Advanced Anticorrosive Coatings Prepared from Polymer-Clay Nanocomposite Materials

Wei-I Hung, Kung-Chin Chang, Ya-Han Chang and Jui-Ming Yeh
Chung Yuan Christian University Taiwan,
R. O. C.

1. Introduction

Corrosion control is an important subject of increasing interest to the modern metallic finishing industry. Surface modification of metallic substrates by organic or polymeric coatings is an essential approach for enhancing surface properties such as wear, oxidation, and corrosion. Various conventional techniques are utilized to depositing the desired materials onto the metallic substrate to achieve surface modifications with better protection for the substrate. Organic or polymeric coatings on metallic substrates provide an effective barrier between the metal and its environment and/or inhibit corrosion through the presence of chemicals. Chromium-containing compounds (CC) have generally been used as effective anticorrosive coatings in the past decades. However, due to the environmental and health concerns, CCs may need to be replaced by alternative materials that would not pose biological and ecological hazards. Thus, research has focused on the development of novel polymeric coating materials that contain effective anticorrosive agents.

During the early stage of corrosion protection engineering, various neat organic or polymeric coatings were developed. These coatings generally function as a physical barrier against aggressive species such as O_2 and H^+ that cause decomposition. Examples of representative polymers are include epoxy resins [MacQueen & Granata, 1996; Dang et al., 2002], polyurethanes [Moijca et al., 2001], and polyesters [Malshe & Sangaj, 2006; Deflorian et al., 1996]. Moreover, conjugated polymers such as polyaniline [Wessling & Posdorfer, 1999; Tan & Blackwood, 2003], polypyrrole [Iroh & Su, 2000, Krstajic et al., 1997], and polythiophene [Kousik et al., 2001], have also been employed as advanced anticorrosive coatings due to their redox catalytic properties, forming metal oxide passivation layers on metallic substrates. Conversely, not all neat polymeric coatings are permanently impenetrable because small defects in the coatings can lead to gateways that allow corrosive species to attack the metallic substrate; thus, localized corrosion can occur. As a second line of defense against corrosion, various nanoscale inorganic additives have been incorporated into various polymer matrices to generate a series of organic–inorganic hybrid anticorrosive coatings.

Recently, montmorrillonite (MMT)–layered silicate (clay) has attracted intensive research interest for the preparation of polymer–clay nanocomposites (PCNs) because its lamellar elements display high in–plane strength, stiffness, and high aspect ratios. Typically, the chemical structures of MMT consist of two fused silica tetrahedral sheets that sandwich an

edge-shared octahedral sheet of either magnesium or aluminum hydroxide. The Na^+ and Ca^{+2} residing in the interlayer regions can be replaced by organic cations such as alkylammonium ions, by a cationic-exchange reaction to render the hydrophilic clay organophilic. The historical development of polymer-clay nanocomposites can be traced back to the work of PCNs reported by Toyota's research group [Usuki et al., 1993]. According to many recently published works, the dispersion of clay was found to boost the thermal stability [Lan et al., 1994], mechanical strength [Tyan et al., 1942], and molecular-barrier [Wang & Pinnavaia, 1998] and flame-retardant [Gilman et al., 2000] properties of polymers. Recently, we reported that the dispersion of MMT platelets into various polymeric materials, in the form of coatings, boosted the corrosion protection of the polymer on metallic electrodes based on a series of electrochemical corrosion measurements, including corrosion potential, polarization resistance, corrosion current, and impedance spectroscopy under saline conditions.

In this chapter, we represent polymer-layered silicate (PLS) nanocomposite materials (including conjugated polymers and non-conjugated polymers) as model coatings to demonstrate the advanced anticorrosive properties of layered silicate-based polymeric coatings by performing a series of electrochemical corrosion measurements.

2. Structure of layered silicates (clay)

The layered silicates commonly used in nanocomposites belong to the structural family known as the 2:1 phyllosilicates. Their crystal lattice consists of two-dimensional layers in which a central octahedral sheet of alumina or magnesia is fused to two external silica tetrahedron by the tip so that the oxygen ions of the octahedral sheet do also belong to the tetrahedral sheets. The layer thickness is around 1 nm, and the lateral dimensions of these layers may range from 300 Å to several microns or larger depending on the particular silicate. These layers organize to form stacks with a regular Van Deer Waals gap between each layer called the interlayer or the gallery. Isomorphic substitution within the layers (for example, Al^{3+} replaced by Mg^{2+} or by Fe^{2+}, or Mg^{2+} replaced by Li^+) generates negative charges that are counterbalanced by alkali or alkaline earth cations situated in the interlayer. As the forces that hold the stacks together are relatively weak, the intercalation of small molecules between the layers occurs readily [Theng, 1974]. In order to render these hydrophilic phyllosilicates more organophilic, the hydrated cations of the interlayer can be exchanged with cationic surfactants such as alkylammonium or alkylphosphonium (onium). Becouse the modified clay (or organoclay) is organophilic, its surface energy is lowered and is more compatible with organic polymers. These polymers may be able to intercalate within the galleries under well-defined experimental conditions. Montmorillonite, hectorite, and saponite are the most commonly used layered silicates. Their structure is given in Fig.1, [Giannelis et al., 1999; Sinha-Ray & Okamoto, 2003] and their chemical formula are shown in Table 1. This type of clay is characterized by a moderate negative surface charge (known as the cation exchange capacity, CEC, expressed in mequiv./100 g). The charge of the layer is not locally constant but varies from layer to layer; therefore, it much be considered as an average value over the whole crystal. Proportionally, even if a small part of the charge-balancing cations is located on the external crystallite surface, the majority of these exchangeable cations are located inside the galleries. When the hydrated cations are ion-exchanged with organic cations such as more bulky alkylammoniums, it usually leads to a larger interlayer spacing. To describe the structure of the interlayer in organoclay, one must

