

# Chapter 1

## Polymer Clay Nanocomposites – An Overview

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### 1.1. ABSTRACT

Polymer nanocomposites are hybrid materials composed of a polymer matrix and another phase which has at least one dimension in the nanometre range, i.e. <100 nm. The present review chapter discuss the recent scientific and technological advances in the field of polymer clay nanocomposites. This include introduction to polymer clay nanocomposites, organic modification of clays, structural characterization of nanocomposite, preparative methods and morphological study, nanocomposite properties, advantages and applications like self assembly and corrosion resistant coatings and finally scope and objectives of the present research work.

### 1.2. INTRODUCTION

Polymer nanocomposites have attracted great interest, both in industry and in academia, because they often exhibit remarkable improvement in materials properties when compared with virgin polymer or conventional micro and macro-composites. The properties found to be improved include mechanical properties, dimensional stability, thermal stability, chemical resistance, surface appearance, flame retardancy, biodegradability of biodegradable polymers and decreased gas

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permeability (Kazutoshi Haraguchi and Huan, 2006; Gilman et al., 2000; Lee et al., 2002 Hwan-Man Park et al., 2002). These unique properties resulted from the combining characteristics of components at nanoscaled level. Clays, graphene, carbon nanotubes, silica, alumina etc are the potential nanofillers that have been in the focus of current research interest (Manias et al., 2001; Wang and Pinnavaia 1998; Yu et al., 2000 Iijima et al., 1991; Chan et al., 2002; et al., Musto 2004; Petrovic et al., 2000)

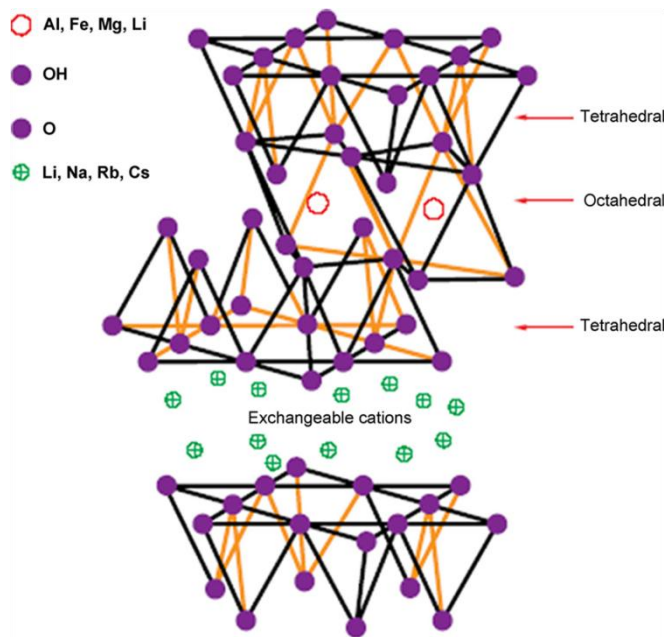
Among these nanofillers, nanometric layered silicates commonly known as clays have been widely used as fillers for thermoplastics like polypropylene, polyethylene, polystyrene and nylon due to its natural abundance, low cost and broadest commercial viability. Although the intercalation chemistry of polymers when mixed with appropriately modified clays has long been known, the field of polymer-clay nanocomposites (PCNs) gained momentum following two major findings. First, the report from Toyota Central Research Laboratory that very moderate clay loading resulted in pronounced improvements in thermal and mechanical properties of the matrix polymer, Nylon 6 (Okada et al., 1990). Second, Giannelis et al., 1993 found that it was possible to melt-mix polymers with clays without the use of organic solvents. The improved properties of PCNs were attributed to the dispersion of clay layers having thickness of one nanometer and lateral dimensions of several nanometers in the polymer matrix. In order to achieve this good compatibility between polymer matrix and the clay, it is very important to understand the structure of clay.

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### 1.3. Clay Structures

Clays are the most popular layered silicates used in polymer nanocomposites preparations. Clays have layered structure. The layers are built from tetrahedral sheets in which a silicon atom is surrounded by four oxygen atoms and octahedral sheets in which a metal like aluminium or magnesium is surrounded by eight oxygen atoms. The tetrahedral (T) and octahedral (O) sheets are fused together by sharing the oxygen atoms. Unshared oxygen atoms are present in hydroxyl form. Tetrahedral and octahedral sheets stack naturally in specific ratios and modes, leading to the formation of 1:1, 2:1 or 2:1:1 layered silicates or phyllosilicates. Among these, 2:1 phyllosilicates have been used for the preparation of PCNs due to the ease of separation of individual silicate layers owing to its structural features. As shown in Figure 1.1 the crystal lattice of 2:1 phyllosilicate consists of 1 nm thick aluminosilicate layers, with an octahedral alumina sheet sandwiched between two tetrahedral silica sheets. The stacks of the platelets are held together by weak Van der Waals force, leaving an interlayer space (or gallery) between the platelets. The clay platelets stacks are usually called as tactoids. Isomorphic substitution of  $Al^{3+}$  in the alumina sheet with cations such as  $Mg^{2+}$  or  $Fe^{2+}$  produces negative charge to the layers. This negative charge is counterbalanced by alkali cations ( $Na^+$ ,  $Li^+$  or  $Ca^{2+}$ ) positioned in the gallery between the aluminosilicate layers which are exchangeable with other inorganic and organic cations and the cation exchange capacity (CEC) is expressed as meq/100 g clay. Clays having high CEC are generally used for the preparation of PCNs. The type of cations positioned in the gallery and its degree of hydration determines the gallery height of pristine clay. 2:1 phyllosilicate include mica,

smectite, vermiculite, and chlorite. The clay minerals most used in nanocomposites are smectites, such as montmorillonite (MMT), saponite and hectorite (Pavlidou & Papaspyrides, 2008). Typical CEC values of selected 2:1 phyllosilicates are listed in Table 1.1. Their crystal structure is essentially the same, but they differ mostly in the chemical composition of the substituent within the tetrahedral and octahedral sheets.



**Figure 1.1.** Structure of 2:1 layered silicate (Beyer G., 2002)

**Table 1.1.** Chemical formula and cation exchange capacity of 2:1 phyllosilicates

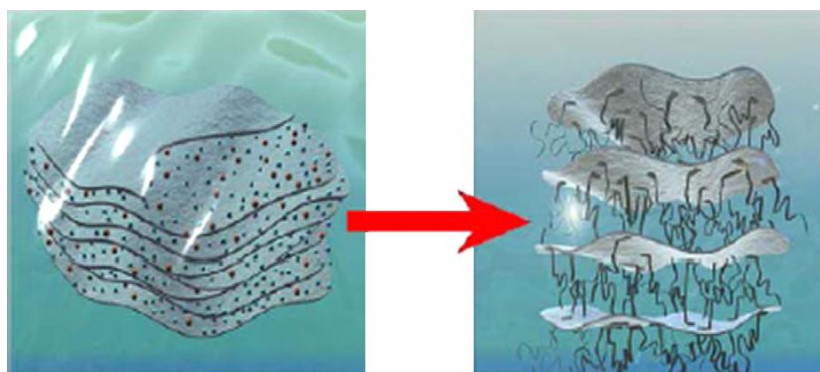
Silicate	Formula	CEC (meq/100g)
<b>Montmorillonite</b>	$M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$	92.6–120
<b>Hectorite</b>	$M_x(Mg_{6-x}Li_x)Si_8O_{20}(OH)_4$	120
<b>Saponite</b>	$M_xMg_6(Si_{8-x}Al_x)Si_8O_{20}(OH)_4$	86.6
<b>Vermiculite</b>	$(Mg,Fe,Al)_3[(Al,Si)_4O_{10}](OH)_2M_{x-n}H_2O$	150

*M represents exchangeable cation and x is the layer charge.*

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## 1.4. Organoclays

In the pristine state hydrophilic clay layers are only miscible with hydrophilic polymers, such as poly(ethylene oxide) and poly(vinyl alcohol). In order to render them miscible with other polymers, the inorganic cations must be exchanged by organic cations as shown in Figure 1.2. This not only serves to match the clay surface polarity with the polarity of the polymer, but it also expands the height of clay galleries. The ion-exchange reaction has two consequences: firstly, the gap between the single sheets is widened, enabling polymer chains to move in between them and secondly, the surface properties of each single sheet are changed from being hydrophilic to hydrophobic. The space between the silicate layers in the organoclay depends greatly on the length of the alkyl chain of organomodifier and the ratio of cross-sectional area to available area per cation (Fischer H., 2003).



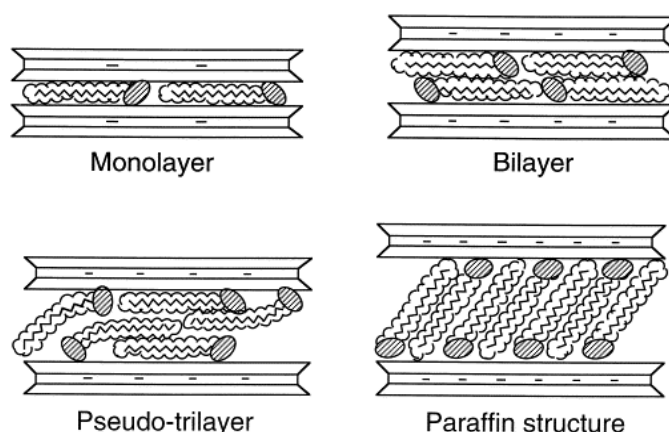
**Figure 1.2.** Schematic picture of an ion-exchange reaction (Fischer H., 2003)

The key issue in the design of PCNs is how to monitor the dispersion of clay platelets at nanometer scale in a polymer matrix. Accordingly, it is necessary to understand the interaction between the clay surfaces and the intercalants. In other words, understanding the structure of organo-clays and the interaction of

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surfactant in clays is of crucial importance in design, fabrication and characterization of PCNs.

