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Polymer/Clay Nanocomposites

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1. Introduction

A composite is any material made of more than one component. Composite materials are solid multiphase materials formed through the combination of materials with different structural, physical and chemical properties. This makes composites different from the other multi component systems such as blends and alloys. Composites are widely used in such diverse as transportation, construction and consumer products (Giannelis, 1996). Composites offer unusual combinations of component materials properties such as weight, strength, stiffness, permeability, electrical, biodegradability and optical properties that is difficult to attain separately by individual components. A composite material can be custom tailored to have specific properties that will meet special requirements. The optimum design of composite component materials and manufacturing process to meet the target properties for specific engineering application is very important.

In a composite, one phase is continuous and is called matrix, while the other is filler material which make the dispersed phase. Composite materials based on the nature of matrix phase can be divided into polymeric, ceramic and metallic composites. Usually the filler phase is embedded to the host matrix phase to make a composite which has properties far from either phase alone. Polymers often have advantages over other materials such as metals and ceramics. They are widely used in various technical applications because of their unique advantages such as ease of production, light weight and ductility. However they have lower mechanical, modulus and strength properties compared to that of metals and ceramics. The commercial importance of polymers and their increasing use, results to the continuous demand for improvement in their properties to meet the necessary conditions. By the composite technology, polymer properties are improved while maintaining their light weight and ductile nature (Jordan et al., 2005).

2. Polymer composites

A polymer composite is made by the combination of a polymer and synthetic or natural inorganic filler. Fillers are employed to improve the desired properties of the polymer or simply reduce the cost. Nowadays, the application of polymer composites as engineering materials has become state of the art. Polymer composites with improved mechanical, thermal, barrier and fire retardancy properties are widely used in very large quantities in variety of applications. However by the application of conventional fillers such as talc, calcium carbonate, fibers, etc, it often requires to use a large amount of filler in the polymer

matrix to have significant improvements in the composite properties which may result to some other undesired properties such as brittleness or loss of opacity (Zhang & Fridrich, 2003).

The final properties of reinforced polymers (composites) are influenced by the nature, properties and content of components, dimensions of components and micro structure of composite and interfacial interactions between matrix and dispersed phase. The efficiency of properties improvements depends strongly on the properties (mechanical) of the filler, the adhesion between matrix and filler and especially on the aspect ratio of the filler. The aspect ratio of the filler is very important and crucial for many properties in composite such as electrical (Al-Saleh & Sundararaj, 2010; Grossiord et al., 2008), mechanical (Zhang et al., 2007) and thermal (Meneghetti & Qutubuddin, 2006) properties. Polymer composites with the high aspect ratio of nano-fillers such as platelet clays, carbon nanotubes and nanofibers are receiving considerable attention due to their unique multifunctional and highly enhanced properties. Combination of filler nanoscale dimension and high aspect ratio with its nanoscale dispersion within polymer matrix leads to the significant improvements in the polymer properties at very low filler volume fractions. As a result of lower filler using, the macroscopic homogeneity and low density of primary polymer retains as well as its opacity in the final nanocomposite system. Polymer nanocomposites are the new class of hybrid materials in this category (Mittal, 2009).

3. Polymer nanocomposites

A nanocomposite is defined as a composite material in which at least one dimensions of at least one component is in the nanometer size scale (< 100 nm). Although the term nanocomposite represent a new and exciting field in material science and technology, the nanocomposites have actually been used for centuries by the nature. Using natural materials and polymers such as carbohydrates, lipids and proteins, nature makes strong nanocomposites such as bones, shells and wood (Hussain et al., 2006). However in recent years the characterization and control of structures at the nanoscale have been studied, investigated and exploited by the learning from the natural surroundings. Consequently the nanocomposite technology has emerged as an efficient and powerful strategy to upgrade the structural and functional properties of synthetic polymers. This is the new nanocomposite science, so referred recently in nanotechnology, and was started by the Toyota report (Usuki et al., 1993) on the superior improvement in the properties of nylon-6 by the preparation of exfoliated nylon-6/clay nanocomposites and has been continued by more recent studies with carbon nanotubes, carbon nanofillers, exfoliated graphite, nanocrystalline metals and fibers modified with inorganic fillers used in polymeric composites (Paul & Robeson, 2008).

