exposed to an electrolyte, the diffusion of the electrolyte follows two processes, which can be classified as fast and slow diffusion [11]. The fast process can occur within a few minutes of exposure, while the slow step can take weeks or months. According to Scantlebury, during the fast process, the electrolyte can reach the surface of the metal, but its electrical properties do not support the corrosion process, while the amount of electrolyte can reduce the adhesion strength of the coating [3].

There are many factors affecting the diffusion of the electrolyte and the corrosive species, namely water and oxygen. Considering the fact that the permeability of a coating depends on the amount of defect present, it can be concluded that the diffusion will be through areas of imperfection. These areas can be considered as free volume including pores and area of

weak cross-linking density. The free volume concentration increases, as the temperature goes above the glass transition temperature (Tg) of the coating. Tg is known as the temperature at which the coating state changes from glassy or solid state to a rubbery state. Above the Tg, the energy of the coating molecules increases, leading to an increase in the movement of these molecules. As a result of this, the free volume can increase, providing more areas for the diffusing species to transport through the coating. Based on that, it is highly recommended to select a coating having Tg higher than the temperature of the process [2, 10]. Film thickness has a great effect on the permeability of the coating. As the film thickness increases, the penetration of the corrosive species through the coating can be delayed. Increasing the film thickness above a critical thickness can increase the probability of having cracks in the coating [2]. Certain pigments have a significant effect on the permeability of coating. It is believed that water and oxygen cannot pass through pigment particles; therefore, the permeability can be reduced with increasing the pigment volume concentration (PVC). The PVC value should not exceed the critical pigment volume concentration (CPVC). Above the value of CPVC, the pigments will introduce voids and gaps inside the coating. These defects can provide an easy way for water and oxygen to go through [2]. It was reported that the pigmentation of inert particles such as nanoclays inside the coating can act as a barrier to reduce the diffusion rate of water and the oxygen through the polymer-clay nanocomposite coatings.

The nanoclays have evoked a great deal of attention lately for the preparation of novel nanocomposite materials for several applications [12]. The uniform dispersion of the layered silicates into polymers matrix leads to the preparation of nanocomposites with improved mechanical properties, thermal stability, and low flammability [13, 14]. This is attributed to their lamellar structures, which are distinguished by having high in-plane strength and stiffness, as well as a high aspect ratio [15]. Additionally, the clays possess excellent stability and low toxicity, and they are cheaper and widely available compared to other nonorganic fillers. Such advancement plays a major role in enhancing the coating industry, specifically for corrosion protection [16, 17]. One main factor attributing to coating failure is its inability to maintain low water and oxygen permeability throughout its service life. The penetration of these elements through the coating leads to corrosion initiation under the coating. The addition of clay to polymeric coatings has great potential to improve the corrosion protection performance of the coatings. This chapter will present the recent advancement in the preparation and utilization of polymer-clay nanocomposites as enhanced coatings for corrosion protection.

2. Structure of layered silicates

The most commonly used layered silicates to produce the polymer-clay nanocomposites belong to a group of clays classified as 2:1 layered or phyllosilicates [18]. This structural family includes natural clays, such as montmorillonite, hectorite, and saponite. Their crystal structure consists of two-dimensional layers made up of two tetrahedral silicon sheets fused to octahedral sheet of alumina or magnesia by the tip so that the oxygen ions of the octahedral sheet also belong to the tetrahedral sheets. The layer thickness of a sheet is of the order of 1 nm, and the lateral dimensions vary from 300 Å to several microns depending on the

specificity of the silicate. The relatively weak Van der Waals force ensures the stacking of the sheets between them and each layer called interlayer [19–21]. Stacking of the layers leads to a regular gap between each adjacent silicate layers called the interlayer or gallery. A negative surface charge is present on the layers due to the isomorphic substitution of tetrahedral silicon or aluminum and octahedral magnesium. The charge deficit is counterbalanced by alkali and alkaline earth cations situated inside the galleries [22].

The most used layered silicates are montmorillonite, hectorite, and saponite [23]. Their chemical formulae are illustrated in the **Table 1** [24]. All these layered silicates are characterized by a high surface area (700–800 m²/g in the case of montmorillonite) and a moderate cation-exchange capacity (CEC) generally expressed in milliequivalents per 100 g (mequiv. per 100 g). The charge indicated by the chemical formula is an average over the whole crystal because the charge varies from layer to layer. Only a small proportion of the charges are located at the surface of the crystal, the majority being mainly in the interlayer spaces [22]. These cations are then exchangeable in solution.