Proper selection of organo-clays depends mainly on the type of polymer matrix used. When the hydrated cations are ion-exchanged with organic cations such as bulky alkyl ammoniums including primary, secondary, tertiary, and quaternary alkylammonium or alkylphosphonium cations, it generally results in larger interlayer spacing. Alkylammonium or alkylphosphonium cations in the organosilicates lower the surface energy of the inorganic host and improve the wetting characteristics of polymer matrix, and result in larger interlayer spacing. Additionally, the alkylammonium or alkylphosphonium cations can provide functional groups that can react with the polymer matrix, or in some cases initiate the polymerization of monomers to improve the strength of the interface between the inorganic and the polymer matrix (Fu and Qutubuddin 2005; . Krishnamoorti et al., 1996). Traditional structural characterization to determine the orientation and arrangement of the alkyl chain was performed using Wide Angle X-ray diffraction.



**Figure1.3.** Orientations of alkyl ammonium ions in the galleries of layered silicates with different layer charge densities (Lagaly, 1986)

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Depending on the packing density, temperature and alkyl chain length, the chains were thought to lay either parallel to the silicate layers forming mono or bilayers, or radiate away from the silicate layers forming mono or bimolecular arrangements as shown in above Figure 1.3 (Lagaly., 1986)

Hence, modification of clay layers with organic cation is necessary, in order to render the clay layers more compatible with polymer chains and also to increase the basal spacing of clay layers. This surface modification reduces the surface energy of clay layers and matches their surface polarity with polymer polarity. The resulting organoclays with lowered surface energy are more compatible with polymers and polymer molecules are able to intercalate within their interlayer space or galleries during nanocomposite preparation (Chigwada et al., 2006). Therefore different techniques used for the nanocomposite preparations have to be studied in detail.

## **1.5. Nanocomposite Preparation Techniques**

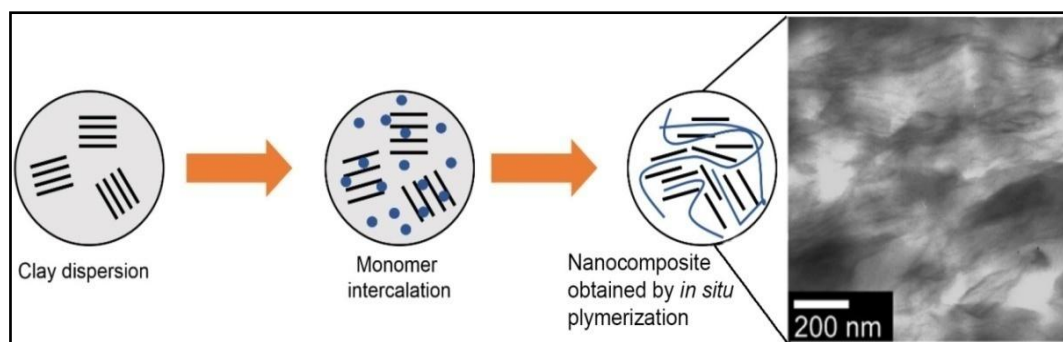
There are mainly three types of nanocomposite preparation technique: *in situ* polymerisation, melt intercalation and solution casting. Each of the three preparative methods may yield exfoliated, intercalated or phase separated structures. The degree of exfoliation versus intercalation depends on experimental conditions such as monomer type, solvents, temperatures, etc.

### **1.5.1. In situ Intercalative Polymerization**

In the case of *in situ polymerization*, the modified clay is swollen within the liquid monomer or a monomer solution so that the monomer diffused into the

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interlayer spacing of the clay, causing delamination (Figure 1.4.) Then, the polymerization reaction occurs between the clay layers and initiated either by heat or radiation, by the diffusion of a suitable initiator, or by an organic initiator or catalyst fixed through cation exchange before the swelling step (Biswas & Sinha-Ray, 2001; Usuki et al., 1993; Okamoto et al., 2000, 2001; Leu et al., 2002; Kim et al., 2003). Caprolactam, polyurethane, polystyrene, polypropylene, polyethylene, poly(ethylene terephthalate) and epoxy resin are some examples of polymers used for in situ intercalation. Exfoliated nanocomposites are mostly prepared using this technique.



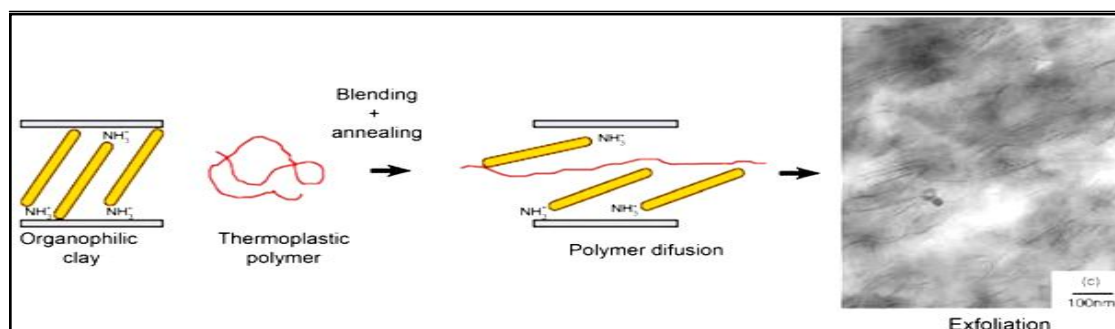
**Figure 1.4.** Schematic representation nanocomposite production of PE/OMMT with *rac*-ethylene bis (4,5,6,7-tetra-hydro-1-indenyl) zirconium dichloride by in situ polymerization. (Ren et al., 2010).

### 1.5.2. Melt Intercalation

The melt Intercalation method involves mixing the organoclay with the polymer in the molten state (Vaia and Giannelis, 1997). Nowadays, the melt intercalation technique has become widely accepted method for the preparation of PCNs. This method has many advantages because it does not require the use of solvents or organic reagents for the preparation of nanocomposites. (Ray et al., 2003). The absence of a solvent makes direct melt intercalation an



environmentally sound and an economically favourable method for industries. Also it is compatible with current industrial processes, such as extrusion and injection molding. Depending on the affinity between the clay and the polymer, the polymer will diffuse into the clay layers to produce an intercalated structure or eventually, to achieve exfoliation (Figure 1.5).



**Figure 1.5.** Schematic representation of PLS obtained by direct polymer melt intercalation of  $\text{M}_2(\text{HT})_2$  with LLDPE (Hotta and Paul., 2004; Beyer., 2002)

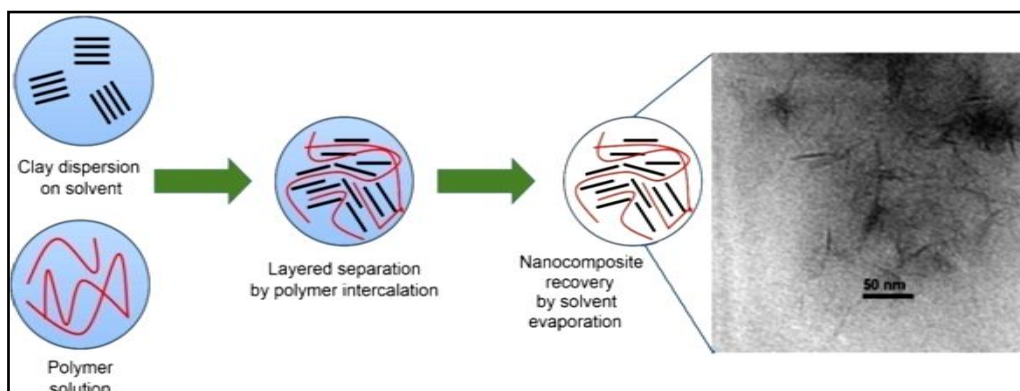
### 1.5.3. Solution casting

In this method the polymer or pre-polymer is dissolved in a solvent and the clay is dispersed in the same solution. The clay is swollen in the solvent and the polymer chains intercalate between the layers. The intercalated nanocomposite is obtained by solvent removal through vaporization or precipitation (Figure 1.6). Clays can be swollen easily in solvents such as water, acetone, chloroform and toluene. The polymer chains are absorbed onto the delaminated sheets. During the solvent evaporation the intercalated structure remains, resulting in nanocomposite.

Water-soluble polymers, such as poly(ethylene oxide) (Aranda and Hitzky., 1992), poly(vinyl alcohol) (Greenland., 1963), poly(vinyl pyrrolidone) (Francis., 1973) and poly(ethylene vinyl alcohol) have been intercalated into the

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clay galleries using this method. Examples from non-aqueous solvents are nanocomposites of poly (caprolactone) and polylactide in chloroform as a co-solvent. The thermodynamics involved in this method are when the polymer is exchanged with the previously intercalated solvent in the gallery; a negative variation in the Gibbs free energy is required. The driving force for the polymer intercalation into layered silicate from solution is the entropy gained by desorption of solvent molecules, which compensates for the decreased entropy of the confined, intercalated chains (Vaia and Giannelis., 1997). Using this method, intercalation only occurs for certain polymer/solvent pairs. This method is good for the intercalation of polymers with little or no polarity into layered structures, and facilitates production of thin films with polymer-oriented clay intercalated layers. However due to the need for use solvent, this technique cannot be applied in industry. The nanocomposite preparation by emulsion polymerization, with the clays dispersed in the aqueous solution, is also categorized as solvent intercalation method (Rehab & Salahuddin, 2005). Toyota group has been used this technique to produce polyimide/clay nanocomposites (Yano et al., 1993).