Polymer nanocomposites have attracted great attention world wide academically and industrially due to the exhibition of superior properties such as modulus, strength, toughness and barrier far from those of conventional micro composites and comparable with those of metals. However polymer nanocomposites have added advantage of lower density and ease of processability. In polymer nanocomposites, the filler has at least one dimension in the nanometer scale and its nanoscale dispersion within the polymer matrix leads to the tremendous interfacial contacts between the polymer and inorganic filler which causes to the superior properties than those of bulk polymer phase. When the dimensions of filler particles are decreased to the nanoscale, their properties change also significantly

(Kumar et al., 2009). This is well-known as nano-effect. In the other word the effect of nanofillers on the polymer properties is different from that of predicted by using the thermodynamical studies for the reduced particle size fillers (Gacitua et al., 2005). Studies and modelings using continuum mechanics reveal that the enhanced properties of nanocomposites are strongly dependent on the particular features of nanofiller system, in particular, its content, aspect ratio and the ratio of filler mechanical properties to those of the matrix (Sheng et al., 2004). The nanoscale is considered where the dimensions of filler particles (diameter), platelets (thickness) or fibers (diameter) are in the size range of 1-100 nm (figure 1).

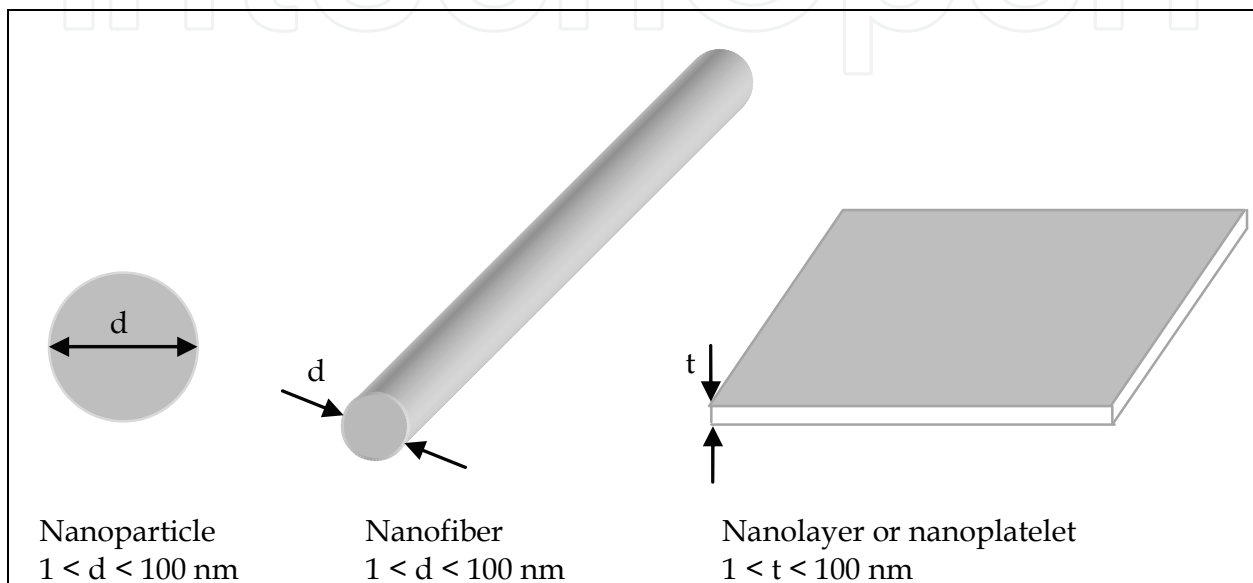


Fig. 1. Scheme of various types of nanofillers or fillers with nanoscale dimensions.

