

Nanotechnology-A New Prospective in Organic Coating - Review

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Abstract—Nanotechnology is regarded as one of the key technologies of the future. The term “nanotechnology” is referred as the manufacturing, analysis and use of structures, for example particles, layers or tubes of less than 100 nanometers (nm) in at least one dimension. Artificially produced nano-sized particles and nanoscale system components have new properties which are of importance for the development of new products and applications.

This paper reviews different types of coatings, different types of pigments used in paint formulation and a special focus is set on the uses of nanomaterials/fillers in coating application. More emphasis was given to bestow an insight in nanocomposite coating.

Index Terms—Coatings, Nanofillers, Pigments, Resin.

I. INTRODUCTION

The composition of organic coating may be simple (a single chemical) or may be a complex formulation of a variety of materials, each having a specific function. Formulations generally have three components intended to be relatively permanent and serve specific functions in dry film. These permanent components are pigment, vehicle and additives. Pigments provide colorant or other functions. The vehicles sometimes called the binders act as the adhesive to stick pigment particles to substrate or to each other. Finally additives are chemicals that modify the properties of the coating in fluid or solid state.

Organic coatings are essentially pigment dispersed in a solution of a binding medium. The binding medium or resin will decide the basic physical and chemical properties of the coating but these will be modified by the nature and proportion of pigments present. The sole function of the volatile component is to control the viscosity of the paint for ease of manufacture and for subsequent application. It is not possible to forecast with any accuracy what combination of properties a particular formulation will possess and the formulation of paints for specific purpose remain very much a technological art. The appearance and appliance of nano-materials brings new opportunities to the coating industry. Addition of nano-materials to the coatings improves the properties of the conventional coatings and produces new multi-functional coating due to their tiny particle size. This paper review different types of coatings, types of pigments used in paint formulation and uses of nano fillers in coating applications.

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II. CLASSIFICATION OF COATING PROPERTIES

Coatings are usually applied as multi-layered systems that are composed of primer and topcoat. However, in some cases – for example automotive coating systems, this may vary from four to six layers. Each coating layer is applied to perform certain specific functions, though its activities are influenced by the other layers in the system. The interactions among different layers and the interfacial phenomenon play an important role in the overall performance of the multi-coat systems [1]. Different properties of coatings are typically associated with specific parts of a coating system [2].

A. Functional Coatings

Coatings are mainly applied on surfaces for decorative, protective or functional purposes, but in most cases it is a combination of these. The term “functional coatings describes systems which possess, besides the classical properties of a coating (i.e., decoration and protection), an additional functionality [3]. This additional functionality may be diverse, and depend upon the actual application of a coated substrate. Typical examples of functional coatings are self-cleaning [4, 5], easy-to clean (anti-graffiti) [6], antifouling [7], soft feel [8] and antibacterial [9, 10]. Although various mechanisms are involved, as well as numerous applications, there is a common feature that is of particular benefit and which satisfies some users’ demands. Most coatings (whether inorganic, organic or ceramic) perform critical functions, but as these fields are extensive it is beyond the scope of this article to include all of them at this stage. Thus, the discussion here is limited to coatings with organic binders.

1) Types and Application of Functional Coatings

Apart from their special properties, functional coatings must often satisfy additional requirements; for example, nonstick, cookware coatings must be resistant to scratching, abrasion and thermal effects. Typical expectations of functional coatings include:

- . durability
- . reproducibility
- . easy application and cost effectiveness
- . tailored surface morphology
- . environmental friendliness

Therefore functional coatings can be classified as several types depending on their functional characteristics.

Functional coatings perform by means of physical, chemical, mechanical, thermal and properties. Chemically active functional coatings perform their activities either at

film–substrate interfaces (anticorrosive coatings), in the bulk of the film (fire-retardant or intumescent coatings), or at air–film interfaces (antibacterial, self-cleaning) [11]. Some applications of functional coatings are discussed in the following sections.

2) *Anitcorrosive Coatings*

It is known that, when iron or steel is exposed to a natural atmosphere, then rust is formed. Although the rusting of iron or steel is usually termed as corrosion, the latter is a general term which is used to define the destructive interaction of a material with its environment. Corrosion usually refers to metals, though nonmetallic substrates such as plastics, concrete or wood also deteriorate in the environment. Corrosion causes enormous industrial losses with a depletion of our natural resources. When two different surface areas of a metallic component are exposed to different operational environments, or differ in their surface structure or composition, electrical potentials developed. Corrosion is in fact an electrochemical process where the electrical cell is composed of an anode (the corrosion site), an electrolyte (the corrosive medium), and a cathode (part of the metal which is active in the corrosion process but does not itself corrode) [12]. In general, organic coatings are applied onto metallic substrates in order to avoid the detrimental effect of corrosion. The anticorrosive performance of the coating depends upon several parameters, including: adhesion to metal, thickness, permeability, and the different properties of the coating. In most cases, the primer is mainly responsible for protecting the metallic substrate and adhering to other coating layers. In this context, surface preparation is essential in order to provide good adhesion of the primer to the metallic substrate [13]. The mechanisms by which organic coatings offer corrosion protection are summarized as follows.

Sacrificial means: The use of a sacrificial anode such as zinc to protect steel is a long standing and well-known industrial practice. The zinc layer on galvanized steel degrades when exposed to an adverse environment, and this protects the underneath surface. Using a similar approach, both inorganic and organic resin based, zinc-rich coatings have been developed to protect a variety of metal substrates [14, 15,]

Barrier effect: In general, polymeric coatings are applied to metallic substrates to provide a barrier against corrosive species. They are not purely impermeable. Moreover, defects or damages in the coating layer provide pathways by which the corrosive species may reach the metal surface, whereupon localized corrosion can occur. Pigments having lamellar or plate-like shapes (e.g., micaceous iron oxide and aluminum flakes) are introduced to polymeric coatings; this not only increases the length of the diffusion paths for the corrosive species but also decreases steel flakes, glass flakes and mica are also used for this purpose[16].

The orientation of the pigments in the coating must be parallel to the surface, and they should be highly compatible with the matrix resin to provide a good barrier effect. Layered clay platelets such as montmorillonite may also be introduced into organic resin systems to increase the barrier effect towards oxygen and water molecules, thereby enhancing the anticorrosive performance of the coating [17].

Inhibition: Traditionally, chromate- and lead-based

pigments are the most common compounds used as corrosion inhibitors to formulate anticorrosive primers for metallic substrate. These substances are considered to be toxic and ecologically unsafe, and therefore the search for new alternative anticorrosive pigments is under way. Today, primers containing metallic phosphate, silicate, titanate or molybdate compounds are available commercially. These pigments form a protective oxide layer on the metallic substrates, and often also form anticorrosive complexes with the binder. To reduce the cost, a number of elements and compounds have been combined to develop an effective anticorrosive pigment, including aluminum zinc phosphate, calcium zinc molybdate, zinc molybdate phosphate, calcium borosilicate, and strontium phosphosilicate. Organofunctionalsilanes have emerged recently as alternative chromate treatments for metals due to their environmental friendliness and good anticorrosion properties [18]. The main disadvantage of using silane is that the substrate must bear hydroxyl groups on its surface. Thus, silane technology offers less flexibility compared to the titanate-based chemistry [19]. Another modern development is the use of intrinsically conductive polymers (ICPs) in the corrosion protection of metals [20, 21,].