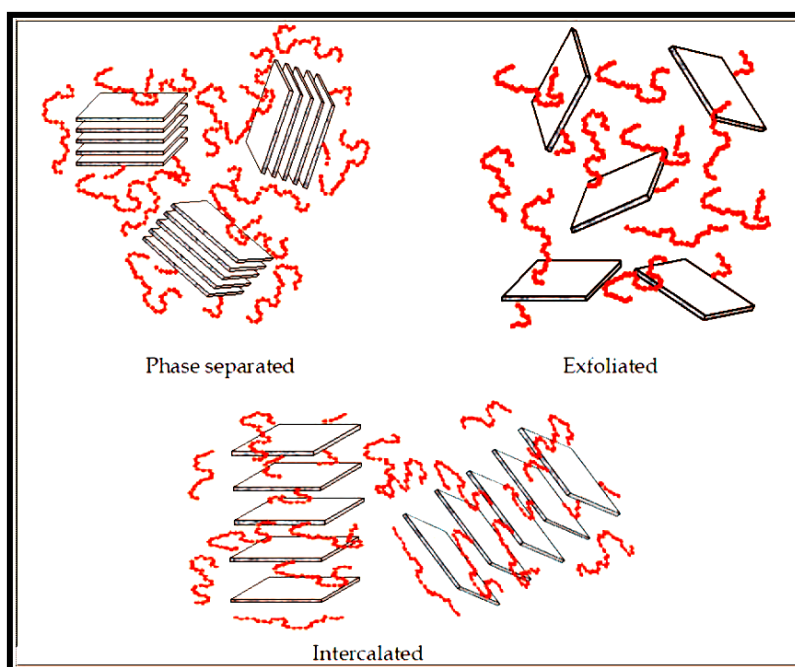


**Figure 1.6.** Schematic representation of EVA/LLDPE/DS-LDH obtained by solution blending (Kuila et al., 2008; Pavlidou and Papaspyrides., 2008)

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## 1.6. Nanocomposite structures

Depending on the level of intercalation and exfoliation of polymer chains into the clay galleries different polymer clay nanocomposite micro-structures can be obtained (Figure 1.7.). Various factors including clay nature, organic modifier, and polymer matrix and preparation method are effective on the intercalation and exfoliation level.



**Figure 1.7.** Schematic representation of three different types of PCNs

### 1.6.1. Phase separated structure

Once the clay is mixed with a polymer, if there is no affinity between the clay and the polymer, the obtained composite structure is considered as “phase separated”. The properties of phase separated polymer/clay composites are in the range of conventional micro composites.

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### **1.6.2. Intercalated structure**

If there is some affinity between the clay and the polymer, the polymer chains tend to penetrate between the interlayer spaces. These results in the increase in the interlayer spacing, but the periodic array of the clay layer still exist to form an intercalated structure. The composite thus obtained is known as intercalated nanocomposite.

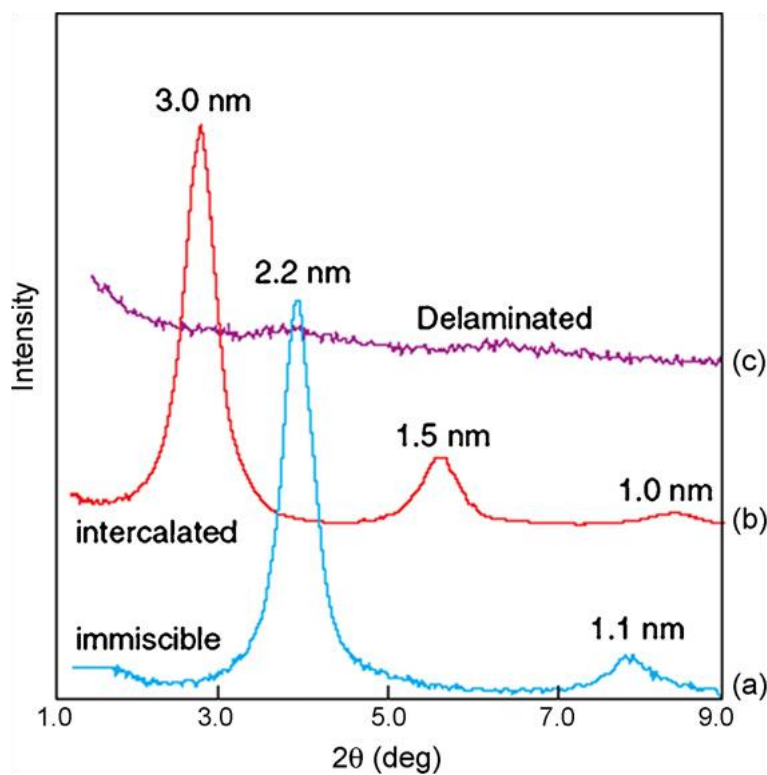
### **1.6.3. Exfoliated structure**

Finally, if the interaction between the clay and the polymer is very good, an exfoliated structure is obtained. In an exfoliated nanocomposite, the individual clay layers are separated in a continuous polymer matrix by an average distance that depends on clay loading. Usually, the exfoliated morphology is most desirable, as in this case the clay layers are well dispersed with the polymer matrix than that of an intercalated nanocomposite.

## **1.7. Nanocomposite Characterizations**

The two most general techniques used for the structure characterizations of PCNs are X-ray Diffraction (XRD) analysis and transmission electron micrographic (TEM) observation. Due to its easiness and availability, WAXD is most commonly used to probe nanocomposite structure (Vaia et al., 1996) and occasionally to study the kinetics of the polymer melt intercalation. By monitoring the position, shape, and intensity of the basal reflections from the distributed silicate layers, the nanocomposite structure (intercalated or exfoliated) may be identified. For example, in an exfoliated nanocomposite, the extensive layer separation associated with the delamination of the original silicate layers in

the polymer matrix results in the eventual disappearance of any coherent X-ray diffraction from the distributed silicate layers. On the other hand, for intercalated nanocomposites, the finite layer expansion associated with the polymer intercalation results in the appearance of a new basal reflection corresponding to the larger gallery height. Only tentative conclusions concerning the mechanism of nanocomposite formation and their structure can be made based on WAXD patterns alone (Figure 1.8).

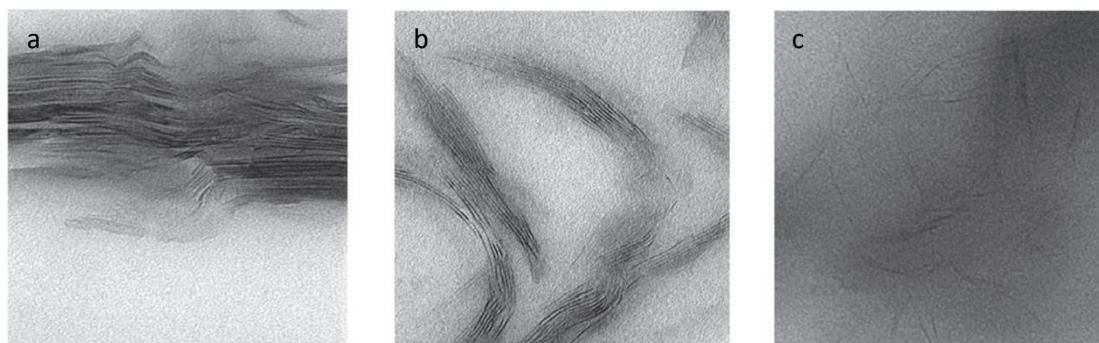


**Figure 1.8.** Typical XRD patterns from PCNs: (a) PE + organoclay (no formation of a nanocomposite), (b) PS + organoclay (intercalated nanocomposite), (c) siloxane + organoclay (delaminated/exfoliated nanocomposite) (Beyer G., 2002)

TEM, however, is extremely useful in providing a direct way of determining PCN morphology (Figure 1.9). TEM allows a qualitative understanding of the internal structure, spatial distribution of the various phases,

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and views of the defect structure through direct visualization. However, special care must be made to make a representative cross-section of the sample. TEM is time-intensive, and only gives qualitative information on the sample as a whole, while low-angle peaks in WAXD allow quantification of changes in layer spacing.



**Figure 1.9.** Transmission electron microscopy images indicating various possible morphologies in the composites as a function of the filler distribution- (a) Unintercalated (b) Intercalated and (c) Exfoliated.

## 1.8. Nanocomposite properties

The main aim for the addition of clay minerals to the polymers is to improve the polymer properties and to produce the polymer/clay nanocomposites with required characteristics for desired applications. Because of the low price, availability, high aspect ratio as well as desirable nanostructure and interfacial interactions, clays can provide dramatic and adjustable improved properties at very lower loadings. Improvements include a higher modulus, increased strength and heat resistance, decreased gas permeability and flammability and increased biodegradability of biodegradable polymers. The main reason for these improvements is the stronger interfacial interaction between the matrix and the

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layered silicate, compared with conventional filler-reinforced systems. However, the nature and properties of components as well as preparation methodology and conditions affects on the final properties of polymer/clay nanocomposite (Ray, 2010). In this section the various improved properties of polymer/clay nanocomposites as well as the effective parameters are discussed.