To produce the nanocomposite with the required properties, the silicate layers should be exfoliated before being dispersed inside the polymer. Indeed, the hydrophilic characteristic of the clay does not allow it to be dispersed in the polymer matrix, which is generally organophilic. To render the mixture compatible, it is necessary to modify the clay before it is dispersed. For this reason, a pretreatment process should take place to weaken the forces holding the structure [24–27]. The main goal of this process is to render the surface of the layered silicate more organophilic. This improves the dispersion process of the layers inside the polymer under well-defined experimental conditions [28]. Given the structure and properties of clay, there are several modification techniques. However, the most commonly used technique for organophilic modification of clay is the ion-exchange reactions with cationic surfactants, including primary, secondary, tertiary, and quaternary alkylammonium cations to replace the hydrated cations with the protonated amine with long-chain alkylammonium cations. Alkylammonium cations in the treated clay decrease the surface energy of the inorganic host and increase interlayer spacing, rendering the modified organoclay is more compatible with organic polymer [29–33]. The above treatment process is basically an intercalating process to increase the spacing and decrease the adhesion forces between the silicate layers. The amine has the ability to achieve such target by acting as an intercalating agent. The efficiency of the intercalating agent is mainly influenced by the agent properties such as its hydrocarbon chain length [1]. It is very important to stress that there are also other original and interesting methods for modifying 2:1 phyllosilicates, such as the use of ionomers or block copolymers, and

Silicate	Chemical formula	Location of isomorphic substitutions	CEC (mequiv./100 g)
Hectorite	$M_x(Mg_{6-x}Li_x)Si_8O_{20}(OH)_4$[a]	Octahedral	120
Saponite	$M_xMg_6(Si_{8-x}Al_x)Si_8O_{20}(OH)_4$[a]	Tetrahedral	86.6
Montmorrillonite	$M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$[a]	Octahedral	110

[a]M = monovalent cation; x = degree of isomorphous substitution (between 0.5 and 1.3).

Table 1. General formula and characteristic parameters of phyllosilicates 2:1.

the grafting of organic substances, such as organosilanes. In the clay, the hydroxyl functional groups are located on the surface of the layers and their edges, and so the silane agents possess the ability to form strong covalently bonds with inorganic clays.

3. Nanocomposite structures

Variations in the strength of interfacial interactions between the polymer matrix and layered silicates result in the formation of three main kinds of nanocomposites as described below [34].

- **Intercalated nanocomposites**: When the polymer is not able to intercalate between the silicate layers, a biphasic composite is obtained, whose properties remain in the same range as the conventional microcomposites structure, in which the clay sheets are not swollen by the polymer and are in the form of clumps or agglomerates in the matrix.

- **Flocculated nanocomposites**: Conceptually, this is similar as intercalated nanocomposites. More polymer molecules are getting inside the layers structure to give more spacing between the silicate layers.

- **Exfoliated nanocomposites**: In this type of nanocomposite, the individual clay layers are separated in a continuous polymer matrix. Usually, the clay content of an exfoliated nanocomposite is much lower than that of an intercalated nanocomposite. The **Figure 1** shows illustrations of the three types of polymer-clay nanocomposites.

Despite the impressive progress that has been reported during the last few years regarding the use of polymer-clay nanocomposites for corrosion protection, its effect on the corrosion performance has rarely been investigated. Although most organo-modified clay nanocomposites
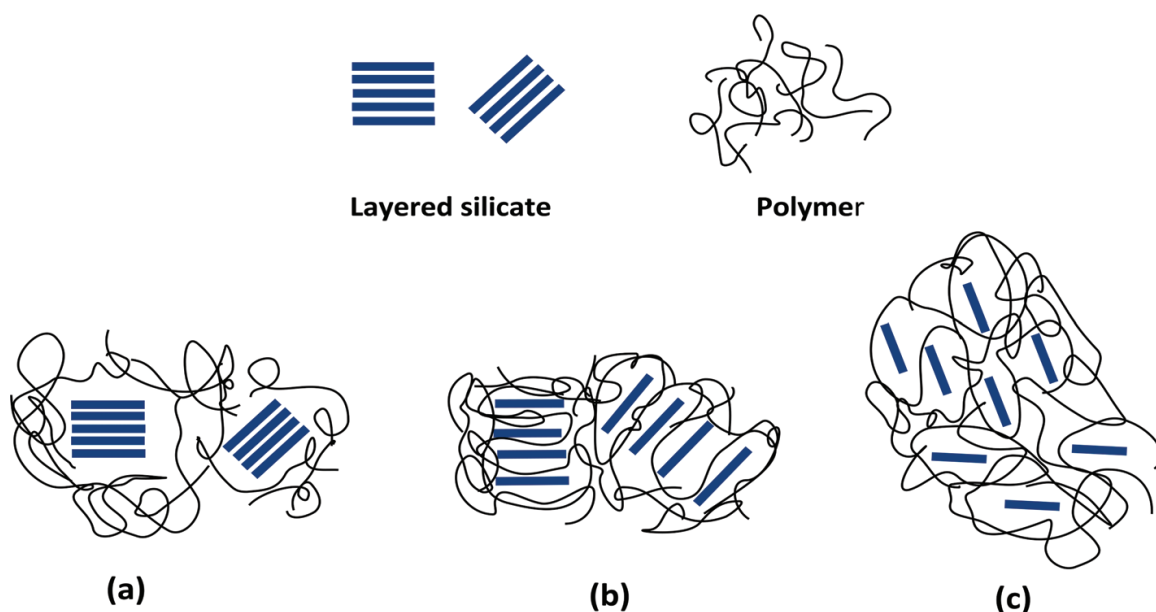