A broad spectrum of polymer properties can be improved by nanocomposite technology such as mechanical, thermal, barrier, durability, chemical stability, flame retardancy, scratch/wear resistance, biodegradability as well as optical, magnetic and electrical properties (Armentano et al., 2010; Cosoli et al., 2008; Ma et al., 2006; Pandey et al., 2005).

The final properties of nanocomposites are determined by the component properties, composition, micro-structure and interfacial interactions. However it has been established that the properties of nanocomposites are strongly influenced by the dimensions and micro structure of filler phase (Sheng et al., 2004). In other word the filler nature has a main effect on the final morphology and properties of the polymer nanocomposite. Clays are one group of nano-fillers which have been widely used for the preparation of polymer nanocomposites. Recently there has been a growing interest for the development of polymer/clay nanocomposites due to their dramatic improved properties compared to the conventional filled polymers in a very low fraction of filler addition (LeBaron et al., 1999; Thostenson et al., 2005). Polymer/clay nanocomposites have received intense attention and research interest driven by the unique properties which can never be obtained by micro size fillers or especially by other nanofillers. The value added properties enhanced without the sacrificing of pure polymer processability, mechanical properties and light weight, make the clays more and more important in modern polymer industry. Clay minerals are belonging to a main group of silicates with layered structure known as layered silicates.

4. Layered silicates

The layered silicates are natural or synthetic minerals consisted of the regular stacks of aluminosilicate layers with a high aspect ratio and high surface area. Layered silicates are easily available and have low cost. The current most popular layered silicates used in polymer nanocomposites preparation are clays.

Clay is referred to a part of soil fraction with the particle size of less than 2 μm . The clay layers have a thickness of about 1 nm which is in the nanoscale. There are many members of clays with some difference in their formula, structure and properties including swelling and exfoliation. Those members who are able to be exfoliated by polymer chains or monomers and distributed as individual clay layers within polymer matrix are suitable for the preparation of polymer nanocomposites. The individual clay layers can cause to the dramatic improvements in polymer properties due to their high aspect ratio and high interfacial interactions with polymer matrix.

4.1 Structure of clays

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. Two main arrangements of tetrahedral and octahedral sheets fused together make the one layer structure of clay. One tetrahedral fused to one octahedral (1:1) is known as kaolin group with the general composition of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_5$ and the layer thickness of ~ 0.7 nm. The crystal lattice consisted of one octahedral sheet sandwiched between two tetrahedral sheets (2:1) with the total thickness of 0.94 nm is well known as phyllosilicates. The 2:1 phyllosilicate layers can be electrostatically neutral with no inter layer ion present known as pyrophyllite. Due to not presence of inter layer ions, the layers do not expand in water. When silicon in tetrahedral sheets is substituted by aluminium, the 2:1 structure is called mica. The negative charge induced by this substitution is balanced by the insertion of potassium cations between layers. Due to the equal size of potassium cation and the hole created by Si/Al tetrahedral sheets, the presence of potassium cation makes no inter layer spacing. Consequently the 2:1 layers are held together strongly and the swelling or exfoliation of layers is not possible. When in neutral pyrophyllite, the aluminum cations in the octahedral layers are partially substituted by divalent magnesium or iron cations the smectite clay group is formed. The negative charge created by this substitution is balanced by inter layer counter sodium or calcium ions. The charge created on the layers is not locally constant and varies from layer to layer. An average charge value is considered for the layers which can be determined by cation exchange capacity (CEC) measurement. Due to the unequal size of inter layer cations with the holes of tetrahedral sheets, the presence of inter layer cations causes to an inter layer spacing. The layers stay near together with a regular gap between them. The gap is called as inter layer or gallery. The thickness of the repeated units in a regular multilayer structure contained of one layer and one inter layer space is called d-spacing (d_{001}) or basal spacing (figure 2). The basal spacing of clays can be measured or calculated from their X-ray diffraction patterns. The inter layer dimension is also dependent to the clay nature and swelling or hydration degree of inter layer cations. The inter layer distance is about 1 nm for montmorillonite.