### **1.8.1. Mechanical properties**

The main purpose of addition of fillers to the polymer is improvement in the mechanical properties and therefore fillers are commonly known as reinforcement agents (Jiang et al., 2005). When rigid filler is added to the soft polymer matrix, it will carry the major portion of applied load to the polymer matrix under stress conditions (Gorrasi et al., 2003). Therefore the larger the interface between filler and matrix, and stronger the interfacial interactions, the great will be the reinforcement effect. Also the modulus increases by increasing the filler ratio in the nanocomposite composition. Because of the rigid structure of clay layers and their high aspect ratio, they have proven to be very effective in the increasing of modulus and stiffness of the polymer matrix in well dispersed condition. Because of very high aspect ratio of nanoclay fillers compared to that of regular fillers such as glass fibers, remarkable improvements in the mechanical properties of nanocomposites are achieved even at very lower nanoclay additions (LeBaron et al., 1999). Also polymer chains, adhesived by strong physisorption forces onto the rigid clay mono layers, exhibit high modulus and equally act as a rigid material. Significant improvement in the modulus was expected on considering the very large interfacial area in well dispersed nanocomposite structures. It has been well demonstrated that the enhancement in the interfacial adhesion properties between

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clay and polymer by surface modification of polymer chains using a suitable polar compatibilizer causes to the increasing in the mechanical properties of nanocomposite (Mittal, 2008). Also the use of organoclay fillers increases both the stiffness and modulus of nanocomposite because of the new intercalation/exfoliation chemistry achieved. Therefore any parameters which helps in the intercalation of polymer molecules within the clay galleries due to interfacial interactions, consequently results in exfoliation of nanocomposite structure and finally results to the greater improvement in the modulus of the nanocomposite.

Usually the incorporation of clay minerals improves the tensile strength of polymers by increasing the filler volume fraction (Fornes et al., 2001; Shelley et al., 2001). However the tensile strength is influenced by the final morphology of nanocomposite. Similar to modulus, any factor affecting on the degree of intercalation/exfoliation has an impact on the tensile strength of nanocomposite. The effect of clay fillers on the stress at break values for polymer nanocomposites depends on the interfacial interactions between polymer and clay layers.

Elongation at break for polymer/clay nanocomposites is similarly dependent to the interfacial interactions of polymer/clay system. Dynamic mechanical analysis studies on polymer/clay nanocomposites have shown that usually storage modulus and glass transition temperature (T<sub>g</sub>) are improved by the addition of clay nanofillers (Nam et al., 2001; Laus et al., 1997)

### **1.8.2. Thermal properties**

Thermogravimetric analysis (TGA) has been usually used to evaluate thermal stability of polymer/clay nanocomposites with that of pure polymer



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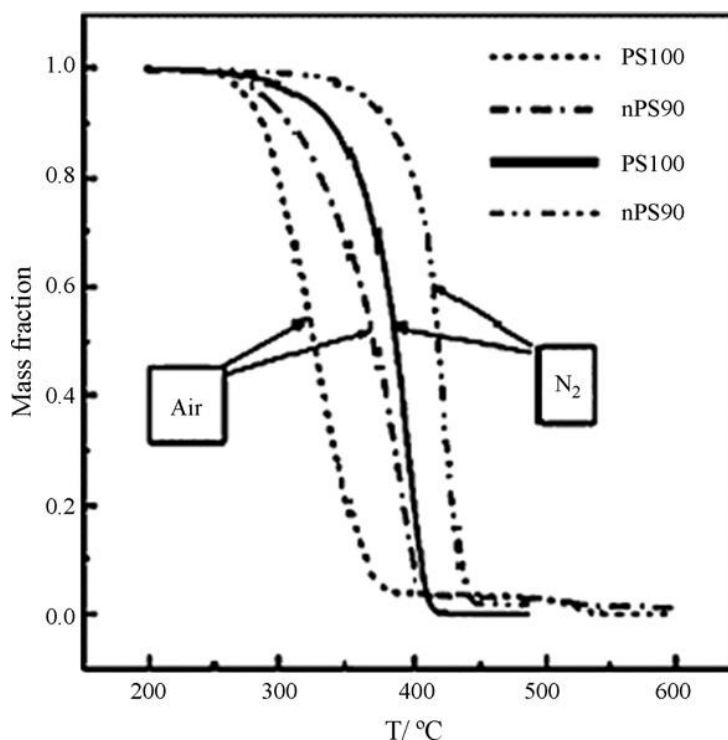
under various oxidative (air) or non-oxidative (inert gases) conditions. In this technique, the weight loss due to the formation of volatile products after degradation at high temperature is monitored as a function of temperature (and/or time). When heating occurs under an inert gas flow, a non-oxidative degradation occurs, while the use of air or oxygen allows oxidative degradation of the samples (Ray and Okamoto., 2003)

Generally, the incorporation of clay into the polymer matrix was found to improve thermal stability by acting as a superior insulator and mass transport barrier to the volatile products produced during decomposition, as well as by supporting in the formation of char after thermal decomposition (Becker et al., 2004; Ray and Okamoto., 2003)

In general, it has been reported that the polymer/clay nanocomposites are thermally more stable than pure polymers (Zanetti et al., 2004; Wang et al., 2002). Also it has been reported that clays help in the formation of layered carbonaceous char during degradation of polymer/clay nanocomposite (Ray et al., 2003). Clay minerals are inorganic materials and are almost stable in the temperature ranges that organic polymers are degraded in to volatile compounds. Therefore in TGA experiments, the clay content of nanocomposites is remain as residue after heating program (Gilman., 1999). The improved thermal stability of PCN was first reported by Blumstein (1965) using PMMA/MMT nanocomposite. The TGA studies showed that PMMA intercalated into the Na-MMT has 40-50°C higher decomposition temperature. The thermal stability of polystyrene/clay nanocomposite compared to pure PS was reported by Vyazovkin et al., (2004). They have showed that PS/clay nanocomposites have

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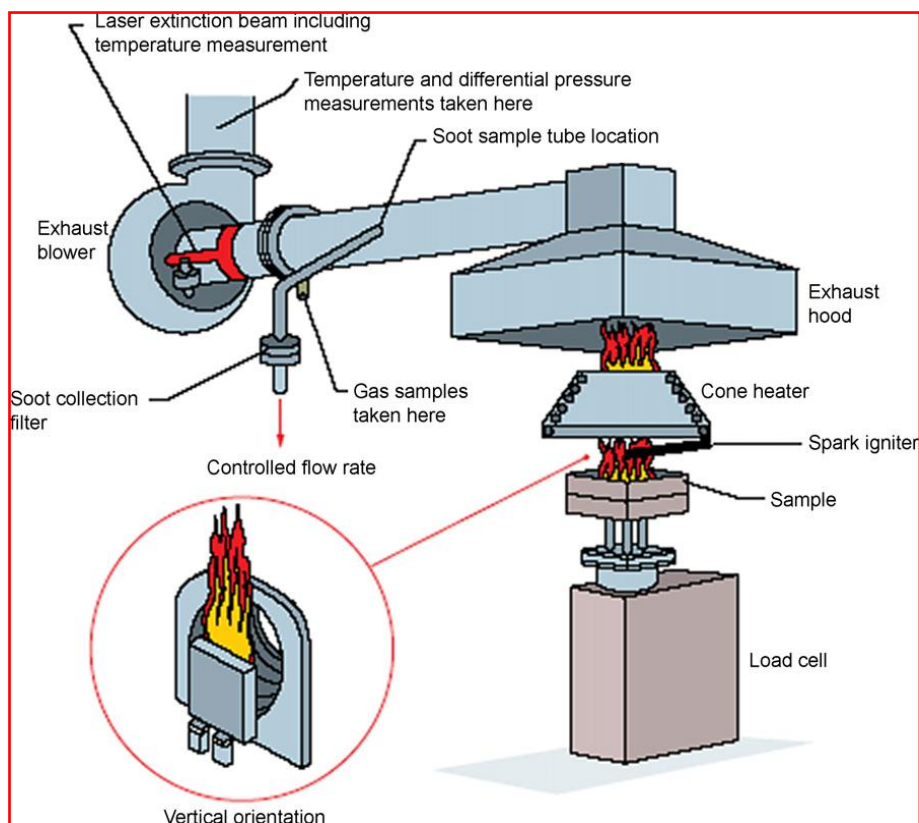
30-40 °C higher degradation temperature compared to pure PS under nitrogen and air heating degradation conditions and also observed that the virgin polymer degrades without forming any residue, whereas the nanocomposite (as expected) leaves some residue (Figure 1.10).



**Figure 1.10.** TGA curves of the degradation of PS100 and nPS90 at a heating rate  $5\text{ }^{\circ}\text{C min}^{-1}$  in air and nitrogen

### 1.8.3. Fire Retardant Properties

Another important property which is improved with the formation of a PCN is flame retardancy. Commonly used equipment to evaluate the resistance to flame propagation of a polymer is the cone calorimeter (Figure 1.11) as it provides valuable information and may even indicate the flame retardancy mechanism.



**Figure 1.11.** Schematic view of the cone calorimeter (Beyer., 2002)

The nanocomposites flame retardant mechanism involves a high-performance carbonaceous-silicate char, which builds up on the surface during burning. This insulates the underlying material and slows the mass loss rate of decomposition products (Porter et al ., 2000).