A different approach is the use of core-shell materials (e.g., a ferric oxide core with a shell of zinc phosphate or anticorrosive titanium dioxide coated with an organic polymer) to develop anticorrosive primers [22,23] and self-priming, chromate-free, corrosion-resistant coating compositions have also been investigated [24]. Smart corrosion-inhibiting coatings such as the inclusion of a pH indicator into a paint formulation that can cause color change when corrosion occurs are presently under investigation. Recent developments also include the use of nanoclay that can exchange anticorrosive agents with the corrosive species when needed. Although these innovative research projects have not yet provided any new commercial products, they offer a variety of interesting routes for future developments.

3) *High Thermal Resistant and Fire Resistant Coatings*

High thermal-resistant coatings are required for a wide variety of metallic substrates that we encounter in everyday life, including nonstick cookware, barbecues and boilers. Fluorine or silicon-based products are used to obtain a high thermal resistance for the above-mentioned products. Fluorinated coatings are not suitable for high-temperature applications as they degrade above ~300 °C and produce toxic by products. Although other binders such as phenolic or epoxy are used to prepare high thermal-resistant coatings, at present silicon containing coatings dominate the market. Silicon-containing polymers offer better thermal resistance due to the high energy required to cleave silicon bonds compared to carbon bonds in analogous molecules.

Recently developed silicon-based coatings are able to resist temperatures of up to 1000°C. Silicon derivatives such as silicone resins (siloxanes) or inorganic silicates are commonly used for high-temperature applications. Silicon containing materials are expensive, however, copolymers or blends of silicones with acrylate, epoxy or urethanes are very often used to save costs. Recent reports have been made of innovative ways to design thermal-resistant coatings; for example, titanium esters in combination with

aluminum flakes have been incorporated into binders that resist temperatures up to 400 °C. Above this temperature “burn off” occurs and a complex coating of titanium-aluminum is formed that deposits on the substrate and enhances thermal resistance up to 800°C [25]. The devastating nature of fire creates havoc and results in great loss of lives and property. Thus, the need to develop fire-retardant coatings is constantly growing. Although protection against fire by the use of coatings for indefinite periods is impossible, the use of fire-retardant coatings can delay the spread of fire or keep a structure intact against fire, thereby allowing sufficient time for safety measures to be taken. Today, several types of fire retardant are phosphorus containing, halogen-based and intumescent fire-retardant systems, each with a different principle of operation.

Phosphorus containing compounds function by forming a protective layer as a glassy surface barrier. Halogen and antimony based fire retardants are both toxic and ecologically unsafe. Intumescent coatings form an expanded carbonaceous layer which acts as a protective barrier against heat transfer and hinders the diffusion of combustible gases and melted polymer to the site of combustion. These coatings are composed of three components: (i) an inorganic acid (dehydrating agent); (ii) a carbonaceous char-forming material; and (iii) a blowing agent. The performance of the intumescent system depends on the choice of the ingredients and their appropriate combination [26, 27]. Nowadays, expandable graphites are available commercially as fire retardant agents; these contain chemical compounds, including an acid, entrapped between the carbon layers. Upon exposure to higher temperatures, exfoliation of the graphite takes place and this provides an insulating layer to the substrate [28]. A combination of polyurethane and phosphate serves as a well-known fire-retardant intumescent system. One problem associated with these systems results from the solubility of phosphates in water and this leads to problems of migration. Nonetheless, this difficulty can be avoided by encapsulating phosphates (di-ammonium hydrogen phosphate) within a polyurethane shell and indeed, the use of microencapsulated fire retardants in polyurethane coatings has shown good fire resistance [29]. Today, silicon or inorganic hydroxide-based fire-retardant coatings are used in a wide variety of industrial applications [30, 31]. Recently, polymer clay (layered silicates) nanocomposites have also been explored for the development of fire-retardant coatings [32,33].

4) Scratch and Abrasion Resistant Coatings

Coatings are susceptible to damage caused by scratch and/or abrasion. Clearly, the consumer prefers to retain the aesthetic appearance of coated materials and for this reason clear coats used on automobiles must have good scratch and abrasion resistance. An added problem is that scratches may also cause damage to the underlying substrate. Many companies worldwide have undertaken the challenge of improving the scratch resistance of a coating without adversely affecting its other properties. Scratch resistance can be obtained by incorporating a greater number of cross links in the coating's binder but unfortunately highly cross linked (hard) films have poor impact resistance due to less flexibility. A less-cross linked (softer) film will show better

performance with regard to other properties such as anti-fingerprint and impact resistance but will have less scratch and abrasion resistance. Thus, in order to obtain optimal scratch resistance, the correct combination of hardness and flexibility is required. In this context, organic-inorganic hybrid films are paving the way for scratch-resistant coating developments. Recent advances in nanotechnology plays an important role in the development of scratch-resistant coatings [34, 35]. Gläsel et al have shown the use of siloxane encapsulated SiO₂ nanoparticles to develop scratch and abrasion-resistant coatings [36, 37]. The coating industries have developed scratch resistant coatings by incorporating SiO₂ nanoparticles into an organic matrix that can migrate to the surface. In this way the scratch resistance is enhanced due to an enrichment of the nanoparticles near the coating surface [38]. Coatings with good abrasion and scratch resistant properties have also been reported by others [39, 40].

5) Self Healing Coatings

Self cleaning coatings, as the name suggests, have a special functional property and today the term Lotus effects and self cleaning are synonymous (fig. 1). Although these surfaces can be soiled, manual cleaning is unnecessary and a shower of rain is sufficient to carry out the cleaning process. In 1997, Barthelott and coworkers showed that the self-cleaning property of lotus leaves was due to their specialized surface morphology and hydrophobicity [41]. This specialized morphology prevents dirt from forming an intimate contact with the surface, while the high hydrophobicity makes the leaf water-repellent. Consequently, as the water droplets roll onto the leaf surface, they carry along the contaminants. The initial discovery by Barthelott, many groups have attempted to mimic this activity to develop self-cleaning or lotus-effect coatings [42]. Detailed discussions on this concept, the underlying mechanism and the different applications of self-cleaning coating surfaces can be found elsewhere [43, 44]. During the past few years, self-cleaning coatings using photo catalytic titanium dioxide (TiO₂; especially the anatase crystalline form) have attracted considerable attention both in academic and industrial sectors. When photo catalytic TiO₂ particles are illuminated with an ultraviolet light source (e.g., sunlight), electrons are seen to be promoted from the valence band (VB) to the conduction band (CB) of the particle [45, 46]. This creates a region of positive charge (h⁺), holes, in the VB and a free electron in the CB. These charge carriers can either recombine or migrate to the surface, while the holes can react with the hydroxyl or adsorbed water molecules on the surface and produce different radicals such as hydroxyl radicals (OH·) and hydroperoxy radicals (HO₂·). By contrast, the electrons combine with the oxygen and produce super oxide radicals. These photo-produced radicals are powerful oxidizing species and can cause the deterioration of organic contaminants or microbials pieces on the particle surface. The other beneficial effect of TiO₂ is its super hydrophilic behavior, commonly known as the “water sheathing effect” [47]. This allows contaminants to be easily washed away with water or rainfall if the coatings are applied to external surfaces.