The electrostatic and van der waals forces holding the layers together are relatively weak and inter layer distance varies depending on the charge density on the layers, inter layer cation radius and its degree of hydration. Because of the inter layer spacing and weak inter layer forces, the cations present between the layer can be hydrated in aqueous solutions well known as clay swelling. The swelling causes to the more increasing of inter layer space. The charge density on the clay layers is different in various clay groups with different clay structures (Mittal, 2009). Due to the inter layer spacing and weak forces between layers, especially in the hydrated form, other molecules also can be intercalate between layers, leads to the expanding of layered lattice and finally may be caused to the separation of individual layers. The unique intercalation/exfoliation behavior of smectite clay minerals which is responsible to the high aspect ratio of this clay type makes them very important and powerful as reinforcing filler for polymers.

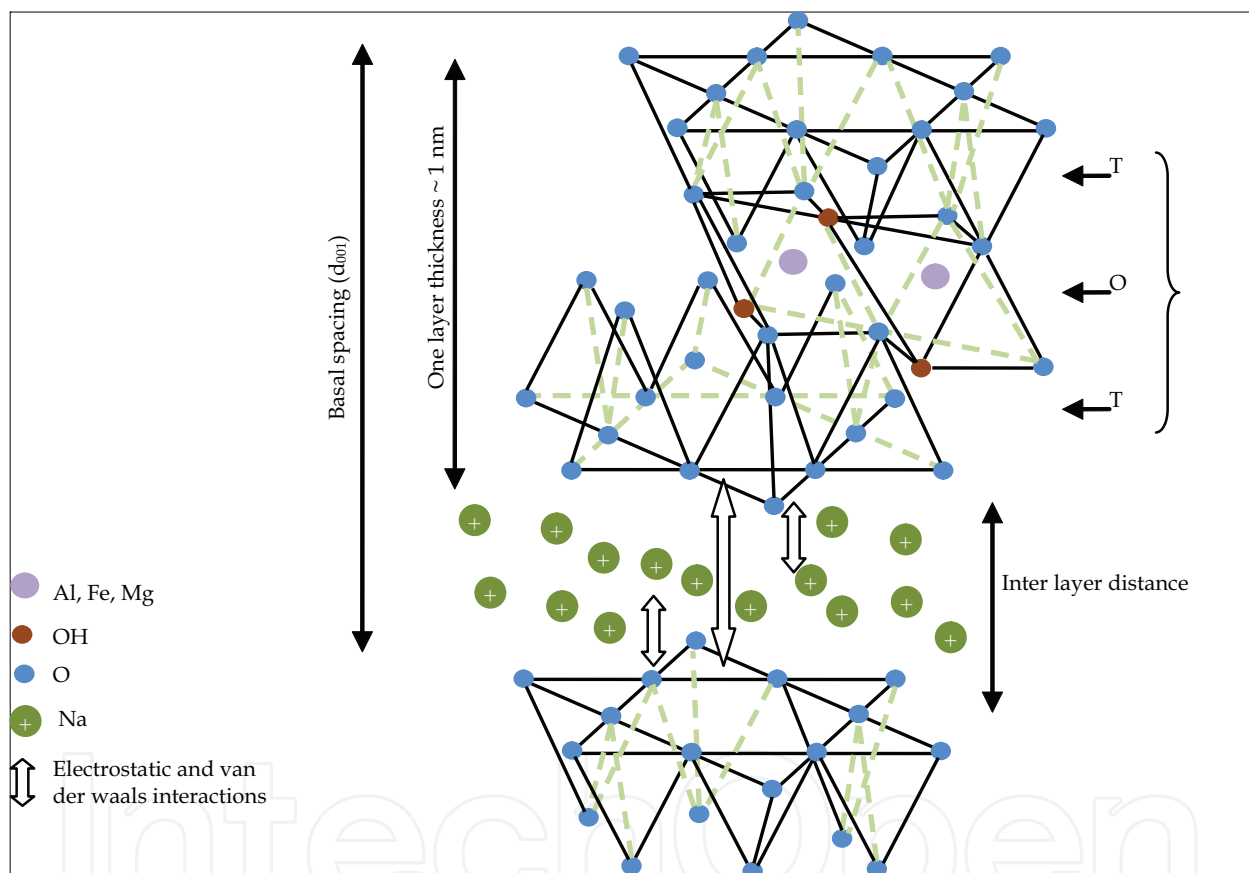


Fig. 2. Scheme of the 2 : 1 smectite clay structure.

The dimension of 2:1 layer structures are about 1 nm in thickness and 30 nm to several microns in lateral depending on the source and preparation method of clay. The clay lateral dimensions and its ability to disperse into separated layers determine the aspect ratio of clay which is strongly important in polymer/clay interfacial interactions. Separation of individual clay layers having about 1 nm thickness display a perfect structure which strongly affects on the improvement of polymer properties. However due to the higher internal surface in high degrees of dispersed structures, the internal forces for agglomeration of individual layers is also increases. Therefore the layers have tendency to hold together or aggregate. Several layers organized parallel together with the total thickness of about 10 nm make “primary clay particles”. Primary particles are laterally

joined together and make “micro aggregates”. “Aggregates” are formed by randomly joining of micro aggregates and primary particles, and finally the staying of aggregates near together makes “association” in the smectite structures.