Generally a number of halogen-based as well as phosphorous compounds have the flame retardant property when incorporated with polymers, without the reduction of their other properties. However the halogenated compounds suffer from environmental contamination characteristics and have pushed the market trends to halogen-free flame retardants (Kiliaris & Papaspyrides, 2010; Levchik, 2007). Investigations on the polymer/clay nanocomposites have been confirmed that incorporation of clay minerals results in flame retardancy along with the

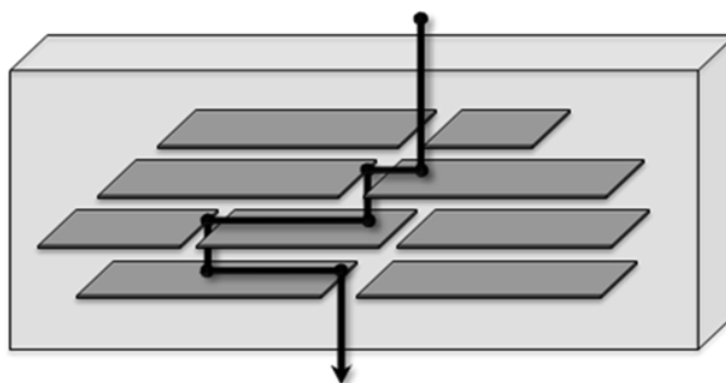
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improvement in the physical and mechanical properties for polymers without any side effects. (Kiliaris & Papaspyrides, 2010).

#### **1.8.4. Barrier Properties**

One of the most significant properties of clays in the polymer matrix is the remarkable improvement of barrier properties of polymers. Clay layers are naturally impermeable. Clays increase the barriers properties of polymers by creating a maze or tortuous path that retards the diffusion of gas molecules through the polymer matrix (Figure 1.12) (Pavlidou & Papaspyrides, 2008; Yano et al., 1993).

The degree of improvement in the barrier properties depends on the degree of tortuosity created by clay layers in the diffusion way of molecules through the polymer film. The tortuous factor is determined by the ratio of actual distance which diffusive molecule is walked to the shortest distance to diffuse (polymer film thickness). This factor is affected by the aspect ratio of clay dispersed in the matrix. Increasing the lateral length of clay sheet as well as increasing of exfoliation or dispersion degree cause to the more barrier enhancement in the polymer matrix. Many studies have reported the barrier properties of polymer/clay nanocomposites against the diffusion of gases and vapours (Tortora et al., 2002; Ray et al., 2003; Lange & Wyser, 2003).



**Figure 1.12.** Formation of tortuous path in Polymer clay nanocomposites.

### 1.8.5. Optical Properties

Micro-sized reinforcing particles scatter light, thus reducing light transmittance and optical clarity (Schmidt and Malwitz., 2003). Even though layered silicates are microns in lateral size, they are just 1 nm thick. Thus, when single layers are dispersed in a polymer matrix, the resulting nanocomposite is optically clear in visible region, whereas, there is loss of intensity in the UV region ( $\lambda < 250\text{nm}$ ) due to scattering by the clay particle (Alexandre and Dubois., 2000). There is no marked decrease in the clarity due to the nano-dispersed fillers even low clay loading( 20wt.%) at This is a general behavior in UV/Vis transmittance for thick films (3–5mm) of polymer/MMT nanocomposites based on PVA, PP, and several epoxies (Manias., 2001).

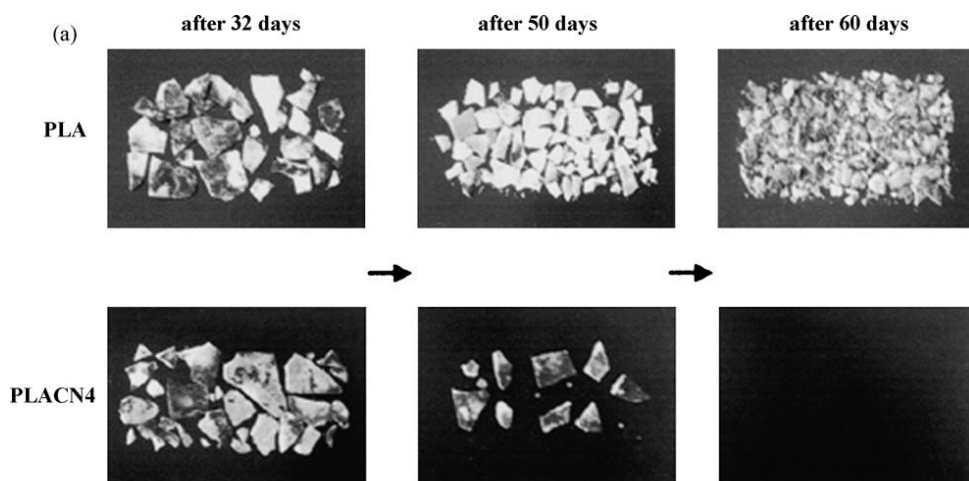
### 1.8.6. Biodegradability

Another interesting aspect of PCNs is the significant enhancement of biodegradability after nanocomposite preparation with organoclay. The improved biodegradability of nanocomposites may be due to a catalytic role of the organoclay in the biodegradation mechanism (Lee et al., 2002). Biodegradability

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improvements have also been reported in the case of PLA- based nanocomposite (Ray et al., 2003). The biodegradability of neat PLA is significantly enhanced after nanocomposite preparation (Figure 1.13). They also suggested that the presence of terminal hydroxylated edge groups of the silicate layers may be one of the factors responsible for this behaviour.

However, contradictory results regarding the effect of clay dispersion on polymer biodegradability were also found in the literature. For example, Lee et al., 2002 prepared nanocomposites based on aliphatic unsaturated polyester and found a decrease in biodegradability under composting with intercalation. They assumed that due to the high aspect ratio and better dispersion of clay in the matrix a more tortuous path formed for penetration of microorganisms into the bulk and hindered their diffusion. From the contradictory results, the increase or the decrease in nanocomposite biodegradation is still under discussion and no conclusion can be driven about mechanisms on the basis of the current literature (Pandey et al., 2005)



**Figure 1.13.** (a) Real pictures of biodegradability of neat PLA and PLACN4 recovered from compost with time. Initial shape of the crystallized samples was 3cm×10 cm×0.1 cm

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### **1.8.7. Heat distortion temperature**

Heat distortion temperature or heat deflection temperature (HDT) is the temperature at which a polymer sample deforms under a specific load. Thus, it is an index of a polymeric material's heat resistance towards applied load and determined by the procedure given in ASTM D-648 (Ray and Okamoto 2003). Increase in the HDT are reported by nanocomposite formation.

A significant increase in the HDT value is achieved for 5 wt.% clay loading and then for higher clay loading the HDT value level off (Sur et al., 2001, Ray et al., 2003). It should be emphasized that the increase of HDT due to clay dispersion is very important for industrial application, but also because it is very difficult to achieve HDT enhancements by chemical modification or reinforcement by conventional fillers (Manias., 2001; Ray and Bousmina., 2005).

Nanodispersion of MMT in a polypropylene matrix has been found to promote a higher HDT. It should be emphasized that the increase of HDT due to clay dispersion is very important, not only from application or industrial point of view, but also because it is very difficult to achieve similar HDT enhancements by chemical modification or reinforcement by conventional fillers (Ray and Okamoto 2003).

### **1.8.8. Rheological properties**

The fundamental understanding of the processibility of polymeric materials can be obtained by the measurement of rheological properties. This is usually done by either dynamic oscillatory shear or steady shear measurement (Ray and Okamoto 2003). Understanding the rheological properties of

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nanocomposite melts is not only important in gaining a fundamental knowledge of the processability, but is also helpful in understanding the structure–property relationships in these materials. The rheological properties of in situ polymerized nanocomposites with end-tethered polymer chains were first described by Krishnamoorti and Giannelis., 1997.

In the case of polymer-layered silicate nanocomposites, the study of rheological properties is instructive for two reasons: First, these properties are indicative of melt processing behaviour in unit operations, such as injection molding. Second, since the rheological properties of particle-filled materials are sensitive to the structure, particle size, shape and surface characteristics of the dispersed phase, rheology potentially offers a means to assess the state of dispersion in nanocomposites, directly in the melt state. Thus, rheology can be envisaged as a tool that is complementary to traditional methods of materials characterization (Cho and Paul 2001; Solomon, Almusallam et al., 2001)

## **1.9. Nanocomposites: Advantages and Applications**

As described above, the main advantage of PCN materials are they often exhibit superior properties compared to conventional composites, such as strength, stiffness, barrier properties, thermal stability, as well as flame retardant behaviour (Schmidt et al., 2002). These improved properties are generally attained at lower silicate content (5 wt.%) compared to that of conventionally filled systems. For these reasons, polymer clay nanocomposites are far lighter in weight than a conventional composite, which makes them relatively reasonable for specific application (Ray and Okamoto., 2003).



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Furthermore, the unique combination of their key properties and potentially low production costs paves the way to a wide range of applications. Recently, some PLS nanocomposites became commercially available, and were applied to the automotive (Garcés et al., 2000) and food packaging industries. Biodegradable polymer based nanocomposites appear to have a very bright future for a wide range of applications as high performance biodegradable materials (Ray and Okamoto., 2003b). Polymer-clay nanocomposites also show improvement in most general polymeric properties. For example, in addition to the decreased permeability of liquids and gases, nanocomposites also show significant improvement in solvent uptake. Scratch resistance is another property that is strongly enhanced by the incorporation of layered silicates (Solyman et al., 2017). The potential use of PANI-based nanocomposites as electrorheologically sensitive fluids or the combination of dispersed layered silicates in a liquid crystal medium is also an attractive application. In addition, nanocomposites have been in the improvement of ablative properties in aeronautics (Hussain et al., 2006). New nanocomposites are currently being developed that have real industrial potential-loading a polymer with a small (ca. 5 %) amount of inorganic nanoparticles is expected to give rise to significant improvement to the materials properties with only a minor increase in cost (Garces., et al. 2000).