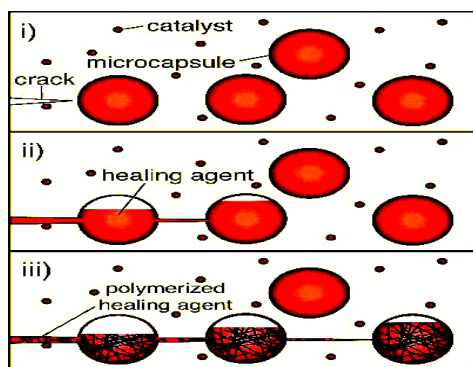


Fig. 1 Self healing action of nano coating

Both photo-catalysis and hydrophilicity occur simultaneously, despite their underlying mechanisms being of an entirely different nature. The addition of silicon oxide to TiO_2 has also been shown to enhance the overall self-cleaning properties [48]. Photo-catalytic TiO_2 particles cannot be incorporated or deposited on the organic coating, as they oxidize the polymer. Recent developments have revealed the use of TiO_2 particles in combination with organic resins [49]. One very recent report noted that lotus leaves may be either hydrophilic or hydrophobic, depending on the contact of water molecules at the leaf surface [50].

6) Antibacterial Coatings

Microorganisms such as bacteria, fungi or viruses represent potential threats for our modern hygienic lifestyle. Microbial growth on coated substrates may have several adverse consequences, including problems of aesthetics (discoloration of the coating), risks to health and hygiene, malodor, biofilm development or microbial corrosion in the case of metallic substrates. Organic coatings are susceptible to microbial attack and the properties of the coating and its composition, the presence of nutrients on the surface and the nature of substrates represent the main parameters that determine the types of micro organisms able to colonize the coating. The classical biocides function is to either by inhibit the growth of bacteria (biostatic) or by kill them (biocidal). However, new legislations, combined with growing pressure from the environmentalists and the possibility of bacterial mutation have forced coating manufacturers to seek new alternatives. Today, more emphasis is placed on the development of bio-repulsive (without killing) antibacterial coatings. A wide variety of organic or inorganic biocides are available commercially and these demonstrate a wide variety of biocidal and biostatic mechanisms[51]. For example biocides containing heavy metal ions function by penetrating the cell wall and inhibiting the bacterium's metabolic enzymes, whereas antimicrobial agents with cationic surfaces cause rupture of the bacterium's cytoplasmic membrane. Examples of organic biocides include polymers, tertiary alkyl amines and organic acids [52,53], while inorganic biocides include silver, zinc oxide (ZnO), copper oxide (CuO), TiO_2 , and selenium [54,55]. Microcapsules containing biocides have also been developed in order to increase the longevity and efficiency of antimicrobial coatings [56, 57].

7) Antifouling Coatings

Marine organisms represent a major threat to all objects used within a marine environment and the unwanted growth or deposition of such organisms being termed as "fouling".

Fouling is generally more prominent in coastal waters where ships or boats are either docked or travel at slow speed. Depending upon the types of marine organism involved, fouling is of two main types, namely micro fouling and macro fouling by marine animals (barnacles, tubeworms) and plants (algae). Both biocidal and nonbiocidal coatings are used to prevent foulings. Biocide-based antifouling coatings function by slow leaching of the incorporated biocides into the coating. For reasons of stringent legislation and toxicity, the use of biocides is restricted on daily basis. For example, tributyl tin (TBT) is a highly efficient marine biocide but it is no longer used due to its toxicity. It is important that the biocide does not have any adverse effects on marine life while carrying out its antifouling activity. For long-term antifouling effects, either controlled-release or contact-active biocides are required [58].

Recently, a number of antifouling products have been developed using micro-encapsulation technology [59, 60,]. For the nonbiocidal approach, polymers with low surface energy are used in order to avoid the adhesion of marine organisms and silicone elastomers are widely used for this purpose. However, this approach is only effective when the vessels move at relatively high speeds, for example ferries. The specialized applications of coatings are almost unlimited and developments of special effect pigments offer new possibilities for the design of functional coatings [61, 62]. In this context, infrared (IR)-reflective pigments are in great demand for the development of "cool roof" coatings, while ultraviolet (UV)-resistant coatings have been developed for outdoor applications [63]. Water-borne functional coatings are becoming more popular than the solvent-borne systems due to their eco-friendly behavior [64].

8) Nanopolymer Coatings

Conducting polymers have evoked a great deal of interest due to their electrochemical properties and their mixed ionic/electronic conductivity properties [65]. They have been used as host matrices in various composite films. Organic or inorganic particles can be mixed with or incorporated in the conducting polymers to modify their morphology, conductivity and different physical properties depending upon the application, such as corrosion protection. Polycrystalline nanocomposites that consist of conductive polymers were found to display novel properties. Nanoparticle dispersions of organic metal polyanilines in various paints at low concentrations can cause tremendous effects in corrosion protection [66]. Melt dispersion of polyaniline leads to fine particles, which self organize into complex ultra fine networks.

Some specific nanoconducting polymers which enhance corrosion resistance are polyaniline, polythiophene and polypyrrole. To enhance the oxidizing power of the polymers, incorporation of strong oxidizing species in the polymer has been envisaged. Polypyrrole nanocomposites with oxides, especially with Fe_3O_4 have prospects for use in corrosion protection of iron [67]. Polypyrrole nanocomposites with montmorillonite clay showed better corrosion protection compared to undoped polypyrrole [68]. Nanostructured materials engineering extends the possibility of engineering 'smart' coatings that can release

corrosion inhibitors on demand when the coating is breached, stressed or an electrical or mechanical control signal is applied to the coating [69].

Inherently conducting polymer (ICP) films containing inhibiting anions as the dopant anions can release them when the film is coupled to a breach in the coating. Research has developed chromate-free corrosion inhibiting additives in which organic corrosion inhibitors are anchored to nanoparticles with high surface areas that can be released on demand [70].

B. Self-Assembled Nanophase Coatings

In the traditional sol-gel method, hydrolysis condensation processes are followed by condensation polymerization upon film application. However, the evaporation process results in voids and channels throughout the solid gel and cannot provide adequate corrosion protection due to the high crack-forming potential. Sol-gel technology has an important limitation related with the maximum coating thickness attainable; typically lower than 2 mm. Studies showed that incorporation of nanoparticles to the sol can make it possible to increase the coating thickness, without increasing the sintering temperature. Electrophoretic deposition of commercial SiO₂ nanoparticles suspended in an acid-catalysed SiO₂ sol on AISI 304 stainless steel substrates leads to coatings as thick as 5 mm with good corrosion resistance [71]. Incorporation of nanoparticles in the hybrid sol-gel systems increases the corrosion protection properties due to lower porosity and lower cracking potential [72]. Incorporation of inorganic nanoparticles can be a way to insert corrosion inhibitors, preparing inhibitor nano reservoirs for self repairing pre-treatments with controlled release properties [72, 73]. Studies showed that sol-gel films containing zirconia nanoparticles present improved barrier properties. Doping this hybrid nanostructured sol-gel coating with cerium nitrate brings additional improvement to corrosion protection. Zirconia particles present in the sol-gel matrix act as nano reservoirs providing a prolonged release of the cerium ions [74]. The recent discovery of a method of forming functionalized silica nanoparticles *in situ* in an aqueous sol-gel process, and then cross linking the nanoparticles to form a thin film, is an excellent example of a nanoscience approach to coatings.