Clay minerals are belonging to the nanoplatelet structured filler particles in polymer composite technology. Montmorillonite, hectorite and saponite are the well known smectites which are most commonly used in the preparation of polymer nanocomposites (table 1) (Pavlidou & Papaspyrides, 2008). Montmorillonite (MMT) has the widest acceptability for use in polymer nanocomposites because of its ease availability, well known intercalation/exfoliation chemistry, high surface area and high surface reactivity. The MMT layer aspect ratio can be in the range 1000 in well dispersed state without breaking of layers and surface area of about 750 m²/g. Usually because of the breaking of clay layers in to small plates during preparation process of nanocomposite, the aspect ratio of MMT layers decreases to about 300-500.

Smectites	Chemical formula
Montmorillonite	$M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$
Hectorite	$M_x(Mg_{6-x}Li_x)Si_8O_{20}(OH)_4$
Saponite	$M_xMg_6(Si_{8-x}Al_x)O_{20}(OH)_4$

Table 1. Chemical structure of commonly used smectite type clays, M: monovalent cation, x: degree of cations isomorphous substitution in octahedral sheets, (Pavlidou & Papaspyrides, 2008).

Other clay materials such as 1:1 structures, 2:1 pyrophyllits and mica are not commonly used in polymer nanocomposites because they have not useful intercalation/exfoliation characteristics or they are not easily separated into layers. Due to the higher charge density on the layers they are strongly stacked together and the hydration of inter layer cations or intercalation of polymer chains between layers are difficult or not possible.

4.2 Modification of clay layers

The preparation of polymer/clay nanocomposites with good dispersion of clay layers within the polymer matrix is not possible by physical mixing of polymer and clay particles. It is not easy to disperse nanolayers in most polymers due to the high face to face stacking of layers in agglomerated tactoids and their intrinsic hydrophilicity which make them incompatible with hydrophobic polymers. Only a few hydrophilic polymers such as poly (ethylene oxide) and poly (vinyl alcohol) can be miscible with clay nanolayers (Pavildou & Papaspyrides, 2008).