Nowadays, applications of polymer clay nanocomposites for self-assembly studies and also as corrosion resistant coatings have attracted the attention of several researchers, both in the academic and the industrial communities. Recent studies have shown that, control of organization of nanometer sized clay platelets at larger scale can be used to extend the range of available morphologies. Fine

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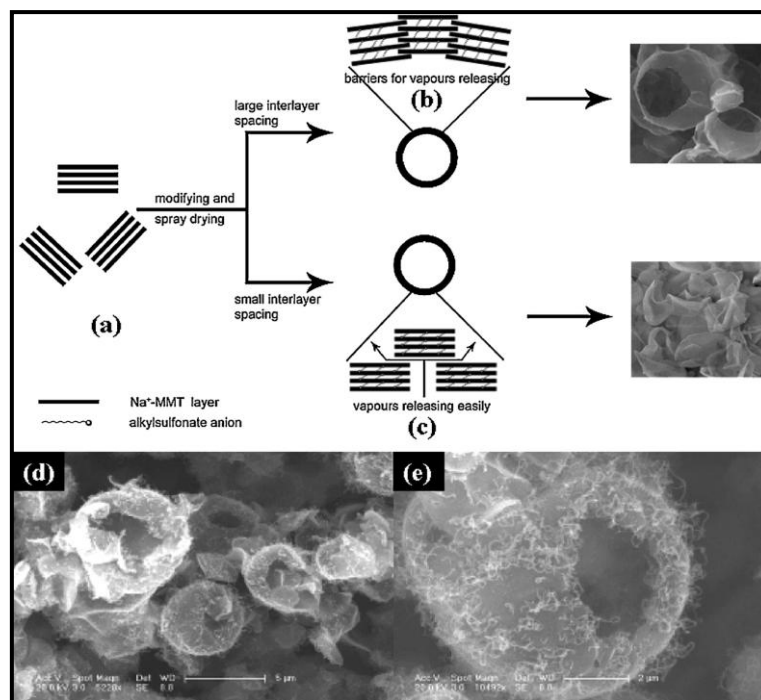
interaction with the nanoclay can influence the morphology of the matrix polymer. Similarly, the use of PCNs as anticorrosion coatings had been explored to be potential candidates used to replace the chromium containing materials, which have negative health and environmental concerns (DeBerry., 1985; Wessling., 1994; Wessling., 1997). Here, the addition of layered silicates, effectively improves the anticorrosive barrier effect of polymer coatings by increasing the length of the diffusion pathways for aggressive species. Clay materials due to their platelet structure and high aspect ratio, in well dispersed state, decrease the permeability of polymer coating films by increasing the diffusion pathways such as shown in above Figure 1.12 and reports available in literature for applications like self-assembling and anticorrosion studies are summarized below.

### **1.9.1. Self-Assembly**

Research and development in the area of clay interactions with organic polymers as well as clay self-assembly with organic polymer was receiving overwhelming interest nowadays. The main two aspects of these non-covalent interactions were: first, plate-like clays can have a considerable impact on polymer properties such as hydrogels and clay films, and also on the encapsulation of bio-molecules. Second, through ionic intercalation with polymeric amine-salts, the clay layered structure units can be modified and enabled to self-assemble into ordered arrays such as rod, dendrite, and fiber like microstructures. The silicate self-assembled morphologies such as worm-like and hollow microspheres were obtained in epoxy matrices and during spray drying,

respectively. A mechanism was proposed for the clay self-assembly in two orientations, platelet face-to face (ionic attraction) and edge-to-edge (organic hydrophobic effect). Further, the layered clays after the exfoliation into random platelets (1 nm in thickness) had strong propensity toward self-piling without any organic influence (Chiu and Lin., 2012).

Direct fabrication of opened hollow microspheres was first reported in 2008 by Du Jiang et al., and the self-organized microstructures were formed due to the incorporation of organic ions into MMT layered structure. (Figure 1.14)

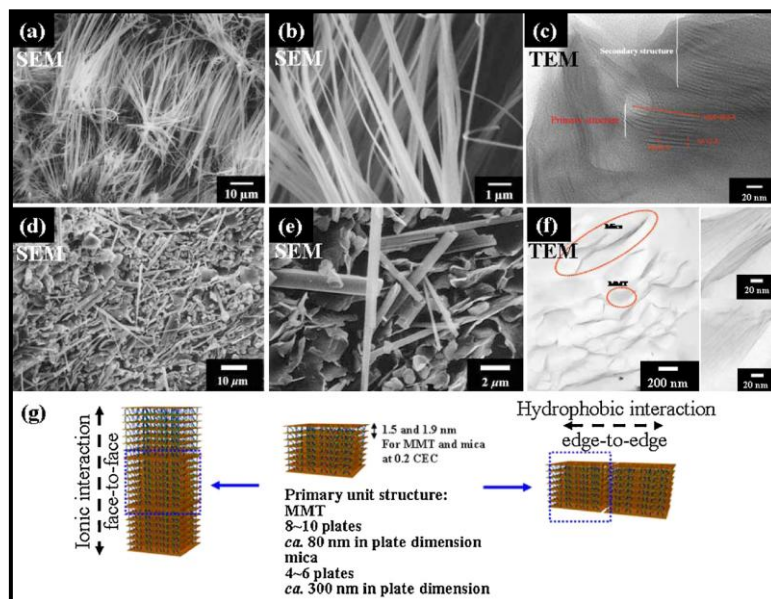


**Figure 1.14.** Schematic diagram of the formation for opened hollow spheres. (a) Na<sup>+</sup>-MMT; (b) a solid shell formed through MMT aggregates intercalating across each other during spray drying; (c) a porous shell formed by MMT aggregates overlapping during spray drying. (d and e) FE-SEM micrographs of clay/CNTs composite at low and high magnifications ( Du Jiang et al., 2008)

Hollow microstructures 3–9 μm in diameter were prepared from self-organization of MMT organoclay units. Under the common spray drying

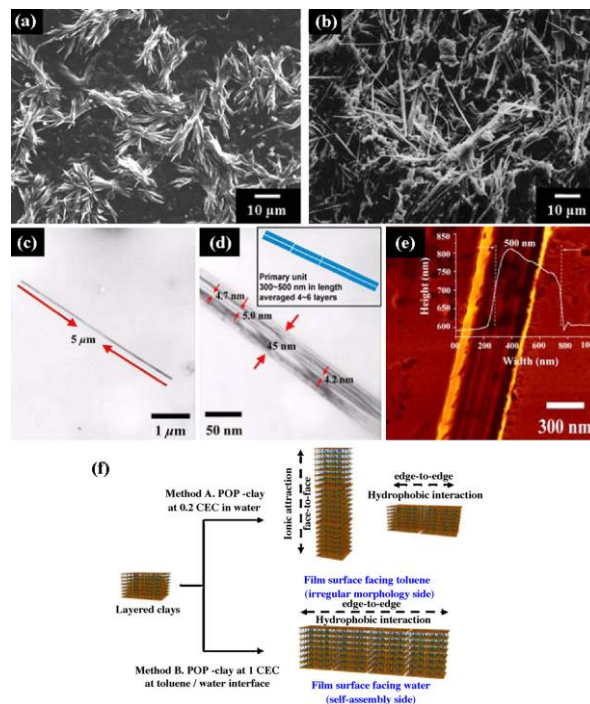
conditions, the formation of hollow spheres from sodium alkylsulfonate intercalated MMT was observed. The mechanism for the formation of unique morphology from organoclay units was explained by comparing two different intercalated organoclays. When the organoclays have a high organic expansion for basal spacing, the aggregates (Figure 1.14b) can cross-intercalate each other to form a solid around droplets during the air-drying as the opened spheres. In contrast, the low intercalating clay produced porous and less ordered microstructure from the unit piling (Figure 1.14c).

It was reported that the Polyoxypropylene (POP)-intercalated MMT organoclay could undergo a self-assembly of lengthy rod-like morphologies, as shown in Figure 15a and b. Rod or fiber like ordered microstructures in high uniformity were observed under SEM. The morphologies with average dimensions of 0.1-0.8  $\mu\text{m}$  in width and 2-100  $\mu\text{m}$  in length for these fibers were recorded. The formation of ordered microstructures from hydrophobic POP-intercalated MMT revealed the non-covalent bonding interactions within the clay basal spacing as well as the unit-to-unit interactions (Lin et al., 2004)



**Figure 1.15.** SEM micrographs of (a,b) fiber-like (d,e) rod-like microstructures from the self-assembling of POP2000/MMT organoclay (Lin et al., 2004; Lin et al., 2008) (c) TEM micrographs of POP2000/MMT microstructure of a thin film (Chou et al., 2003) (f) TEM micrographs of POP2000-intercalated synthetic mica and MMT (Lin and Chen., 2004) (g) Conceptual explanation for the formation of these rod-like arrays

The water-evaporation method for organoclay self-assembly was suitable for low levels of POP clay interaction. With high POP intercalation or hydrophobic organoclays, a toluene dispersed bi-phasic self-assembling was reported (Lin et al., 2008). The increase of POP levels up to 50–60 wt% in silicates made the organoclays hydrophobic and dispersible in toluene.