know that, as the negative charge originates in the silicate layer, the cationic head group of the alkylammonium molecule preferentially resides at the layer surface, leaving the organic tail radiating away from the surface. In a given temperature range, two parameters then define the equilibrium layer spacing: the CEC of the layered silicate, driving the packing of the chains, and the chain length of the organic tail(s).
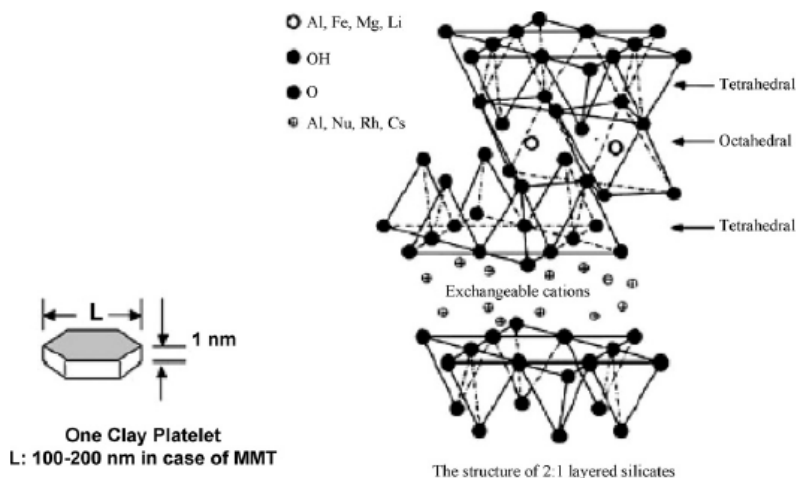

Fig. 1. Structure of 2:1 layered silicate showing two tetrahedral sheets of silicon oxide fused to an octahedral sheet of aluminum hydroxide.

Silicate	Location of isomorphous substitution	Formula
Montmorillonite	Octahedral	$M_x[Al_{4-x}Mg_x](Si_8)O_{20}(OH)_4$[a]
Hectorite	Octahedral	$M_x[Mg_{6-x}Li_x](Si_8)O_{20}(OH)_4$[a]
Saponite	Tetrahedral	$M_x[Mg_6](Si_{8-x}Al_x)O_{20}(OH)_4$[a]

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

Table 1. Structure and chemistry of commonly used layered silicates

According to X-ray diffraction (XRD) data, the organic chains have been long thought to lay either parallel to the silicate layer, forming mono or bilayers, or, depending on the packing density and the chain length, to radiate away from the surface, leading to mono or even bimolecular tilted "paraffinic" arrangements [Lagaly, 1986], as shown in Fig. 2. A more realistic description has been proposed by Vaia et al., 1994, based on Fourier transform infrared (FTIR) spectroscopy experiments. By monitoring frequency shifts of the asymmetric CH_2 stretching and bending vibrations, they found that the intercalated chains exist in states with varying degrees of order. Generally, as the interlayer packing density or the chain

length decreases (or the temperature increases), the intercalated chains develop more disordered, liquid-like structure resulting from an increase in the gauche/trans conformer ratio. When the available surface area per molecule is within a certain range, the chains are not completely disordered but maintain some orientation order close to that in the liquid crystalline state, as shown in Fig. 3. Recently, this interpretation has been confirmed by molecular dynamics simulations in which a strong layering behavior with a disordered liquid-like arrangement that can evolve towards a more ordered arrangement by increasing the chain length has been found [Hackett et al., 1998]. As the chain length increases, the interlayer structure appears to evolve in a stepwise fashion, from a disordered to a more ordered monolayer, and then "jump" to a more disordered pseudo-bilayer.
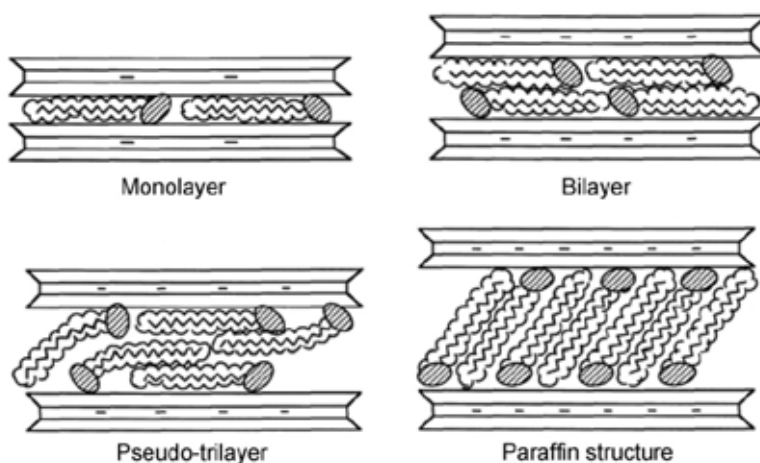

Fig. 2. Orientations of alkylammonium ions in the galleries of layered silicates with different layer charge densities.
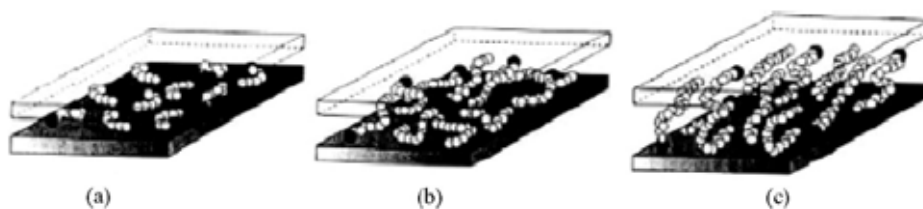

Fig. 3. Alkyl chain aggregation models (a) Short alkyl chains: isolated molecules, lateral monolayer; (b) intermediate chain lengths: in-plane disorder and interdigitation to form quasi-bilayers; (c) longer chain length: increased interlayer order, liquid crystalline-type environment.