This self-assembled nanophase particle (SNAP) surface treatment based on hydrolysed silanes, containing a cross linking agent substantially is free of organic solvents and Cr-containing compounds promotes adhesion of overcoat layers more effectively. Unlike chromate based treatments, SNAP coatings provide barrier-type corrosion resistance but do not have the ability to leach corrosion inhibitors upon coating damage and minimize corrosion of the unprotected area. The SNAP surface coating could replace the currently used chromate containing surface treatment and can provide the basis of long-lived coating for aluminum alloys [75]. The ability to design coating components from the molecular level upward offers potential for creating multifunctional coatings. Molecular simulation approaches have been used to enhance the understanding of complex chemical interactions in coating based on self-assembled nanophase particle (SNAP) surface treatment [76]. SNAP

coatings provide barrier type corrosion resistance but do not have the ability to leach corrosion inhibitors upon coating damage and minimize corrosion of the unprotected area. The SNAP surface coating could replace the currently used chromate containing surface treatment and can provide the basis of long-lived coating for aluminum alloys.

1) Self-Cleaning and Biocidal Coatings

There is a great interest in the design and development of surfaces that not only provide biocidal activity but are also easy to clean and even self-cleaning. Most of such coatings acquire their biocidal/self-cleaning capacity by incorporating specific nanoparticles: basically silver (Ag) and titanium oxide (TiO₂) [77, 78]. Nano TiO₂ is used for developing anti-UV, anti-bacterial and self-cleaning paints. This possesses self-cleaning hydrophobic properties, which causes water droplets to bead-off of a fully cured surface picking up dirt and other surface contaminants along the way.



Fig. 2 Self cleaning action of nano coating

This self-cleaning action (Fig. 2) helps clean and maintain important surfaces and to accelerate drying, leaving the surface with minimal spotting. A recent study by Cai *et al* [79] utilizes corona treatment technique, inert sol-gel coating and anatase TiO₂ layer. With the corona treatment, an organic surface was activated to allow a uniform TiO₂ sol-gel coating. Nanoparticles of surfacetreated Al₂O₃ molecules help increase hydrophobicity and increase scratch resistance. Microbial evolution on a wide variety of surfaces can cause corrosion, dirt, bad odour and even serious hygiene and health problems. AMBIO (Advanced Nanostructured Surfaces for the Control of Biofouling), a European Union research project [80] is investigating how to prevent the build-up of organisms on surfaces under marine conditions to avoid biofouling. The project aims to use nanostructuring to significantly reduce the adhesion of organisms to surfaces in aquatic environments, and thus control the fouling process without the use of toxic biocides such as copper and organotin compounds that prevent fouling by killing organisms.

Nanostructuring of the surface alters the wetting properties and is intended to signal that the site is not suitable for the organisms to settle. The project aims to synthesize new nanostructured polymers that are stable under marine conditions. Although no alternatives to the use of biocides are available at present, creation of nanostructured surfaces could offer an innovative and environment-friendly solution to the problem of biofouling [80]. Research has developed new biocidal coating systems that prolong biocidal activity by immobilizing such

additives on nanoparticles; the embedded biocides are designed to be released into the environment only when needed, thus extending the lifetime of the biocidal activity [81].

III. PIGMENTS FOR PAINT FORMULATIONS

Pigments are added to paint resins to confer improved physical properties and/or to provide corrosion inhibitive or protective properties to the paint film. Since paint film always possess a degree of permeability to moisture and water, the reinforcement of the protective action of paint by corrosion inhibitive pigments is necessary. However, inhibitive pigments are relatively ineffective for this purpose in the presence of high concentration of chlorides such as seawater [82]. Paints pigmented with zinc dust are useful as prime coats. The function of the zinc is to cathodically protect the steel in the same manner as galvanized coatings. Such paints are some times used over partly rusted galvanized surfaces because they also adhere well to zinc. The minimum amount of zinc dust pigment required to provide cathodic protection depends on several factors including zinc particle size, nature of the resin, amount of ZnO and other pigments that may be present.

The metallic zinc content of such Zinc-rich paints is generally of the order of 92-95% of the dry film weight. The initial penetration of water through the binder causes zinc to corrode sacrificially producing zinc hydroxide. Carbon dioxide also diffuses through the binder to react with the hydroxide and form a carbonate. Zinc corrosion product fills the pores in the paint film and produces an impervious, compact and adherent layer. High zinc content in the dry paint film is essential if the first part of the reaction is to succeed in blocking the pores and once the film is sealed the loss of electrical contact between the pigments particles is not so important. Studies of zinc rich primers have shown a reduction in their galvanic action with time [83]. This is thought to be due to the oxidation of the zinc particles that interrupts the electrical flow between adjacent zinc particles and between the zinc and the steel substrate. However, corrosion protection may be maintained by the barrier mechanism that occurs.

Aluminum in flake form is often used as protective pigment but the protective action arises not from cathodic protection as with zinc but by extension and blockage of permeability pathways within the binder. It is possible that some degree of cathodic protection occurs when the dried film is mechanically damaged so that the alumina film of the flakes is disrupted and there is cathodic protection of the steel substrate while the film is being established but the effect is essentially short-term if present at all. Aluminium additions of 30-60% by weight are common.

Other metallic pigments such as stainless steel powder have been proposed as protective pigments and in severe service conditions, such pigments have been found to be highly satisfactory. The mode of protection appears to be akin to that of aluminum, namely barrier action rather than by reaction with the substrate or the binder as with zinc. Inhibitive pigments generally contain leachable ions that act as passivators towards the substrate metal. Typically

chromates such as zinc chromates are widely used as pigments for protective paint coatings for a variety of metal substrates, when moisture permeates the paint film, leaching of chromate ions occurs and these migrates to the metal substrate where passivation occurs. Zinc molybdate has been suggested as inhibiting pigments for paints and it is less toxic than chromates.

Zinc phosphate which was introduced as a nontoxic alternative to zinc chromate has been adopted in many paint formulation. To improve the performance of zinc phosphate, a modified zinc phosphates has been developed with inorganic aluminum phosphate and molybdenum oxide. These pigments work better in some binder systems and on some substrate than others. Modified zinc phosphate is particularly suited for coatings for non-ferrous substrates such as aluminum. Modified polyphosphate pigments were developed to provide improved electrochemical activity and match the performance of chromates where modified zinc phosphates could not. Environmental issues concerning zinc and the classification of zinc as a heavy metal have let to the development of new anticorrosive pigments based on calcium phosphate. In general, the pigment selection is the result of a compromise in the desirable properties of the final paint film.