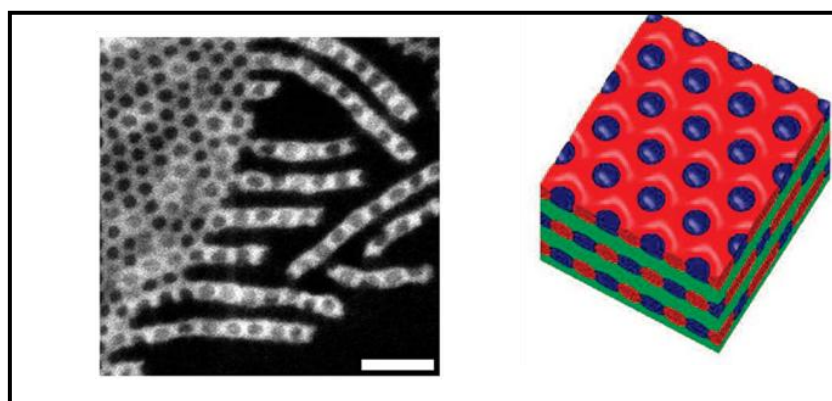


**Figure 1.16.** SEM, TEM and AFM images of self-assembled POP/clay (1.0 CEC) at the toluene/water surface and conceptual diagram of POP/clay self-assembling procedures

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The particular CEC (1.0) sample was hydrophobic and dispersible in toluene rather than in water. When the primary units of the POP-intercalated clays were subjected to a two phase standing, self-assemblages into ordered structures occurred. Thin film of unit self-piling at the toluene-water interface was generated by a long term standing of the toluene dispersion with static water phase (Figure 1.16).

Toombes et al., 2008 observed hexagonally patterned lamellar morphology in ABC triblock copolymer poly (ethylene-*alt*-propylene-*block*-ethyleneoxide-*block*-*n*-hexyl methacrylate)-clay nanocomposites. Level set modelling confirmed that this patterning of the PEO-aluminosilicate sheets is consistent with micellar PEP domains forming either pillars through the sheet (Figure 1.17). The hybrid materials possess structure within the PHMA and PEO aluminosilicate domains at the 1-3 nm length scale. These results establish that ABC triblock copolymers can be used to direct the assembly of inorganic precursors into hybrid materials with complex, hierarchical structures.

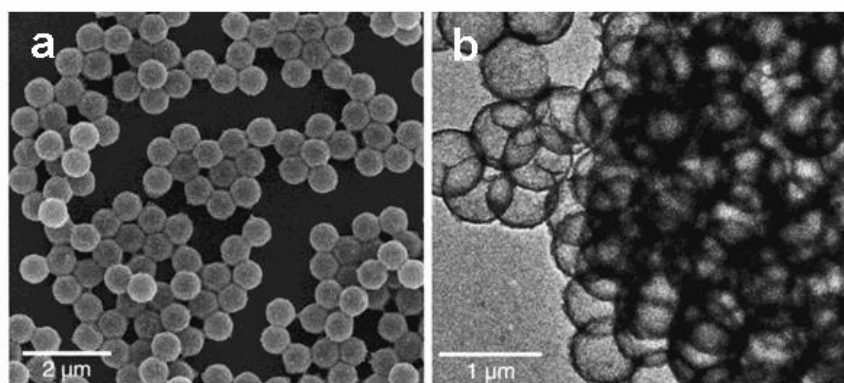


**Figure 1.17.** Hexagonally patterned lamellar morphology in ABC triblock copolymer poly (ethylene-*alt*-propylene-*block*-ethyleneoxide-*block*-*n*-hexyl methacrylate)-clay nanocomposites

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Negrete-Herrera et al., 2007 also reported the formation of transparent polymer-laponite nanocomposite films, which contained an unconventional honeycomb laponite network, whose microstructure resulted from the original morphology of the composite latex particles. The films were obtained by drying a suspension of latex particles synthesized through emulsion polymerization of styrene and butyl acrylate (BuA) in the presence of laponite clay particles intercalated with cationic initiator molecules.

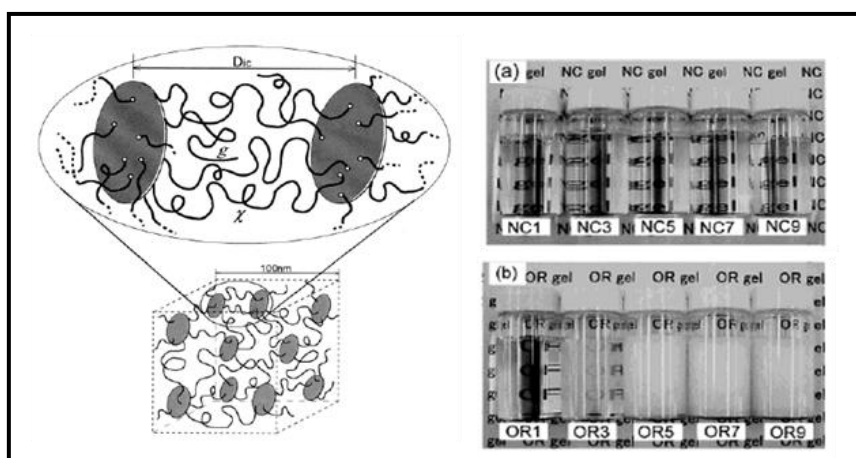
Using a similar approach Caruso et al., 2001 prepared laponite hollow spheres using composite particles comprising a PS core and well defined laponite nanoparticle/PE multilayers fabricated by using the layer-by-layer approach. The hybrid core-shell particles were subsequently calcined to create well-defined hollow spheres with predetermined diameters (Figure 1.18).



**Figure 1.18.** SEM (a) and TEM (b) images of hollow laponite spheres obtained after calcination of PS spheres (640 nm)

Haraguchi et al., in 2006 developed a method by making hydrogels of an organic-inorganic network using laponite clay (Figure 1.19). They used nanoclay instead of the chemical cross-linker. These nanocomposite gels are novel, and destroy the prevailing common sense on conventional gels. It was found that

mechanical properties of the nanocomposite gels were improving with clay content. For gels with low clay content, the clay platelets may be aligned perpendicular to the stretch direction. However, in nanocomposite gels with high clay content, it was estimated from the changes in mechanical properties that the clay platelets may be orientated parallel to the stretch direction. Because of the high concentration of clay and their cooperative alignment toward the stretch direction on elongation, the orientation as well as the strain is partially retained, even after long relaxation times, resulting in much-improved mechanical properties.



**Figure 1.19.** Hydrogels of an organic-inorganic network using laponite clay

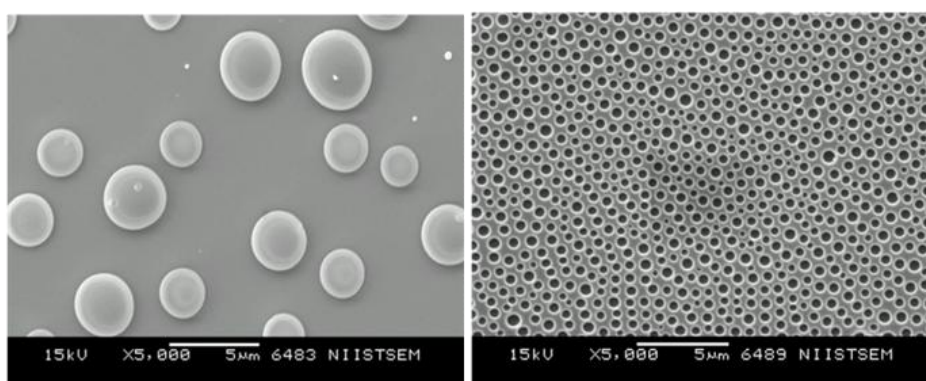
Similarly, self-assembly of silicate layers to form microvesicles and micropatterned polymer film has become an important part of research due to enormous advantage of using nanoclay in polymer matrix, as compared to the convectional fillers. Vesicles have been receiving intense research interest due to their potential applications in drug encapsulation/delivery system, dyes and ink, catalysis, as microcontainers, or reactors and sensors. Various methods approved



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for the synthesis of polymer, inorganic and organic-inorganic hybrid vesicles which include solvent-assisted self-assembly of amphiphilic polymers, rod-coil diblock polymers, dendrimers, and foldamers and sacrificial template method. As compared to polymer vesicles, an inorganic and organic-inorganic hybrid vesicle shows superior strength and resistance. Various attempts have been reported in literature for the preparation of hybrid vesicles by solvent-assisted self-assembly.

Recently, formation and mechanism of polymer clay nanocomposite particle, vesicle and micropatterned film using POSS-modified clay nanocomposite was reported. Nair et al., 2009 reported the concentration dependent self-assembling property of polystyrene-clay nanocomposite particles in THF. The composites were synthesized by in situ intercalative polymerization of styrene with vinyl POSS amine-modified organoclay. While the particles from dilute solution of 0.001 mg/mL showed a lateral dimension of 190-800 nm and thickness of 120 nm, microvesicles of diameter of 2.5-3.5  $\mu\text{m}$  and average membrane thickness of 85 nm were produced from solution concentration of 2.5 mg/ mL by consuming the particles (Figure 1.21).



**Figure 1.20.** Self-assembly of polystyrene-clay nanocomposite particles as  
a) Vesicles and b) Micropatterned film

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The particle possessed a sandwich structure consisting of polystyrene(PS)-POSS-intercalated clay tactoid of thickness of 12.6 nm at the core and PS chains growing from the tactoid surfaces on either side, exposing the hydroxylated edges of the silicate layers. Vesicle was formed by edge-edge association of the silicate layers so that the layers lie flat along the vesicle membrane. Guest-encapsulated vesicles were obtained when prepared from solutions containing guest molecules.