3. Nanocomposite structures

In general, layered silicates have layer thickness on the order of 1 nm and very high aspect ratio (e.g., 10–1000). A few weight percent of layered silicates that are properly dispersed

throughout the polymer matrix create much higher surface area for polymer/filler interaction compared to conventional composites. Depending on the strength of interfacial interactions between the polymer matrix and the layered silicate (modified or not), three different types of polymer/layered silicate nanocomposites are thermodynamically achievable (Fig. 4)

a. Intercalated nanocomposites: In intercalated nanocomposites, the insertion of a polymer matrix into the layered silicate structure occurs in a crystallographically regular fashion, regardless of the clay to polymer ratio. Intercalated nanocomposites are normally interlayered with a few molecular layers of polymer. Properties of the composites typically resemble those of ceramic materials.

b. Flocculated nanocomposites: conceptually this is the same as intercalated nanocomposites. However, silicate layers are sometimes flocculated due to hydroxylated edge–edge interaction of the silicate layers.

c. Exfoliated nanocomposites: In an exfoliated nanocomposite, the individual clay layers are separated in a continuous polymer matrix by an average distance that depends on the clay loading. Usually, the clay content of an exfoliated nanocomposite is much lower than that of an intercalated nanocomposite.
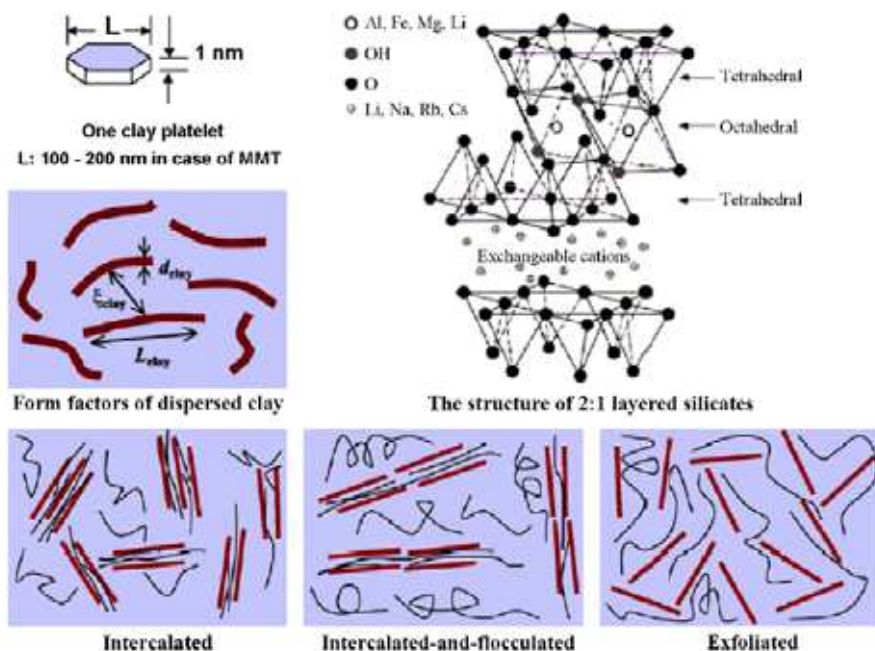

Fig. 4. Schematic illustration of three different types of thermodynamically achievable polymer/layered silicate nanocomposites.

4. Methods used for the synthesis of PLS nanocomposites

Intercalation of polymers in layered hosts, such as layered silicates, has proven to be a successful approach to synthesize PLS nanocomposites. The preparative methods are

divided into three main groups according to the starting materials and processing techniques

a. Intercalation of polymer or pre-polymer from solution (Fig. 5) [Xu et al., 2001; Yano et al., 1993; Aranda & Ruiz-Hitzky, 1992; Jimenez et al., 1997; Jeon et al., 1998 ; Tseng et al., 2001]: This is based on a solvent system in which the polymer or pre-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 PLS nanocomposites.
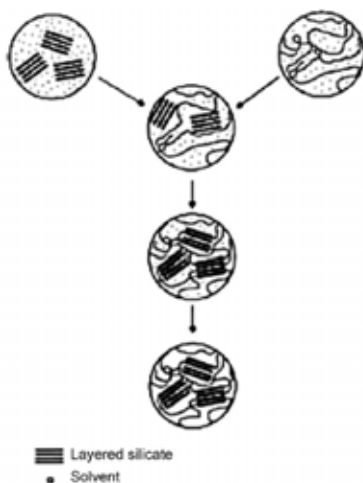

Fig. 5. Schematic representation of a PLS nanocomposite obtained by intercalation of polymer from solution.
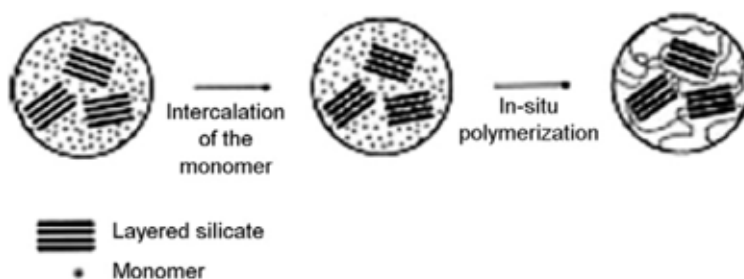

Fig. 6. Schematic representation of a PLS nanocomposite obtained by in-situ polymerization.

b. In-situ intercalative polymerization method (Fig. 6) [Biswas & Sinha-Ray, 2001; Kojima et al., 1993; Usuki et al., 1993; Okamoto et al., 2000, 2001; Leu et al., 2002; Kim et al., 2003]: In this method, the layered silicate is swollen within the liquid monomer or a monomer solution so that polymer formation can occur between the intercalated sheets. Polymerization can be initiated either by heat or by radiation, by the diffusion of a

suitable initiator, or by an organic initiator or catalyst fixed through cation exchange inside the interlayer before the swelling step.

c.   Melt intercalation method (Fig. 7) [Vaia & Giannelis, 1997; Vaia et al., 1993, 1995; Fornes et al., 2002; Wang et al., 2001; Usuki et al., 2002; Chisholm et al., 2002 ; Huang et al., 2000]: This method involves (statically or under shear), a mixture of the polymer and organically modified layered silicates (OMLS) above the softening point of the polymer. This method has advantages over either in situ intercalative polymerization and polymer solution intercalation. First, this method is environmentally benign due to the absence of organic solvents. Second, it is compatible with current industrial process such as extrusion and injection molding. The melt intercalation method allows the use of polymers that were previously not suitable for in-situ polymerization or solution intercalation.
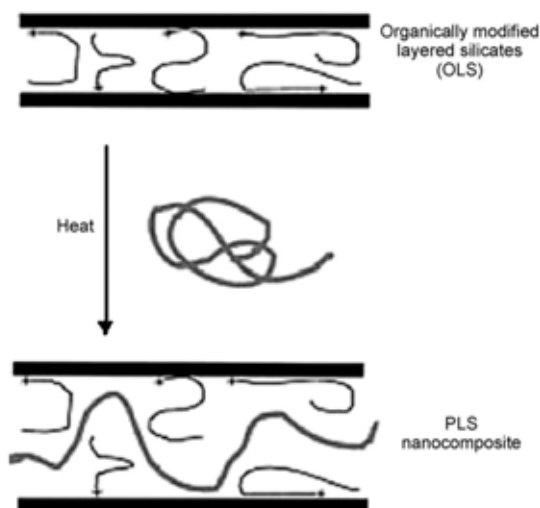

Fig. 7. Schematic representation of a PLS nanocomposite obtained by direct melt intercalation.