Various non-inhibitive but protective pigments are also widely used notably red iron oxide, micaceous iron oxide and these pigments are protective by virtue of barrier action. Pigments are incorporated into paints by means of mixers and mills having a strong shearing action whereby the finely divided pigments become dispersed and completely wetted by the paint resin. The mixing process can involve several hours depending on the nature and particle size of the pigments, viscosity of resin, type of resin and solvent present. Formulation based on zinc and aluminum is now successful in marine locations [84]. All present day paints are permeable in some degree to water and oxygen and some binders are less permeable than others, but their better performance as a diffusion barrier applies only to well adhering multiple coat applications that effectively seal up pores and other defects. Pigmentation levels for barrier coatings are less critical than are pigmentation levels for zinc and inhibitive based primers [85]

Kalendova (86) studied mechanisms of the action of zinc powder as an anticorrosive pigment in coating compositions based on binders that are composed of a two-component epoxy, a single-component polyurethane, and epoxy-ester resins. The results of the study have shown that neutralisation and barrier mechanisms contribute more than the electrochemical mechanism to the effectiveness of the anticorrosion protection. During the investigation, the results obtained in corrosion tests were evaluated by investigating the morphology of coatings by means of electron microscopy procedures.

Santagata et al [87] investigated the effect of different kind of pigments on the corrosion resistance properties of an epoxy paint using electrochemical impedance spectroscopy and open circuit potential measurements. Painted naval steel samples were studied during the exposure to artificial sea water. The epoxy paint coatings were prepared employing red lead, zinc, red iron oxide or titanium dioxide as pigment with 0.8 of PVC/CPVC ratio.

From the EIS and corrosion potential data analysis, it was found that the anticorrosive protection given by an anticorrosive (pigmented with red lead) and a top coat (pigmented with red iron oxide) epoxy painting scheme was both more lasting and more effective. This was attributed to the effective adhesion provided by the chemical bonding between the steel surface and the epoxy paint groups and the constant high barrier effect afforded by this type of top coat.

Emira et al [88] evaluated magnesium ferrite pigments in anticorrosive water borne paints. The study includes the use of two different anticorrosive pigment volume concentration (APVC), 15 and 25 per cent in paint formulations. Epoxy and acrylated alkyd resins were used as binders. The paints were evaluated by accelerated salt spray tests, corrosion tests and electrochemical evaluations. The results obtained were compared with reference paints containing zinc ferrite and zinc phosphate pigments. A lower per cent, i.e. 15 per cent of APVC was found to be sufficient to provide satisfactory anticorrosion protection.

Zinc phosphate pigment as anticorrosive pigment in waterborne epoxy paints for steel protection was investigated by Caprari et al [89]. The main variables considered were PVC and the anticorrosive pigment content. Accelerated tests (salt spray, humidity chamber, and electrochemical tests) were performed to evaluate the paints' anticorrosive performance. Good correlation was found using salt spray and impedance tests. From analysis of the time dependence of all the experimental results it was concluded that an efficient steel protection could be obtained using a waterborne epoxy primer pigmented with zinc phosphate. Such protection is attained through the barrier effect afforded by the paint film as well as the precipitation of a pretty stable ferric phosphate layer under the intact and damaged coating areas.

Bodo muller [90] studied the effect of zinc pigment in water borne paint resin and found that the epoxy ester resin loses its corrosion inhibiting properties after film formation, because of losing its mobility, which seems to be a requirement for corrosion inhibition. So, zinc dust is inhibited in the liquid waterborne paint but still shows its sacrificial action in the solid primer coating. Abd -Ghaffar et al [91] in their study, Ca, Zn and Ca-Zn phosphomolybdates were prepared and characterized by chemical analysis and spectrophotometric measurements, X-ray diffraction (XRD) and scanning electron microscopy (SEM), in addition to thermal gravimetric analysis (TGA). Their anticorrosive properties were evaluated by incorporation in anticorrosive paint formulations using medium oil alkyd resin as a binder. The paint films were tested in artificial seawater for 28 days. The results showed superior anticorrosive protection properties of the pigments prepared were superior over other nontoxic pigments. Batis et al [92] investigated the possibilities for the exploitation of the powder by-product of oxygen converter slag from the ferronickel industry as pigment in anticorrosive non-toxic paints. Paints with this powder, either unrefined or processed, as a pigment and chlorinated rubber resin were produced and tested by the following methods: half-cell potential, mass loss, chloride diffusion and EIS. The results indicated that protection of steel was achieved to a

satisfactory level. A comparative electrochemical study was carried out between conventional zinc rich and novel zinc containing paints by Faidei et al [93]. Current and potential were monitored with immersion time in 3.5%NaCl. Zinc rich paint offered cathodic protection for about 7 days compared with 40 days for the new paint. Thereafter a reversal in polarity was obtained once rust formed. Thus author concluded that established cathodic protection criteria can not be solely used to assess the protection properties of zinc containing paint.

IV. NANOPARTICLES/FILLERS FOR COATINGS

Nanoparticles are generally considered to be a number of atoms or molecules bonded together with radius of 100nm. A cluster of one nanometer radius has approximately 25 atoms, but most of them are on the surface of the cluster [94]. In typical nanomaterials, the majority of the atoms located on the surface of the particles, whereas they are located in the bulk of conventional materials. Thus the intrinsic properties of nanomaterials are different from conventional materials since the majority of atoms are in a different environment (Fig. 3).

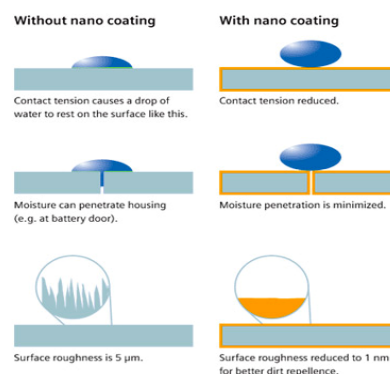


Fig. 3 Nano coating Vs conventional coating

Nanomaterials represent almost the ultimate in increasing surface area and they are chemically very active because the number of surface molecules or atoms is very large compared with the molecules or atoms in the bulk of the materials. Substances with high surface areas have enhanced physical, chemical, mechanical, optical and magnetic properties and this can be exploited for a variety of structural and non-structural application. Nanoparticles / fillers find application in wear-resistant, erosion-resistant and corrosion resistant [95].

Typical nanoparticles like carbon black are used in car tyres to increase the life of the tyre and provide the black colour. Nanocoatings are coatings that are produced by usage of some component at nanoscale to obtain desired properties [96]. Because of greater surface activity of nano particles, they can absorb more resins compare to conventional pigments and thus reduce the free space between the pigment and the resin. Thus, nanoparticles increase the transport path of corrosive species and enhance the protective properties and performance. Nanocomposites represent a new prospective branch in the various fields of polymer materials science and technology. It has been shown that an overall enhancement of properties of resins can be achieved under certain conditions by the addition of

nanoparticles. Min Zhi Rong et al demonstrated the importance of TiO_2 –nanoparticles dispersion in an epoxy resin matrix on the materials tribological properties when sliding against a smooth steel counterpart. It was found that the friction and wear behavior of polymeric nanocomposites under sliding environment was rather sensitive to the dispersion states of the nanoparticles and when the micro structural homogeneity of the nanocomposites was improved, their wear resistance could be increased significantly[97].