Layered silicate   **Polymer**

(a)   (b)   (c)

Figure 1. The main types of nanocomposite. (a) Intercalated, (b) flocculated, and (c) exfoliated.

reported so far are intercalated, exfoliated structures are more desirable in property improvement of the polymeric materials. In this context, Chen and co-workers described the processing of epoxy-layered silicate nanocomposites with different properties as corrosion resistant coatings on aluminum surfaces [35]. Based on their studies, they concluded that there is a slight enhancement in anticorrosion properties for the exfoliated nanocomposites coatings and no enhancement for the intercalated nanocomposites. Finding shows that these criteria are related to the better dispersion of silicate nanosheet in some epoxy matrix than the other grades of resin matrix. However, these findings were not very conclusive, and it appears that an epoxy with a lower barrier resistance or higher permeability will help in discriminating the corrosion behavior through the introduction of clay into the matrix. Similarly, Sakai and co-workers found that the exfoliated clay structures were more fixed in polymeric matrix compared to intercalated and conventional clay structures [36]. Additionally, exfoliated clay structures exhibited better corrosion performance compared to intercalated coatings nanocomposites. This is mainly attributed to the larger clay interlayer distance, smaller clay aggregate, and uniform homogeneity of exfoliated clay structures inside the epoxy matrix. In some case, a mixture of intercalated and exfoliated nanocomposites was obtained, and it was difficult to evaluate the effect of nanocomposite structures on the corrosion performance of the prepared nanocomposites [37].

4. Methods used for the synthesis of nanocomposites

Several methods were reported to prepare clay-based polymer nanocomposites. These include in-situ polymerization, melt intercalation, and solution casting, according to the starting materials and processing techniques:

1. **Intercalation of polymer from solution.** This is based on a solvent system, in which the polymer is soluble and the silicate layers are swellable. The layered silicate is first swollen in a solvent, such as water, chloroform, or toluene. When the polymer and layered silicate solutions are mixed, the polymer chains intercalate and displace the solvent within the interlayer of the silicate. Upon solvent removal, the intercalated structure remains, resulting in nanocomposite [38, 39].

2. **In-situ intercalative polymerization.** In this method, the layered silicate is swollen within the liquid monomers or a monomer solution so that the polymer formation can occur between the intercalated sheets. Polymerization can be initiated either by heat or radiation [40, 41]. This method technique was used to prepare nanocomposites based on polyamide, poly(e-caprolactone), polystyrene, polyolefien, and polyethylene terephthalate [41].

3. **Melt intercalation.** The melt intercalation involves annealing, statically or under shear, a mixture of the polymer and modified clays. This method has great advantages over either in-situ intercalative polymerization or polymer solution intercalation. Firstly, this method is environmentally benign due to the absence of organic solvents. Secondly, it is compatible with current industrial process [42, 43]. This process is widely used to design nanocomposites based on polyamide, such as polyethylene terephthalate and nylon 6 [12]. **Table 2** shows the advantages and the limitations of different methods used to prepare the polymer-clay nanocomposites.