5. Measures of corrosion prevention

Material selection

a.   Metals and alloys: The most common method for preventing corrosion is the selection of the proper metal or alloy for a particular corrosive service [Harple & Kiefer, 1953; Vernon, 1948].

b.   Metal purification: The corrosion resistance of a pure metal is usually better than that of one containing impurities or small amounts of other elements. However, pure metals are usually expensive and are relatively soft and weak. In general, pure metals are used in relatively few , special cases [Harple & Kiefer, 1953; Vernon, 1948].

c.   Nonmetallics: This category involves integral or solid nonmetallic construction (mainly self-supporting) and sheet linings or coverings of substantial thickness (different from paint coatings). The five general classes of nonmetallics are (1) rubbers (natural and

synthetic), (2) plastics, (3) ceramics, (4) carbon and graphite, and (5) wood [Harple & Kiefer, 1953; Vernon, 1948; Worspop & Kingsburf, 1950; Rohring, 1935].

d. Changing mediums: Altering the environment provides a versatile means for reducing corrosion. Typical changes in the medium that are often employed include (1) lowering the temperature, (2) decreasing the velocity, (3) removing oxygen or oxidizers, and (4) changing the concentration. In many cases, these changes can significantly reduce corrosion, but they must be performed with care [Harple & Kiefer, 1953; Vernon, 1948; Welder & Partridge, 1954].

e. Inhibitors: An inhibitor is a substance that, when added in small concentrations to an environment, decreases the corrosion rate. In a sense, an inhibitor can be considered a retarding catalyst. There are numerous inhibitor types and compositions. Most inhibitors have been developed by empirical experimentation, and many inhibitors are proprietary in nature thus, their composition is not disclosed. Inhibition is not completely understood because of these reasons, but it is possible to classify inhibitors according to their mechanism and composition [Harple & Kiefer, 1953; Vernon, 1948; Rosenfeld, 1981].

Cathodic and anodic protection

a. Cathodic protection: Cathodic protection was employed before electrochemistry had been developed. Humphrey Davy used cathodic protection on British naval ships in 1824. The principles of cathodic protection may be explained by considering the corrosion of a typical metal in an acid environment. Electrochemical reactions include the dissolution of the metal and the evolution of hydrogen gas:

$$M \rightarrow M^{n+} + ne$$

$$2H^{+} + 2e \rightarrow H_2$$
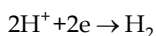
b. Anodic protection: In contrast to cathodic protection, anodic protection is relatively new; it was first suggested by Edeleanu in 1954. This technique was developed using electrode kinetics principles and is somewhat difficult to describe without introducing advanced concepts of electrochemical theory. Simply, anodic protection is based on the formation of a protective film on metals by externally applied anodic currents [Acello & Greene, 1962; Locke & Sudbury, 1960].

Coatings

a. Metallic and other inorganic coatings: Relatively thin coatings of metallic and inorganic materials can provide a satisfactory barrier between a metal and its environment. The chief function of such coatings (aside from sacrificial coatings such as zinc) is to provide an effective barrier. Metal coatings are applied by electrodeposition, flame spraying, cladding hot dipping, and vapor deposition. Inorganics are applied or formed by spraying, diffusion, or chemical conversion. Spraying is usually followed by baking or firing at elevated temperatures. Metal coatings usually exhibit some formability, whereas the inorganics are brittle. In both cases a complete barrier must be provided. Porosity or other defects can result in accelerated localized attack on the basic metal because of two-metal effects [Draper, 1982; McCafferty et al., 1982; Moore & McCafferty, 1981; Potter et al., 1983].

b.   Organic coatings: These involve a relatively thin barrier between the substrate material and the environment. Paints, varnishes, lacquers, and similar coatings protect more metal per ton than any other method for combating corrosion. Exterior surfaces are most common, but inner coatings or linings are also widely utilized. Approximately 2 billion dollars per year are expended in the United States on organic coatings. A myriad of types and products are involved, and some are accompanied by outlandish claims. Substantial knowledge of this complex field is required for successful performance. The best procedure for those who are inexperienced is to consult a reputable producer of organic coatings. As a general rule, these coatings should not be used where the environment would rapidly attack the substrate material [Garrett, 1964]. Aside from proper application, the three main factors to consider for organic coatings, listed in order of importance, are (1) surface preparation, (2) selection of primer or priming coat, and (3) selection of top coat or coats. Polymeric (or organic) coatings have been employed to protect metals against corrosion for a long time. The primary effect of a polymeric coating is to function as a physical barrier against aggressive species such as O_2 and H^+. However, not all polymeric coatings are permanently impenetrable, and once there are defects in the coatings, pathways will be formed for the corrosive species to attack the metallic substrate, and localized corrosion will occur. Therefore, as a second line of defense for corrosion, various pigments with a lamellar or plate-like shape, such as micaceous iron oxide and aluminum flakes, have been introduced into the polymeric coating to effectively increase the length of the diffusion pathways for oxygen and water as well as to decrease the permeability of the coatings. A number of electrochemical measurements have been used to evaluate the anticorrosion performance of polymeric coatings, including conjugated (e.g., polyaniline) or nonconjugated (e.g., polystyrene) polymers. Wei et al., 1995, demonstrated the anticorrosive performance of conjugated polyaniline and nonconjugated polystyrene by performing a series of electrochemical measurements of corrosion potential and corrosion current on the sample-coated cold-rolled steel (CRS) electrode under various conditions. Li et al., 1997, investigated the corrosion-resistance properties of polyaniline-coated mild steel in saline and acid by electrochemical impedance spectroscopy. Recently, PLS nanocomposites used as enhanced anticorrosion coatings have been reported by Yeh group [Yeh et al., 2001, 2002, 2003, 2004, 2005, 2006, 2007; Chang et al., 2006, 2007, 2008; Lai et al., 2007; Yu et al., 2004]. For example, conjugated polymers (e.g., polyaniline, polypyrrole, and poly(3-hexylthiophene)), thermoplastic polymers (e.g., poly(methyl methacrylate), polystyrene, poly(styrene-co-acrylonitrile), polysulfone, and polyacrylate), and thermosetting polymers (e.g., polyimide and epoxy) all had been blended with organo-modified clay or raw Na^+-MMT clay through different preparative routes such as in-situ polymerization or solution dispersion, to make a series of novel advanced anticorrosion coatings based on a series of electrochemical corrosion parameter measurements of corrosion potential, polarization resistance and corrosion current at room temperature.