A large number of studies dedicated to coating systems containing nanofillers have already been published such as on epoxy/ TiO_2 , Latex/silica [98, 99] and these studies show that compared to conventional organic coatings containing microfillers, the use of nanofillers has advantages such as improvement in scratch, abrasion, heat, radiation and swelling resistance and decrease in water permeability and increase in hardness, wetherability, modulus [100]. To make a successful ‘nanoorganic coating’ it is imperative to disperse the binder. If this is not achieved, agglomerates will form and the expected properties will not be obtained. When the uniform incorporation is difficult, such with lamellar silicates, a chemical modification of the nanofiller surface might be necessary [101]. Sometimes to retain the desired properties of the nanoparticles, a stabilizer must be used to prevent further reaction. This enables them to be wear-resistant. The inclusion of nanopigments in binder results in new and interesting macroscopic properties due to the extended ‘inter-phase’ created around the nanopigment particles. Nanotechnology promises to unleash vast potential in the field of coatings and it deals with incorporating nanoparticle that enhance specific features. Structure of a coating influences its protective properties and plays a crucial role in surface protection and incorporation of nanofillers can improve protective properties of coating. A studies on preparation of epoxy-clay nanocomposite coating by M.R.Bagherzadeh et al [102] shown that incorporating nanoclay (Fig.4) particles into organic coatings improves anti-corrosive properties of coating. In their study, the desired amount of resin and nanoclay was mixed together. The mixing process was performed in an oil bath (50-70 degree).Then the mixture was subjected to sonication for 8-12h. For fabrication of nanocoating after addition of some additives to epoxy –clay mixture, the stoichiometric amount of the hardener was added to mixture.

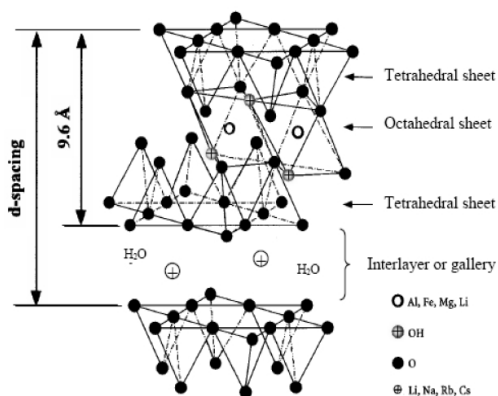


Fig. 4 Structure of nanoclay

By this method, three samples containing different

amount of clay (1.3 and 5%) were prepared. It was found that as the clay loading increases the barrier and anti-corrosive properties increases, so in this work the best anti-corrosive performance of coatings was obtained at 3 and 5 wt % clay concentrations. The EIS results with 3 and 5wt% clay concentration samples were relatively similar but using 3wt% is economically prepared. H.J.Yu et al prepared nano- CaCO_3 modified powder coatings using epoxy resin/nano CaCO_3 Composite which were obtained by in situ and inclusion polymerization. They compared with unmodified powder coatings and found that the tensile properties and neutral salt spray corrosion resistance of the modified ones were remarkably improved. They concluded that the dispersion of nanoparticles in the resultant films effects on the properties of resultant powder coatings greatly and method of in situ and inclusion polymerization is obviously an efficacious way to disperse nano- CaCO_3 in the powder coatings effectively. And this method can be a reference to make other kinds of nanoparticle modified powder coatings [103].

M.Sangermano et al prepared nanosilica containing coatings by UV curing of an epoxy system. They found that surface properties were modified with an increase on hardness in the presence of filler. Finally the strong decrease on water uptake in the presence of SiO_2 was noticed. They concluded that these nanocomposite materials can be a good choice for gas barrier coatings applications [104]. Linda Fogelstrom et al investigated the possibility of creating a nanocomposite resin in order to prepare UV-curable system. The hydroxyl group on hyper branched polyester Boltron H30 was acrylated using direct esterification with acrylic acid. Both 30 % and 70 % acrylated Boltron H30 were synthesized. However, when clay had been added before acrylation, outcome of the fictionalization was affected, rendering an uneven acrylation. This in turn affected the coating properties, which was clearly demonstrated in the coating characterization. The nanocomposite preparation was successful both when clay added before and after the acrylation and better dispersion of the nanoparticles was obtained in the 30% acrylated matrix than in the 70 % acrylated matrix. This would imply that the 30 % acrylated Boltron H30 with clay added before the acrylation would give the best coating. However the uneven acrylation caused by clay added before the acrylation counteracted many of the positive effects of the nanoparticles addition. Consequently ,it was the coating prepared from 30% acrylated H30 with clay added after the acrylation, having a mainly exfoliated structure according to X-Ray and TEM exhibited the largest property improvements compared with the coating without nanofiller[105]

Andrea Kalendova studied of the zinc particle sizes and shape effects on the anticorrosive coating properties. As a binder the epoxy ester resin is used. The zinc particle size and shape effects were investigated from the mechanical coating properties, film permeability to water vapor and pigment anticorrosion protection efficiency points of view. The connection between the spherical particle sizes and the coating anticorrosive efficiency was found. The smaller particle sizes mean better anticorrosive coating properties. The lamellar zinc particles exhibit the highest anticorrosion

efficiency at a concentration around 20 vol. % [106]. Different forms of nanocomposite finds application in coating industry (Fig.5).

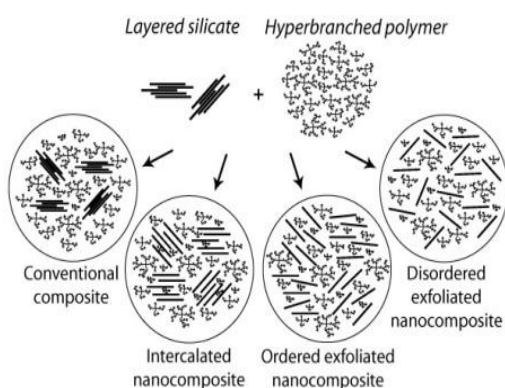


Fig. 5. Different forms of nanocomposite coatings

A series of polymer–clay nanocomposite (PCN) materials that consist of siloxane-modified epoxy resin and inorganic nanolayers of montmorillonite (MMT) clay has been prepared through a thermal ring opening polymerization using 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane as a curing agent. These PCN materials at low clay concentration in the form of coating on cold-rolled steel (CRS) were found to be much superior in corrosion protection over those of pure epoxy resin when tested for performance in a series of electrochemical measurements of corrosion potential, polarization resistance, corrosion current, and impedance spectroscopy in 5 wt % aqueous NaCl electrolyte. The as-prepared materials were characterized by infrared spectroscopy, wide-angle X-ray diffraction, and transmission electron microscopy. After measurements, it was found to have advanced protection against corrosion on CRS coupon compared to bulk epoxy resin. Molecular (e.g., O₂, N₂, and H₂O) permeability of epoxy resin–clay nanocomposite membranes was found to be lower than that of bulk epoxy resin based on the studies of gas and vapor permeability analysis. Moreover, the epoxy resin–clay nanocomposite materials have significant advantages over standard epoxy resins such as lower water absorption, lower cure shrinkage, moderate glass transition temperature (T_g), and higher tensile strength [107].