Processing methods	Advantages	Limitations
Intercalation of polymer from solution	• More suitable at laboratory scale • Uniform dispersion of the clay particles inside the polymer • Preparation of intercalated nanocomposites based on polymers with low polarity	• Environmentally unfriendly due to the use of large amounts of solvents • Limited to certain polymer/solvent pairs, in which the polymer is soluble and the silicate layers are swellable
In-situ intercalative polymerization	• Easy method, based on the dispersion of the filler in the liquid monomer	• Monomer and clay must have similar hydrophobicity to mix • Limited applications • Suitable monomer is not always available • Difficult control of intragallery polymerization
Melt intercalation	• Environmentally benign • Compatible with industrial polymer process • Use of polymers not suited for other methods	• Limited applications to polyolefins • Organo-modified clay must be thermally stable at the softening point of the polymer

Table 2. Summary of different methods used for the synthesis of nanocomposites.

Concerning the characterization of polymer-clay nanocomposites, the small-angle X-ray scattering (SAXS), transmission electron microscopy (TEM), and scanning electron microscopy (SEM) are the main techniques used to identify the structure of nanocomposites. Indeed, the SAXS allows to monitor the position, shape, and the intensity of the peak, while TEM provides information on the spatial disposition of the internal structure and the spatial distribution of the various phases. SEM is employed to identify the response of the clays to the cationic exchange reaction.

5. Corrosion and organic coatings

Corrosion is defined as the gradual oxidation of metallic materials by converting them to their original state of oxide, sulfide, carbonate, or other stable salts in the ambient environment. Corrosion results from a combination of reactions occurring at the metal-solution interface by involving electrons and the chemical species. More specifically, the oxidation of the metallic material naturally occurs at the metal-environment interface and constitutes the anodic reaction, whereas the reduction of oxygen typically takes place in solution and often constitutes the cathodic reaction [44]. The cathodic and anodic reactions form an electrical circuit, which is completed by conduction of electrons in the metal and by ionic conduction through the electrolyte. There are various forms of corrosion that can take place depending on the surrounding environment and the design of the equipment that suffers corrosion. The galvanic, pitting, intergranular, crevice, and uniform corrosions are the most investigated corrosion

in the literature [45, 46]. In general, the corrosion protection methods commonly used are mainly organic and metallic coatings, inhibitors, cathodic, and anodic protection. This latter is relatively new, and it was first demonstrated and tested by Edeleanu 1954 [47].

The use of organic coatings on metal is usually an effective way to protect metal surfaces from corrosion while still preserving the desirable physical and mechanical properties of the metal [47, 48]. Corrosion on a bare metal surface is very complex process in itself, as the morphology of the corrosion layers formed on the surface and corrosion rate depends on several factors [49]. To evaluate the performance of any organic coatings, several parameters must be taken into consideration such as the permeability to water and oxygen, adhesion performance to the metal, coating thickness, ionic conductivity, as well as pore size distribution [50]. Commonly, the corrosion mechanism of an organic coating to protect the metal against corrosion can be divided into three groups: the electrochemical effect, the physicochemical effect, and the adhesion to the substrate [8]. The organic coating is a complex formulation of variety of materials each having a specific function. Examples of those materials include, but not limited to the following: polymeric materials, solvents, pigments, and various additives. Organic coating simply acts as a barrier between the metal surface and the surrounding environment. The barrier ability of such coating might be attributed to its structure or due to some additives or pigments implemented inside the coating. For this reason, understanding the nature and the constituents of the coating to be applied is essential to predict the performance of this coating as a corrosion protective technique. There are several reasons that can lead to failures in the coating applied, and the most common failures and the reasons leading to such failures are the permeability of the coating, adhesion, blistering, and cathodic delamination. Importantly, it was reported that a poor coating applied to a well-prepared surface is better than a good coating applied to a poorly prepared surface [51]. Contaminations on the surface of the metal can cause a direct failure to the applied coating. These contaminations can be the reason for a poor coating adhesion, which is one of the most critical factors controlling the quality of the coating. It is also well known and documented that no matter how good the coating is, the corrosion still can take place under the coating if the surface is contaminated.