6. Anticorrosive properties

In a non-conjugated system, Yeh et al., 2002, reported a series of PCN materials that consisted of poly (methyl methacrylate) (PMMA) and layered MMT clay that were prepared by effectively dispersing the inorganic nanolayers of MMT clay in an organic PMMA matrix

via in-situ thermal polymerization. Organic methyl methacrylate monomers were first intercalated into the interlayer regions of organophilic clay hosts followed by a typical free-radical polymerization. The as-synthesized PCN materials were characterized by infrared spectroscopy, wide-angle powder XRD (Fig. 8), and transmission electron microscopy (TEM; Fig. 9). PCN coatings with low clay loading (e.g., 1 wt %) on CRS showed superior anticorrosion properties compared with those of bulk PMMA based on a
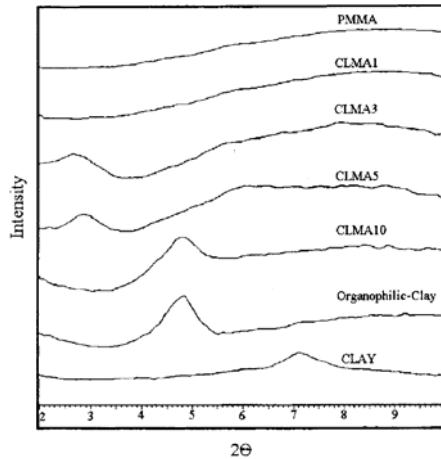

Fig. 8. Wide-angle powder X-ray diffraction patterns of organophilic clay, PMMA, and a series of PMMA−clay nanocomposite materials.
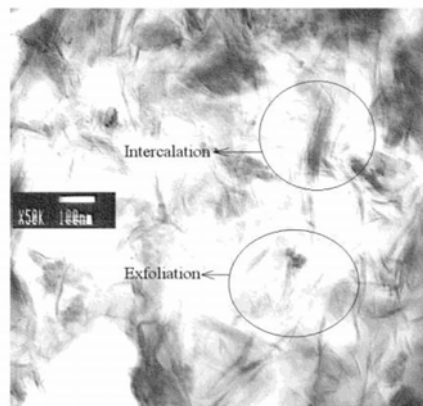

Fig. 9. Transmission electron microscopy of CLMA5.

series of electrochemical measurements of corrosion potential, polarization resistance, corrosion current, and impedance spectroscopy in 5 wt% aqueous NaCl electrolyte (Table 2 and Fig. 10−11). The molecular weights of PMMA extracted from PCN materials and bulk PMMA were determined by gel permeation chromatography (GPC) with tetrahydrofuran as an eluant. Effects of the material composition on the gas and water permeability (Fig. 12), optical clarity, and thermal stability of PMMA and PCN materials, in the form of both

free-standing films and fine powders, were also studied by molecular permeability analysis, ultraviolet-visible transmission spectra, differential scanning calorimetry, and thermogravimetric analysis, respectively.

compound code	feed composition (wt %)		inorganic content found in product[b] (wt %)	electrochemical corrosion measurements				
	PMMA	MMT		E_{corr} (mV)	R_p (kΩ·cm²)	i_{corr} (nA/cm²)	R_{corr} (MPY)	thickness[c] (µm)
bare				−604	2.7	1.9×10^4	36.7	
PMMA	100	0	0	−485	3.2×10^2	1.2×10^2	2.3×10^{-1}	110
CLMA1	99	1	1.2	−379	9.2×10^2	4.5×10^1	8.0×10^{-2}	112
CLMA3	97	3	3.5	−278	6.4×10^3	9.4	1.8×10^{-2}	121
CLMA5	95	5	6.9	−78	7.5×10^3	5.7	1.1×10^{-2}	113
CLMA10	90	10	18.1	−19	1.8×10^4	2.3	4.4×10^{-3}	117
CLMA·N10	90	10	22.1					

[a] A saturated calomel electrode was employed as the reference electrode. [b] As determined form TGA measurements. [c] As measured by a digimatic micrometer.