In this research, both commercially available and synthesized organolayered silicates, which are compatible with the epoxy resins, were used to make epoxy nanocomposites. The epoxy resin used in this research includes Epon 862/curing agent W (the aerospace epoxy resin), the Epon 828 / Epi-Cure curing agent 8290-Y-60 (used as the primer layer for corrosion prevention in aircraft coating) and Epon 828/Jeffamine D400. The morphology of the nanocomposites was characterized using wide-angle X-ray diffraction (WAXD), small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). The morphology development for the aerospace epoxy-organoclay nanocomposite was monitored through in situ SAXS and analyzed. The solvent absorption of the exfoliated aerospace epoxy-organoclay nanocomposite in acetone was examined and the diffusion coefficients of solvent in the nanocomposites were reduced. The organoclay / Epon 828 / Y-60 and organoclay / Epon 828 / D400 nanocomposite were used to make coatings on an Al

surface. The anticorrosion properties of the nanocomposite coatings were evaluated and an improvement in the anti-corrosion behavior of epoxy clay nanocomposite was found [108]. The effect of the pigment/binder ratio (P/B) on the corrosion resistance properties of polyurethane paints on carbon steel was investigated by AC impedance techniques. Painted steel electrodes were studied during exposure to 3.5% NaCl solution for up to 1000 h. Two series of polyurethane paints were used: conventional ZnO or nano-ZnO as pigments. The results showed that the corrosion resistance is affected by the P/B ratio, the optimum amount of zinc oxide of conventional zinc oxide (P/B = 1) was less than that of nano-zinc oxide (P/B = 0.3). Therefore, better anticorrosive protection is achieved by the coatings pigmented with nano-ZnO and a lesser amount of nano-ZnO is required [109].

Tetrapod-like nano-particle ZnO/acrylic resin composite was prepared by a direct dispersing method forming a multi-function coating. The composite with uniform distribution of nano-ZnO in the acrylic resin have both anti-electrostatic and antibacterial functions. The coatings can be used for plastic materials or others. The mechanisms of the electrostatic and antibacterial functions were also analyzed. On the aspect of antibacterial function, tetrapod-like nano-ZnO has higher antibacterial effect against colibacillus and *Staphylo-coccus aureus* [110].

A molybdenum based treatment based nano-particles by sol–gel method has been investigated as a replacement for toxic chromate. A treatment process in which the surface was etched followed by oxide thickening prior to molybdate treatment is being proposed. The process involves surface cleaning, etching followed by oxide thickening in distilled water and then, treatment in molybdate sol. The effect of surface preparation prior to molybdate treatment on the corrosion resistance of AA6061-T6 in 3.5% NaCl solution was measured using ac impedance spectroscopy and DC polarization techniques. Optical microscope and SEM showed a marked decrease in the number and depth of pits for the samples pre-etched and oxide thickened as compared to the non-etched treatments. XPS analysis revealed presence of relatively higher amount of Mo₃Pp1 and Mo₃P₃ for the samples etched followed by oxide thickening compared with the non-etched samples. Conversely, non-etched samples revealed high amount of Mo₃P₃ than the etched samples. Accordingly, it was suggested that the protection is due to conversion of molybdate from less corrosion resistant species such as Mo₃P₃ to more corrosion resistant oxides such as Mo₃P₁ and Mo₃P₃. AFM showed that the film formed in the etched samples is more compact and has smoother appearance than the non-etched ones. It has been shown that the etching process prior to oxide thickening enhances formation of a uniformly distributed highly protective compact molybdate oxide film [111].

The preparation of PMMA / Na⁺-MMT clay nanocomposites was investigated by using sodium dodecylbenzenesulfonate (SDS) and potassium peroxodisulfate (KPS) as a surfactant and chain initiator for an in situ emulsion polymerization reaction, respectively. The as-prepared nanocomposites were then characterized by Fourier transformation infrared (FTIR) spectroscopy, wide-

angle X-ray diffraction (WAXRD) patterns and transmission electron microscopy (TEM). It should be noted that the nanocomposite coating containing 1 wt% of clay loading was found to exhibit an observable enhanced corrosion protection on cold-rolled steel (CRS) electrode at higher operational temperature of 50 °C, which was even better than that of uncoated and electrode-coated with PMMA alone at room temperature of 30°C based on the electrochemical parameter evaluations (e.g., E_{corr} , R_p , I_{corr} , R_{corr} and impedance). In this work, all electrochemical measurements were performed at a double-wall jacketed cell, covered with a glass plate, through which water was circulated from a thermostat to maintain a constant operational temperature of 30, 40 and 50 ± 0.5 °C. Moreover, a series of electrochemical parameters shown in Tafel, Nyquist and Bode plots were used to evaluate PCN coatings at three different operational temperatures in 5 wt% aqueous NaCl electrolyte. The molecular barrier properties at three different operational temperatures of PMMA and PCN membranes were investigated by gas permeability analyzer (GPA) and vapor permeability analyzer (VPA). Effect of material composition on the molecular weight and optical properties of neat PMMA and PCN materials, in the form of solution and membrane, were also studied by gel permeation chromatography (GPC) and UV-vis transmission spectra [112].

A series of novel advanced environmentally friendly anticorrosive materials have been successfully prepared by effectively dispersing nanolayers of Na⁺-montmorillonite (Na⁺-MMT) clay into water-based polyacrylate latex (i.e., vinyl acrylic terpolymers). First of all, a polyacrylate latex was synthesized through co-polymerizing organic monomers of MMA, BMA and styrene using conventional emulsion polymerization technique with SDS, 1-pentanol and KPS as surfactant, co-surfactant and initiator, respectively. Subsequently, the commercial purified hydrophilic Na⁺-MMT was effectively dispersing into the polyacrylate latex through the direct solution dispersion technique.