6. Anticorrosive properties of layered silicate nanocomposites

It is well known that polymeric coatings are not permanently impenetrable, as the presence of defects in the coatings will lead to the formation of the pathways for the corrosive species to reach and attack the metallic surface, and a localized corrosion will be initiated. Various fillers such clays as were incorporated into the polymeric coatings to improve their barrier properties by reducing their permeability and increase the length of the diffusion pathways for oxygen and water species [52]. Indeed, the addition of clay as filler creates a maze that impedes the diffusion of corrosive molecules as illustrated in **Figure 2**. The use of clay as pigments appears to be one of the promising solutions to enhance the corrosion performance of nanocomposites. This section presents an overview on the recent advances of using of polymer-clay nanocomposites for corrosion protection.
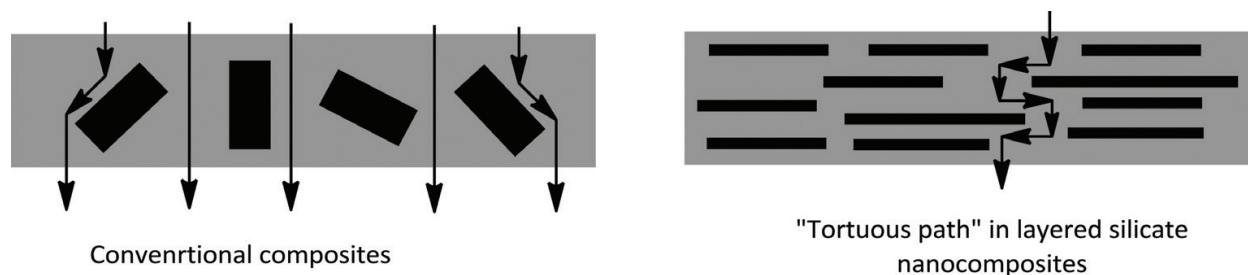
Convenrtional composites

"Tortuous path" in layered silicate nanocomposites

Figure 2. The difference between conventional composite and nanocomposites.

Different kinds of polymers were used to prepare nanocomposites coatings such as conjugated polymers and thermoplastic polymers [53]. Using the in-situ thermal polymerization, Yeh and colleagues prepared a series of polymer-clay nanocomposite by dispersing layered montmorillonite (MMT) clay into an organic poly(methyl methacrylate) matrix [54]. Firstly, methyl methacrylate monomers were intercalated into the montmorillonite that was exfoliated by cation-exchange reaction with quaternary alkylammonium cations or alkylphosphonium cations followed by a typical free-radical polymerization. The as-synthesized polymer-clay nanocomposites exhibited enhanced Tg compared to pure polymer. TEM analysis revealed that after the dispersion of the clay, the prepared nanocomposite displayed a mixed nanomorphology with well-exfoliated silicate layers into the polymer matrix. The electrochemical measurements using polarization resistance, corrosion current, and impedance spectroscopy revealed that nanocomposites coatings with the low clay loadings (e.g., 1 wt%) exhibited better anticorrosion protection for steel compared to the pure poly(methyl methacrylate). In an independent study, the same group has also designed several nanocomposite materials containing polyaniline (PANI) and layered montmorillonite clay and investigated their corrosion performance for cold-rolled steel [55]. Firstly, the organophilic montmorillonite was prepared via cation-exchange reaction with cocamide-propylhydroxysultaine before being mixed with aniline monomers in diluted hydrochloric acid followed by one-step oxidative polymerization. TEM analysis of as-synthesized nanocomposite revealed that the prepared materials possessed mixed nanomorphology, and the silicate layers were found to be well dispersed in the polyaniline matrix. The electrochemical measurements of potentiodynamic (e.g., Tafel plots) of a series of polyaniline nanocomposites with varying clay loadings at room temperature are illustrated in **Table 3**. Electrochemical corrosion current values of polyaniline nanocomposites were found to be decreasing progressively with further increment in clay loading. Importantly, visual inspection of the corrosion products revealed the presence of grayish oxide layer formed over polyaniline nanocomposites, showing better corrosion performance. It is very important to stress that the incorporation of the montmorillonite in polyaniline matrix resulted in a decrease in mechanical strength and in thermal decomposition temperature. This could be attributed to the significantly decreased molecular weight of polyanilines formed in the montmorillonite. Same research group evaluated the effect of adding organo-modified clay on the corrosion protection performance of conducting polymer/layered silicate, such as poly(o-methoxyaniline) and poly(3-hexylthiophene) [56]. The experimental findings revealed that the conducting polymer/layered silicate nanocomposites with low clay loading (3 wt.%) were found exhibiting better anticorrosion properties compared to the pure conducting polymer.

Compound code	Feed composition (wt.%)		Inorganic content found in the product (wt%)[a]	Electrochemical corrosion measurements[b]			
	PANI	MMT		E_{corr} (v)	R_p (KΩ cm^2)	$I_{corr \times 10}^{-6}$ (A/cm^2)	R_{corr} (mm/year)
Bare	—	—	—	−0.641	0.8	44.4	86.1
PANI	100	0	0	−0.590	3.4	12.0	23.3
CLAN0.25	99.75	0.25	0.70	−0.581	13.7	2.9	5.6
CLAN0.5	99.25	0.50	1.50	−0.568	15.4	2.7	5.2
CLAN0.75	99.00	0.75	3.80	−0.555	20.0	2.4	4.5
CLAN1	99.00	1.00	4.70	−0.551	36.2	1.1	2.1
CLAN3	97.00	3.00	7.10	−0.543	57.9	0.5	1.0

[a]As determined by thermogravimetric analysis.
[b]Saturated calomel electrode was employed as reference electrode.