Table 2. Relationships of the composition of PMMA–MMT clay nanocomposite materials with the Ecorr, Rp, icorr, and Rcorr measured using electrochemical methodsa
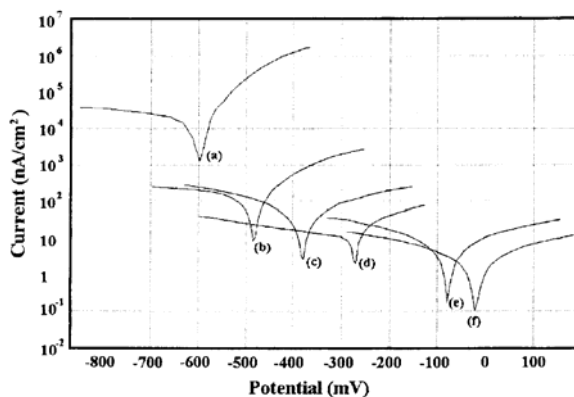

Fig. 10. Tafel plots for (a) uncoated, (b) PMMA-coated, (c) CLMA1-coated, (d) CLMA3-coated, (e) CLMA5-coated, and (f) CLMA10-coated CRS measured in 5 wt% NaCl aqueous solution.
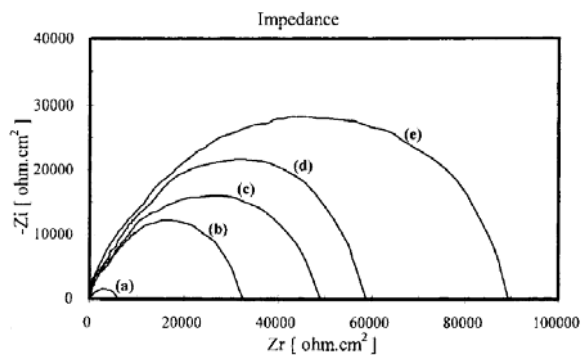

Fig. 11. Nyquist plots of five CRS samples in 5 wt% NaCl aqueous solution (a) PMMA-coated, (b) CLMA1-coated, (c) CLMA3-coated, (d) CLMA5-coated, and (e) CLMA10-coated.
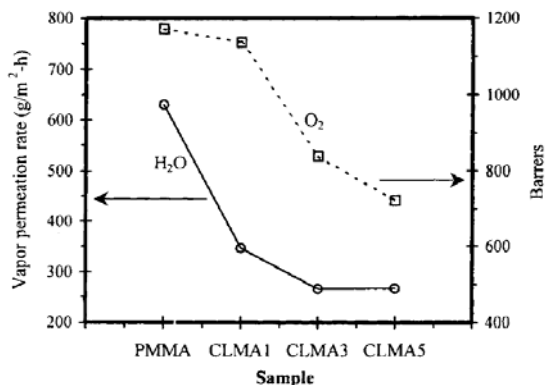
Fig. 12. Permeability of H_2O and O_2 as a function of the MMT clay content in the PMMA−clay nanocomposite materials.

According to the results above, the enhanced corrosion protection effect of PMMA nanocomposites compared to bulk PMMA might have resulted from dispersing silicate nanolayers of clay in the PMMA matrix to increase the tortuosity of oxygen gas diffusion pathways.
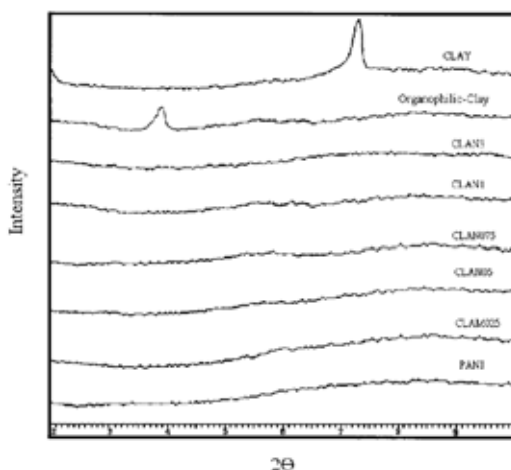

Fig. 13. Wide-angle powder X-ray diffraction patterns of organophilic clay, polyaniline, and a series of PMMA-clay nanocomposite materials.

In conjugated system, Yeh et al., 2001, investigated a series of nanocomposite materials consisting of an emeraldine base of polyaniline and layered (MMT) clay that were prepared by effectively dispersing the inorganic nanolayers of MMT clay in an organic polyaniline matrix via in-situ polymerization. Organic aniline monomers were first intercalated into the interlayer regions of organophilic clay hosts and followed by a one-step oxidative polymerization. The as-synthesized polyaniline–clay lamellar nanocomposite materials were characterized by infrared spectroscopy, wide-angle powder XRD (Fig. 13), and TEM (Fig. 14). Polyaniline–clay nanocomposites in the form of coatings with low clay loading (e.g.,

0.75 wt%) on CRS showed superior corrosion protection compared to those of conventional polyaniline based on a series of electrochemical measurements of corrosion potential, polarization resistance, and corrosion current in 5 wt% aqueous NaCl electrolyte (Fig. 15).
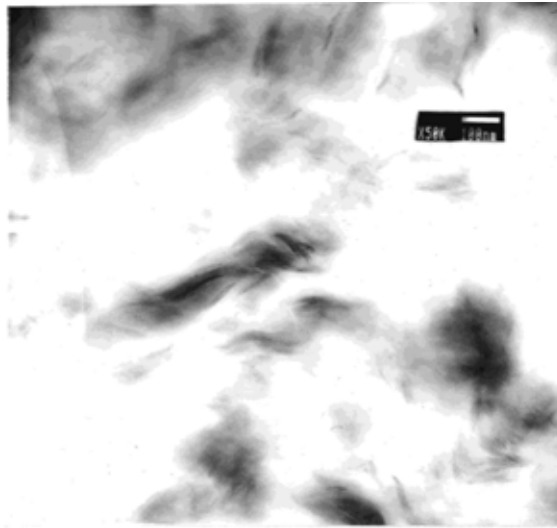

Fig. 14. TEM of CLAN3: with exfoliated single, double, and triple layers and a multilayer tactoid.
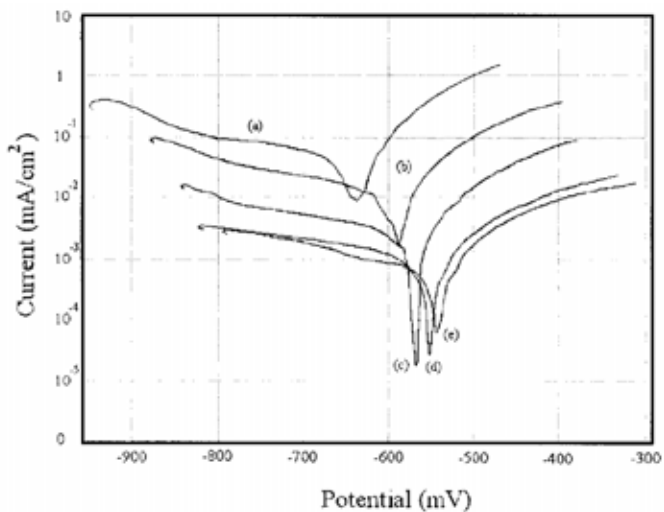

Fig. 15. Tafel plots for (a) uncoated, (b) PANI-coated, (c) CLAN025-coated, (d) CLAN05-coated, and (e) CLAN075-coated CRS measured in 5 wt% NaCl aqueous solution.