The as-prepared neat polyacrylate and the series of water-based polyacrylate/Na⁺-MMT clay nanocomposite (Na⁺-PCN) materials were subsequently characterized by FTIR spectroscopy, XRD, TEM and GPC. The water-based Na⁺-PCN materials loaded with low content of Na⁺-MMT when in the form of coating on the cold rolled steel (CRS) coupons was found to be remarkably superior in anticorrosion efficiency over those of neat polyacrylate based on a series of electrochemical measurements of corrosion potential, polarization resistance, corrosion current, and impedance spectroscopy in saline water. Effect of material composition on the molecular barrier, optical clarity and thermal stability were also studied by molecular permeability analysis, ultraviolet and visible transmission spectra, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), respectively. Organo-PCN materials were also prepared as a control experiment for comparative studies [113]. A series of poly (o-methoxyaniline) (PMA) / Na⁺montmorillonite (MMT) clay nanocomposite materials have been successfully prepared by in situ emulsion polymerization in the presence of inorganic nanolayers of hydrophilic nanoclay with DBSA and APS as

surfactant and initiator, respectively. The as-synthesized nanocomposite materials were characterized by Fourier-transformation infrared (FTIR) spectroscopy, wide-angle powder X-ray diffraction (XRD) and transmission electron microscopy (TEM). Nanocomposite materials in the form of coatings with low loading of nanoclay (e.g., 5 wt.%, CLMA5) on cold rolled steel (CRS) were found much superior in corrosion protection over those of neat PMA based on a series of electrochemical measurements of corrosion potential, polarization resistance, corrosion current and impedance spectroscopy in 5 wt.% aqueous NaCl electrolyte. The molecular weight of PMA extracted from nanocomposite materials and neat PMA were determined by gel permeation chromatography (GPC) with NMP as eluant. Effects of material composition on the optical properties, electrical conductivity, thermal stability and surface morphology of neat PMA and/or a series of nanocomposite materials, in the form of solution, powder-pressed pellet and fine powder, were also studied by ultraviolet and visible spectra, four-point probe technique, thermogravimetric analysis (TGA) and scanning electron microscopy (SEM), respectively [114].

DBSA - doped polyaniline (PANI) / Na⁺montmorillonite (MMT) clay nanocomposite (PCN) materials have been successfully prepared with dodecylbenzenesulfonic acid (DBSA) as emulsifier and dopant for the emulsion polymerization of aniline. The as-prepared DBSA-doped samples were subsequently characterized by FTIR spectroscopy, WAXRD patterns and TEM. It should be noted that the nanocomposite coating containing 1 wt % of clay loading was found to exhibit an observable enhanced corrosion protection on cold-rolled steel (CRS) electrode at higher operational temperature of 50°C, which was even better than that of uncoated and electrode-coated with PANI alone at room temperature of 30°C based on the electrochemical parameter evaluations (e.g., E_{corr} , R_p , I_{corr} , R_{corr} and impedance). In this work, all electrochemical measurements were performed at a double-wall jacketed cell, covered with a glass plate, through which water was circulated from a thermostat to maintain a constant operational temperature of 30, 40 and 50 ± 0.5 °C. Moreover, a series of electrochemical parameters shown in Tafel, Nyquist and Bode plots were all used to evaluate PCN coatings at three different operational temperatures in 5 wt % aqueous NaCl electrolyte. Effect of material composition on the molecular weight and optical properties of PANI and PCN materials, in the form of solution, were studied by gel permeation chromatography (GPC) and UV vis spectra, respectively. Finally, electrical conductivity at three different operational temperatures of PANI and PCN powder-pressed pellets doped with different inorganic acids such as HCl, HNO₃ and H₂SO₄ was also investigated through the measurements of standard four-point-probe technique [115].

Nanoscale montmorillonite (MMT) clay fillers dispersed in a polyphenylenesulfid (PPS) matrix through the processes of octadecylamine (ODA) intercalation and molten PPS co-intercalation and exfoliation. Cooling this molten exfoliated material led to the formation of a PPS / MMT nanocomposite. The MMT nanofiller conferred three advanced properties on the semi-crystalline PPS: First, it raised its melting point by nearly 40 to 290 °C; second, it

increased its crystallization energy, implying that an excellent adherence of the nanofillers surfaces to PPS in terms of a good interfacial bond and third, it abated the degree of its hydrothermal oxidation due to sulfide and sulfite linkage transformations. When this advanced PPS nanocomposite was used as a corrosion preventing coating for carbon steel in a simulated geothermal environment at 300 °C and adequately protected the steel against hot brine-caused corrosion. In contrast, an MMT-free PPS coating of similar thickness was not nearly as effective in mitigating corrosion as was the nanocomposite; in fact, the uptake of corrosive ionic electrolyte by the unmodified coating increased with an extending exposure time[116].

A series of polyaniline (PANI) / Na⁺-montmorillonite (MMT) clay and PANI/organo-MMT nanocomposite materials have been successfully prepared by in situ emulsion polymerization in the presence of inorganic nanolayers of hydrophilic Na⁺-MMT clay or organophilic organo-MMT clay with DBSA and KPS as surfactant and initiator respectively. The as-synthesized Na⁺-PCN and organo-PCN materials were characterized and compared by fourier transformation infrared (FTIR) spectroscopy, wide-angle powder X-ray diffraction (XRD) and transmission electron microscopy (TEM). Na⁺-PCN materials in the form of coatings with low loading of Na⁺-MMT clay (e.g., 3 wt. %, CLAN3) on cold-rolled steel (CRS) were found much superior in corrosion protection over those of organo-PCN materials with same clay loading based on a series of electrochemical measurements of corrosion potential, polarization resistance, corrosion current and impedance spectroscopy in 5 wt % aqueous NaCl electrolyte. The molecular weights of PANI extracted from PCN materials and PANI were determined by gel permeation chromatography (GPC) with NMP as eluant. Effects of material composition on the gas permeability, optical properties and electrical conductivity of neat PANI and a series of PCN materials, in the form of free-standing film, solution and powder-pressed pellet, were also studied by gas permeability analyzer (GPA), ultraviolet and vis spectra and four-point probe technique, respectively[117].

Tribological and electrochemical corrosion properties of Al₂O₃/polymer nanocomposite coatings were studied by using micro-hardness test, single-pass scratch test, abrasive wear test, and finally electrochemical technique such as potentiodynamic polarization measurement. The coatings containing Al₂O₃ nanoparticles showed improvement in scratch and abrasive resistance compared with that of polymer coating. The improvement in scratch and abrasive resistance is attributed to the dispersion hardening of Al₂O₃ nanoparticles in polymer coatings. Corrosion test results showed that the embedded Al₂O₃ nanoparticles in polymer matrix do not sacrifice the corrosion resistance of the polymer itself [118].

V. CONCLUSIONS

In this review we overviewed different types of organic coating based on their function, pigments used for coating formulation and nanoparticles/nanofillers for coating

application. Protective coatings perform important functions based on types of coatings. Paint industry has made significant progress in improving protective coatings and the formulation of paints for specific purpose remain very much a technological art. The application of nanotechnology in the corrosion protection of metal has recently gained momentum as nanoscale materials have unique physical, chemical and physicochemical properties, which may improve the corrosion protection in comparison to bulk- size materials. Significant work on nanoscale coatings is underway globally in the area of the area of nanocoating in the way of incorporating nanoparticles in coating formulation that enhance specific features. Nanotechnology promises to unleash vast potential in the field of coatings. The future of these special coating markets will further expand in different industry such as marine, building and defense. In the opinion of a great number of experts, nanotechnology has a positive potential not only for economic development. Considerable improvement is also expected with regard to the protection of the infrastructure and human health. Thus, nanotechnology development may conserve our natural resources and improve the overall performance of corrosion protection.

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A.Mathiazhagan, biography and photograph not available at the time of publishing.

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