Table 3. Relations of the composition of polyaniline (PANI)-MMT clay nanocomposite materials with the E_{corr}, R_p, I_{corr}, and R_{corr} measured from electrochemical methods[a].

In a subsequent study, the same research group investigated the corrosion properties of polyaniline/clay nanocomposites prepared from Na$^+$-montmorillonite or organo-modified montmorillonite with dodecylbenzene sulfonic acid using in-situ emulsion polymerization in the presence of aniline monomer [57]. The authors conducted a series of electrochemical measurements and concluded that the polyaniline nanocomposites coatings modified with low loading of Na$^+$-montmorillonite exhibited better anticorrosion performance compared to conventional polyaniline on cold-rolled steel. This was attributed to the co-existence of the redox catalytic properties of polyaniline and the barrier effect of montmorillonite dispersed in the nanocomposites. Yeh and colleagues were also reported the anticorrosive properties of thermosetting polymer-layered silicate nanocomposites, such as polyimide and epoxy nanocomposites, prepared by solution dispersion procedure and thermal ring opening polymerization [58, 59]. The standard electrochemical measurements such as impedance spectroscopy, corrosion potential, and corrosion current revealed that the prepared thermosetting polymer/layered silicate nanocomposites exhibited enhanced protection against the corrosion on cold-rolled steel compared to bulk polymers. Danaee and co-workers investigated the effect of adding nanoclay on corrosion protection of zinc-rich epoxy coatings on steel [60]. The TEM findings revealed that the clay nanolayers were effectively dispersed and successfully separated between zinc particles in coating. The electrochemical measurements revealed that the incorporation of 1 wt.% clay enhanced the cathodic protection duration and sacrificial properties of the coatings. These findings clearly demonstrate that the incorporation of clay into the coating decreased the electrical contact between the zinc particles without affecting the zinc sacrificial properties. The authors indicated that high clay loadings lead to the increment of the porosity in coatings and the decrease in the intercalation of clay which could decrease the long-term protective performance of the coating. Spathis and co-workers investigated the performance of epoxy-clay nanocomposite coatings for steel protection [61].

The montmorillonite clay was firstly modified with quaternary or primary octadecylammonium cations before being mixed with the epoxy resin. The experimental findings revealed that the mechanical and thermomechanical of all epoxy-organoclay nanocomposites were enhanced compared to those of the pure epoxy polymer. The electrochemical impedance measurements indicated that the epoxy-montmorillonite clay modified with primary octadecylammonium cations exhibited better protection performance compared to those modified with quaternary octadecylammonium cations. Indeed, the total resistance value, R_{tot}, after 4 days exposure in the corrosive environment, improved from 1.03×10^2 of bare steel, to 5.34×10^3 in the case of pure epoxy resin, to 7.40×10^3 in the case of epoxy-loaded with clay modified with quaternary octadecylammonium ions, and to 2.96×10^4 (Ωcm^2) in the case of nanocomposite made from modified clay with primary octadecylammonium ions. Importantly, the total resistance values decrease continuously in case of bare steel, with exposure time and the relation between these two factors were observed to be linear, indicating a constant corrosion rate. Importantly, the protective corrosion protection performance of the nanocomposite coatings was found to depend on the clay loading up to the saturation level. The excellent mechanical properties and thermal stability, as well as the high corrosion protection of these epoxy-clay nanocomposites, make them attractive candidates for various demanding coating applications. Al-Shahrani and colleagues demonstrated that the incorporation of modified bentonite with intercalating agents in the epoxy-based coatings resulted in the development of epoxy-bentonite nanocomposites with intercalated structures as shown in the **Figure 3** [62]. The presence of the silicate layers was evident in the TEM images with different degree of intercalation. The corrosion resistance abilities of a series of epoxy-bentonite nanocomposites, as coatings on carbon steel, were evaluated by electrochemical impedance spectroscopy, in 3.5% NaCl solution, at room temperature and compared to unpigmented epoxy. The experimental findings indicated that the presence of nanolayers has successfully improved the corrosion protection of epoxy resin as shown in **Table 4**. Furthermore, the amount of bentonite has an influence of the performance of the coating as the epoxy modified with 3% of bentonite led to
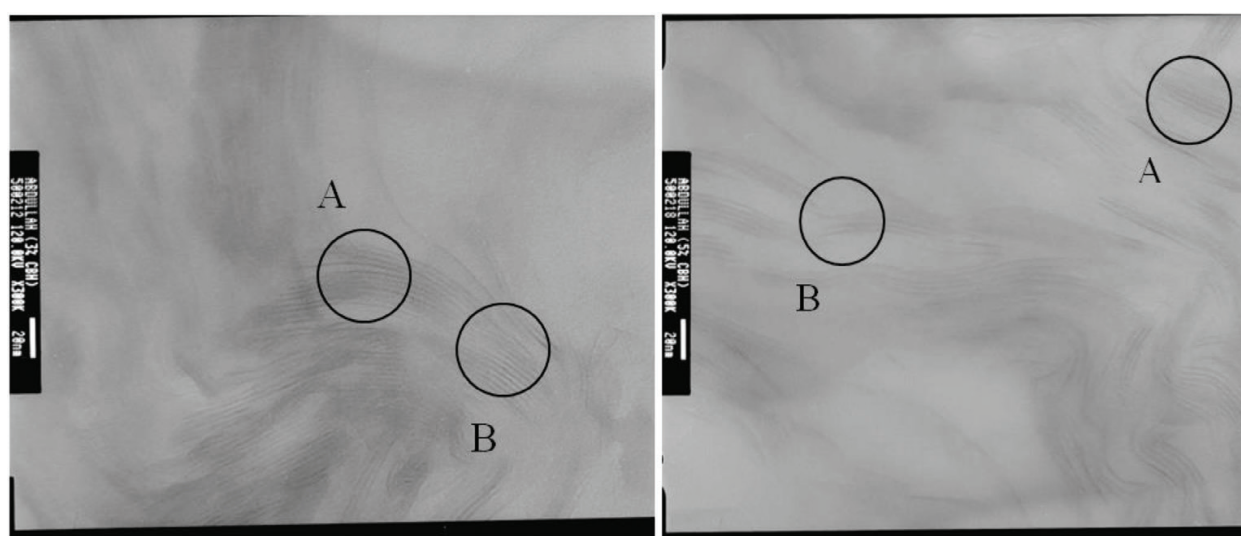