The molecular weights of polyaniline extracted from polyaniline–clay nanocomposite materials and bulk polyaniline were determined GPC. Effects of the material composition on

the gas barrier property (Fig. 16), thermal stability, and mechanical strength of polyaniline and polyaniline–clay nanocomposite materials, in the form of both fine powders and free-standing films, were also studied by gas permeability measurements, differential scanning calorimetry, thermogravimetric analysis, and dynamic mechanical analysis.
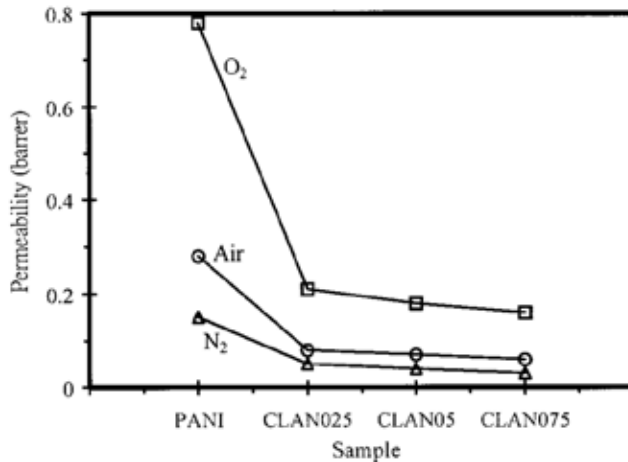

Fig. 16. Permeability of O_2, N_2, and air as a function of the MMT clay content in the polyaniline–clay nanocomposite materials.
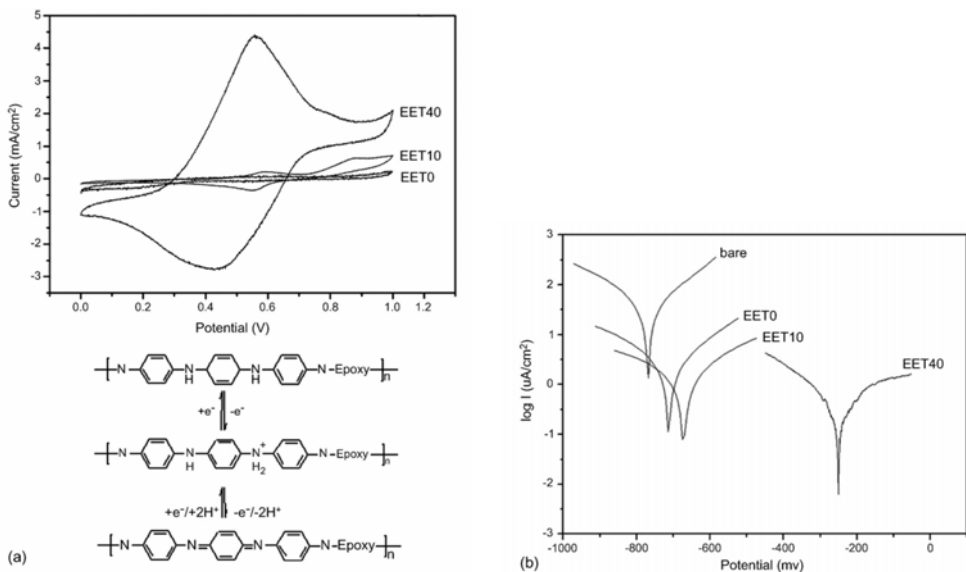

Fig. 17. (a) Redox behavior of EET40-, EET10-, and EET0-coated Pt foil electrode measured in 1.0M H_2SO_4 aqueous solution. (b) Tafel plots for EET40, EET10, EET0-coated and bare CRS electrodes measured in 5 wt% NaCl aqueous solution.

Huang et al., 2009, reproted a series of electroactive epoxy thermosets (EETs) containing conjugated segments of electroactive amino-capped aniline trimer (ACAT) units that were successfully prepared and characterized. Furthermore, the redox behavior of as-prepared EET materials was identified by electrochemical cyclic voltammetry studies. Higher concentrations of ACAT components in the corresponding as-prepared EETs led to remarkably enhanced corrosion protection effects on CRS electrodes based on sequential electrochemical corrosion measurements in 5 wt% NaCl supporting electrolyte (Fig. 17). The mechanism for the enhancement of corrosion protection of EET coatings on CRS electrodes might be attributed to the redox catalytic capabilities of ACAT units that existed in EETs, leading to the formation of passive metal oxide layers, as further evidenced by SEM and ESCA studies (Fig. 18−20).
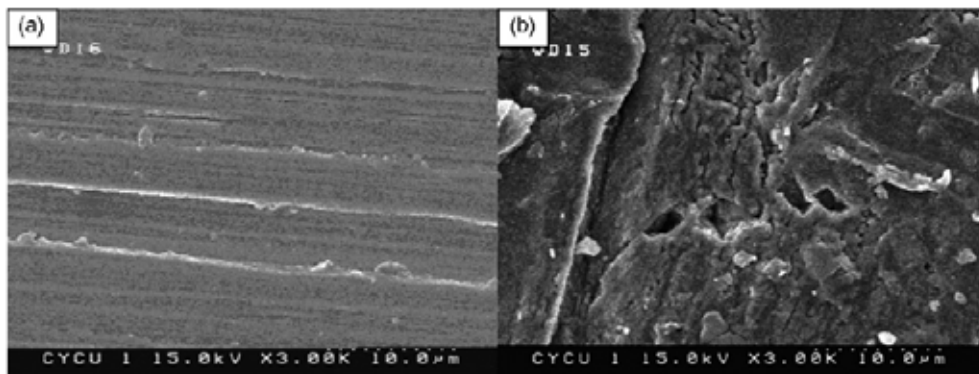