They also report micropatterned polystyrene-clay nanocomposite surfaces with concavities by moisture-induced phase separation of PSC particles (Nair et al., 2010). Micropatterned film with concavity size of 800 nm to 1.3  $\mu\text{m}$  and a high number density of 2-108 features/ $\text{cm}^2$  was obtained by drop-casting PCN solution (20 mg/mL PCN/THF) under ambient relative humidity of 70-80% (Figure 1.20). It is proposed that water droplets were channelled through the hydrophilic interfaces between the PCN particles, and the two-dimensional array of concavities was formed by spontaneous phase separation due to the presence of rigid clay platelets.

### **1.9.2. Anticorrosive Coatings**

Relatively thin coatings of metallic and inorganic materials can offer a suitable barrier between a metal and its environment. The chief function of such coating is to provide an effective barrier for attacking species. Metal coatings are applied by electrodeposition, flame spraying, cladding, hot dipping, and vapour deposition. Inorganics are applied or formed by spraying, diffusion, or chemical conversion. Metal coatings usually exhibit some formability, whereas the inorganics are brittle. In both cases a complete barrier must be provided.

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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].

In the case of organic coatings there involve a relatively thin barrier between the substrate material and the environment. Paints, varnishes, lacquers, and similar coatings protect more metal than any other method for combating corrosion. 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. Primarily polymeric coatings act as physical barrier against the diffusion of aggressive species such as  $O_2$  and  $H^+$  to the metal surface. 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 defence for corrosion, various pigments with a lamellar or plate-like shape 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.

#### **1.9.2.1. Organic-Inorganic hybrid coatings:**

In recent years, many reports were given in literature including the addition of platelet fillers like as layered silicates (clay), as effective anticorrosive coatings by increasing the length of the diffusion pathways for aggressive species.

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Clay materials due to their platelet structure and high aspect ratio, in well dispersed state, decrease the permeability of polymer coating films by increasing the diffusion pathways such as already shown in Figure 1.9. The nanocomposite of various polymeric materials such as polystyrene, poly(styrene-coacrylonitrile), polyaniline, polypyrrole, polysulfone, polyacrylates, polyimide and epoxy with unmodified and organically modified clays have been investigated as anticorrosive coatings on metals.

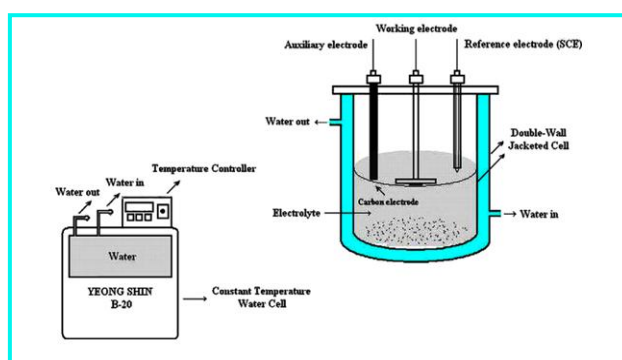
A number of electrochemical measurements have been used to evaluate the anticorrosion performance of polymeric coatings, including conjugated (e.g., polyaniline) or nonconjugated (e.g., polystyrene) polymers. Wei et al., 1995, demonstrated the anticorrosive performance of conjugated polyaniline and nonconjugated 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., 2001a, 2001b, 2002a, 2002b, 2003, 2004a, 2004b, 2004c, 2005, 2006, 2007; Chang et al., 2006, 2007, 2008, 2011; Lai et al., 2007; Yu et al., 2004a, 2004b). 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<sup>+</sup>-MMT clay through different

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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. Reports available of corrosion resistant coatings containing clay as fillers in literature are summarized below.

Chang et al., 2007 reported the preparation of PMMA–clay nanocomposites using sodium dodecylbenzenesulfonate (SDS) and potassium peroxydisulfate (KPS) as a surfactant and chain initiator for an in situ emulsion polymerization reaction, respectively (Figure 1.21). 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.,  $E_{\text{corr}}$ ,  $R_p$ ,  $I_{\text{corr}}$ ,  $R_{\text{corr}}$  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  $50 \pm 0.5$  °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. The

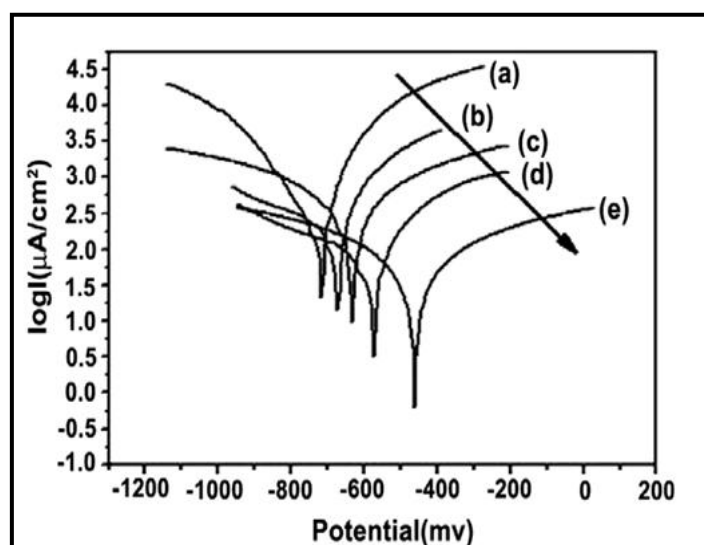
molecular barrier properties at three different operational temperatures of PMMA and PCN membranes were investigated by gas permeability analyzer (GPA) and vapor permeability analyzer (VPA). Effect of material composition on the molecular weight and optical properties of neat PMMA and PCN materials, in the form of solution and membrane, were also studied by gel permeation chromatography (GPC) and UV–vis transmission spectra.



**Figure 1.21.** Electrochemical measurements 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  $50 \pm 0.5 \text{ }^\circ\text{C}$

Similarly, Yeh et al., 2007 reported a series of poly(o-methoxyaniline) (PMA)/ $\text{Na}^+$  montmorillonite (MMT) clay nanocomposite ( $\text{Na}^+$ -PCN) materials by in situ emulsion polymerization in the presence of inorganic nanolayers of hydrophilic  $\text{Na}^+$ -MMT clay with DBSA and APS as surfactant and initiator, respectively (Figure 1.22). The as-synthesized  $\text{Na}^+$ -PCN materials were characterized by Fourier-transformation infrared (FTIR) spectroscopy, wide-angle powder X-ray diffraction (XRD) and transmission electron microscopy (TEM).  $\text{Na}^+$ -PCN materials in the form of coatings with low loading of  $\text{Na}^+$ -MMT clay

(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 Na<sup>+</sup>-PCN 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 Na<sup>+</sup>-PCN materials, in the form of solution, powder-pressed pellet and fine powder, were also studied by ultraviolet-visible spectra, four-point probe technique, thermogravimetric analysis (TGA) and scanning electron microscopy (SEM), respectively.



**Figure1.22.** Tafel plot of a series of poly(o-methoxyaniline) (PMA)/Na<sup>+</sup> montmorillonite (MMT) clay nanocomposite corrosion protection studies.

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## 1.10. Scope and Objectives of the Present Investigation

Polymer clay nanocomposites have attracted great interest during the past two decades because they often exhibit remarkable thermal, mechanical and barrier properties due to the dispersion of silicate layers of nanometer dimensions in a polymer matrix. It was reported that nanocomposites with various structures/morphology, properties and applications can be produced by tuning the polymer-clay interactions. The use of reactive organomodifiers with unsaturated bonds or other reactive functional groups for clay is a good strategy to improve the strength of the interface between the inorganic and the polymer matrix. These groups are expected to react with the growing polymer chains so that the polymer chains remain attached to the clay surface. Recently, the formation and mechanism of polymer nanocomposite particle, vesicle and micropatterned film using POSS-modified clay nanocomposite was reported by Nair et al., 2010. Here, the polystyrene composites were synthesized by in situ intercalative polymerization of styrene with silane modified organoclay. Silanes were costly and the modification procedures were tedious and time consuming.

So, the aim of our present work was to synthesize organoclay using easily available and cost effective Acid-Amine Adduct. Adduct modified organoclays with reactive functional groups will be particularly attractive in this regard. It was for the first time adducts modified clay containing reactive functional groups were used to prepare polymer clay nanocomposite. Advantage of this method include, adoption of simple Acid-Amine adduct for the clay modification instead of commonly used quaternary ammonium salt as intercalating agent.



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**The objectives of the present work are:**

- 1) To prepare Acid–Amine adduct modified clay having reactive functional groups using CTAB and unsaturated acids like Acrylic acid, Oleic acid, and Cinnamic acid, so that the unsaturated acid part intercalated in the clay can take part in polymerization reactions and the CTAB part involves in the cation exchange process.
- 2) To study the structure and characteristics of the Adduct modified clays and hence its usefulness for the synthesis of polymer-clay nanocomposites.
- 3) To study the structure and properties of polymer-clay nanocomposites prepared from Adduct modified clays using various characterization techniques.
- 4) To study the concentration dependant self-assembling property of Polystyrene clay nanocomposite using different Adduct modified clay using optical microscopy, SEM and Fluorescence spectroscopy.
- 5) To study the anticorrosive characteristics of polystyrene clay nanocomposite coatings using potentiodynamic and electrochemical impedance spectroscopy measurements in 3.5 wt.% aqueous NaCl electrolyte at different clay loading on Aluminum 6061 alloy and also the effect of modifier concentration on cold rolled steel .