Figure 3. TEM micrographs of epoxy/bentonite nanocomposites: 3% (left) and 5% (right).

Coatings systems	Resistance (KΩ.cm²)	Capacitance (F)
Neat epoxy	5.60	4.00E-04
Epoxy and 1 wt.% clay nanocomposites	4.5E + 05	1.04E-10
Epoxy and 3 wt.% clay nanocomposites	5.60E + 05	9.65E-11
Epoxy and 5 wt.% clay nanocomposites	1.60E + 05	5.00E-10

Table 4. The resistance and capacitance of coated samples from electrochemical impedance spectroscopy calculations after 40 days of immersion.

a high protection level. 5 wt% clay loading showed the lowest performance, indicating that it exceeded the saturation level of clay into the epoxy and consequently generated areas of agglomeration that can be identified as weaknesses in the coating. Such findings suggest that there is a critical loading value above which the coating might be affected [63, 64].

Navarchian and co-workers prepared polyaniline and polyaniline/montmorillonite nanocomposites via in-situ oxidative polymerization, and the resulted nanoparticles were incorporated into the epoxy resins and coated on steel substrates [65]. The anticorrosion performance of prepared epoxy-based coatings was conducted through electrochemical Tafel and electrochemical impedance spectroscopy tests. It was reported that the epoxy coating modified by polyaniline/montmorillonite nanocomposite particles exhibited improved corrosion protection compared to unpigmented epoxy and epoxy/polyaniline coatings as it can be seen in **Table 5**. Furthermore, these findings indicated also that the incorporation of polyaniline and organo montmorillonite (OMMT) into epoxy coating improves its anticorrosion performance compared to polyaniline/montmorillonite and neat polyaniline. Similar findings were reported by Kalaivasan and Shafi using polyaniline/montmorillonite clay nanocomposites prepared by mechanochemical intercalation method [66].

It is worth noting that the effect of clay in the polymer/layered silicate nanocomposites coatings was commonly evaluated at room temperature, and the investigation of the corrosion performance of these materials at higher temperature has attracted little attention. Do the coatings operated at high temperatures still maintain their good corrosion efficiency as even compared to that of electrode coated with neat polymer at room temperature? In this context, Yeh and colleagues performed the electrochemical corrosion parameter measurements of water-based conducting polyaniline/montmorillonite nanocomposites of polyaniline with

Sample code	$I_{corr} \times 10^6$ (A/cm²)	$E_{corr} \times 10^3$ (v)	R_p (KΩ cm²)	R_{corr} (mm/year)
Epoxy	1.170	−483	11.35	0.013
Epoxy/PANI	0.798	−463	17.24	0.009
Epoxy/PANI/MMT	0.651	−459	19.97	0.007
Epoxy/PANI/OMMT	0.467	−418	28.51	0.005

Table 5. The Tafel plot data for steel panels coated with neat and modified epoxy in NaCl (3.5 wt. %) solution.