Fig. 18. SEM image of (a) polished CRS metal and the surface of the (b) EET40 coating on the CRS metal.
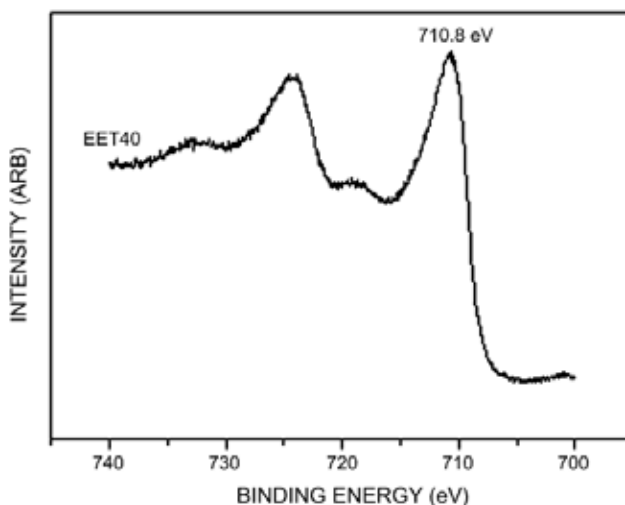

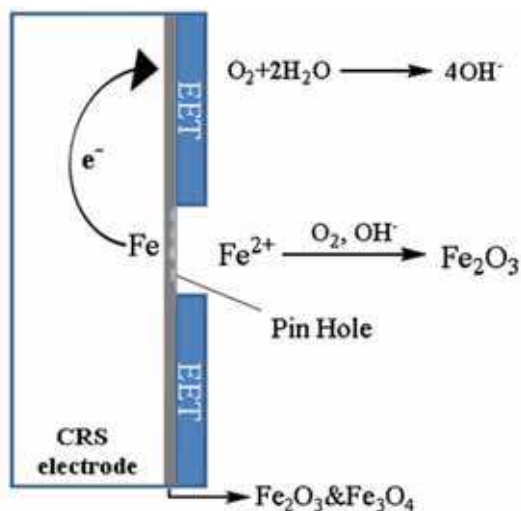Fig. 19. ESCA Fe 2p core spectrum of EET40.

Fig. 20. Schematic diagram of mechanism of the CRS passivation by EET coatings.

In conjugated polymers used for anticorrosion, higher concentration of conjugated ACAT units in as-prepared led to higher redox currents in the CV studies. Corrosion protection of EET coatings cast onto CRS electrodes was systematically investigated by performing sequential electrochemical corrosion measurements under saline conditions. Electrochemical corrosion experimental results showed that higher concentrations of ACAT segments in as-prepared EETs resulted in better corrosion protection efficiency of the corresponding sample-coated CRS electrode. The remarkable enhancement of corrosion protection for EET coatings on CRS electrodes might probably be attributed to the redox catalytic (i.e., electroactivity) properties of conjugated ACAT units in the as-prepared electroactive EETs, leading to the formation of passivation metal oxide layers, as demonstrated by SEM and ESCA studies. The passive oxide layer is predominately composed of Fe_2O_3, above a very thin Fe_3O_4 layer.

7. Conclusion

Smectite clays can be effective reinforcing agents in the synthesis of polymer/layered silicate nanocomposites that display superior properties, even at low clay content (<3 wt%). Nanocomposites show enhanced physical properties even with a small amount of added clay, because the nanoscale dimensions of the clay particles yield a large contact area between the polymer matrices and the filler. The structure of clays, with layers of high aspect ratio, also imparts excellent barrier that provide low gas permeability and enhanced anticorrosive properties.

Anticorrosive properties of non-conjugated polymer nanocomposites with layered silicates have been discussed herein. The as-prepared nanocomposites, in the form of coatings, showed advanced protection against corrosion on CRS coupons compared to bulk polymers based on a series of standard electrochemical corrosion measurements, including corrosion potential, polarization resistance, corrosion current, and impedance spectroscopy. The

enhanced corrosion protection effect of nanocomposites compared to bulk polymers might have resulted from dispersing silicate nanolayers of clay in the polymer matrix to increase the tortuosity of diffusion pathway for H_2O and O_2 molecules and is further evidenced by the O_2 and H_2O permeability studies on the free-standing film of as-prepared nanocomposites.

It is noteworthy to mention that the investigations on the corrosion protection efficiency of coujugated polymer–layered silicate nanocomposite coatings were divided into two separate phases. First, neat conjugated polymeric coatings significantly enhanced corrosion protection on CRS electrodes compared to non-conjugated polymeric coatings, and this might be attributed to the redox catalytic property of electroactive aniline trimers in the formation of passive layers of metal oxides. Second, the advanced anticorrosive properties of conjugated polymer coatings were revealed by the introduction of layered silicate into the matrix to form conjugated polymer–layered silicate nanocomposite materials.

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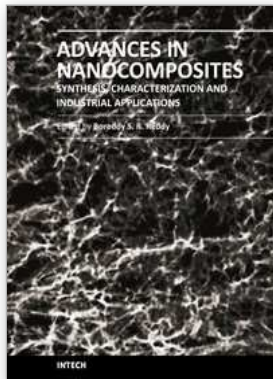
Advances in Nanocomposites - Synthesis, Characterization and Industrial Applications

Edited by Dr. Boreddy Reddy

Advances in Nanocomposites - Synthesis, Characterization and Industrial Applications was conceived as a comprehensive reference volume on various aspects of functional nanocomposites for engineering technologies. The term functional nanocomposites signifies a wide area of polymer/material science and engineering, involving the design, synthesis and study of nanocomposites of increasing structural sophistication and complexity useful for a wide range of chemical, physicochemical and biological/biomedical processes. "Emerging technologies" are also broadly understood to include new technological developments, beginning at the forefront of conventional industrial practices and extending into anticipated and speculative industries of the future. The scope of the present book on nanocomposites and applications extends far beyond emerging technologies. This book presents 40 chapters organized in four parts systematically providing a wealth of new ideas in design, synthesis and study of sophisticated nanocomposite structures.

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