Compound code	Feed composition (wt.%)		Inorganic content found in the product (wt.%)[a]	Electrochemical corrosion measurements[b]			
	PMBS	MMT		E_{corr} (v)	R_p (KΩ cm²)	$I_{corr} \times 10^{-6}$ (A/ cm²)	R_{corr} (mm/year)
Bare	—	—	—	−0.670	1.91	80.00	37.24
PMBS	100	0	4.56	−0.644	13.87	31.40	14.62
CLMA1	99.00	1.00	6.13	−0.568	20.86	11.60	5.40
CLMA3	97.00	3.00	7.05	−0.528	67.36	10.20	4.75
CLMA3 (M)	97.00	3.00	7.28	−0.575	50.33	15.20	7.08

[a]As determined by thermogravimetric analysis.
[b]Saturated calomel electrode was employed as reference electrode.

Table 6. Relations of the composition of polyacrylate-latex clay nanocomposite materials with the E_{corr}, R_p, I_{corr}, and R_{corr} measured by electrochemical methods.

raw Na⁺-montmorillonite clay [67]. In this study and based on the electrochemical tests such as corrosion potential, polarization resistance, corrosion current corrosion rate, and electrochemical impedance spectroscopy, the nanocomposite coating containing 1 wt% of clay exhibited an noticeable improved corrosion efficiency on cold-rolled steel electrode at high temperature of 50°C and was found even much better than that of no coated and electrode coated with unpigmented polyaniline at room temperature. Indeed, the Ecorr of polyaniline nanocomposites measured at 50°C (E_{corr} = −572.5 mV) was lower than that of uncoated (E_{corr} = −664.1 mV) and polyaniline-coated electrode measured at room temperature.

Yeh and colleagues recently reported the anticorrosive properties of water-based polyacrylate/layered silicate nanocomposites [68]. Raw Na⁺-montmorillonite clay and organo montmorillonite clay were used for the preparation of nanocomposites. The anticorrosion performance of cold-rolled steel coupons coated with as-prepared unpigmented polyacrylate (denoted PMBS) and a series of nanocomposite latexes were evaluated by operating sequential electrochemical corrosion parameters, such as corrosion potential, polarization resistance, corrosion current, and corrosion rate as illustrated in **Table 6**. It should be noted that nanocomposite latexes with Na⁺-MMT clay exhibit better corrosion protection efficiency on cold-rolled steel coupons than that of with organo-MMT clay based on the studies of E_{corr}, R_p, I_{corr}, R_{corr}, and R_{ct}.

7. Concluding remarks

In conclusion, an impressive progress has been reported during the last few years regarding the preparation and the use of polymer-clay nanocomposites for corrosion protection. These materials offer a number of advantages, such as excellent mechanical and thermal stability, improved anticorrosion protection, and wide accessibility of clay. The corrosion protection properties of these materials were found influenced by the type of the clay and curing agents

used to process the nanocomposites. Despite the significant progress of research efforts, a number of challenges remain untapped to understand the complex structure in clay-based nanocomposites. For example, exfoliation of clay layers into polymers matrix is still ambiguous to understand. This is very critical to prepare new nanocomposite with enhanced corrosion properties. A highly exfoliation of the clay inside the polymer matrix is usually difficult to attain. In addition, the most of works reported in the literature revealed the absence of direct relationship between the nanocomposite structures and their final anticorrosive properties most probably, thanks to negligence of the interface properties in determination of final anticorrosion performance. An in-depth understanding of the effect of morphology of clays on the corrosion performance of nanocomposites is necessary to design an ideal coating. With these present challenges combined with emergent interest in the use of polymer-clay nanocomposites for corrosion protection, it is certain that this field will continue to be a fast-moving research topic for the next several years.

Acknowledgements

Author details

Abdullah Al-Shahrani*, Ihsan Taie, Aziz Fihri and Gasan Alabedi

*Address all correspondence to: abdullah.shahrani.13@aramco.com

Oil and Gas Network Integrity Division, Research and Development Center, Saudi Aramco, Dhahran, Saudi Arabia

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