The intrinsic incompatibility of hydrophilic clay layers with hydrophobic polymer chains prevents the dispersion of clay nanolayers within polymer matrix and causes to the weak interfacial interactions. Incompatibility and weak interfacial interactions hinders the exfoliation and preparation of dispersed stable nanocomposite with improved properties. Modification of clay layers with hydrophobic agents is necessary in order to render the clay layers more compatible with polymer chains. This is a surface modification which causes to the reduction of surface energy of clay layers and match their surface polarity with polymer polarity. The organoclays with lowered surface energy are more compatible with polymers and polymer molecules are able to intercalate within their interlayer space or galleries under well defined experimental conditions.

The surface modification of clay layers can be achieved through a cation exchange process by the replacement of sodium and calcium cations present in the inter layer space or clay galleries by alkylammonium or alkylphosphonium (onium) cations (Ahmad et al., 2009). In addition to the surface modification and increasing the hydrophobicity of clay layers, the insertion of alkylammonium or alkylphosphonium cations into the galleries causes to some degree of increasing in the inter layer spacing which promotes the following intercalation of polymer chains into the galleries during nanocomposite preparation (Chigwada et al., 2006). Also the alkylammonium or alkylphosphonium cations can provide functional groups which interact with polymer chains or initiate the polymerization and therefore increase the interfacial interactions. Figure 3 schematically shows the organically modification of clay layers using alkylammonium cations via the ion exchange process.

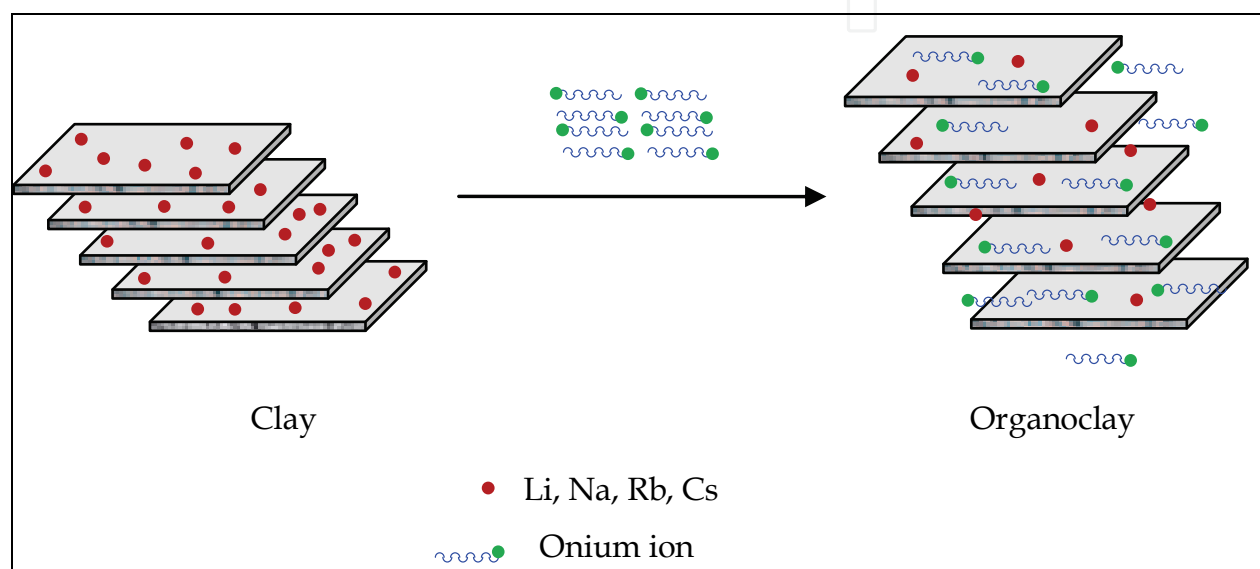


Fig. 3. Scheme of the modification of clay layers by organic onium cations.

The ion exchange process is carried out in aqueous solution with the hydrated inter layer cations. The affinity of monovalent sodium cations to hydration promotes the ion exchange process and increases the efficiency of organic modification of clay layers. Clays containing divalent counter cations such as calcium can not be easily hydrated and therefore their replacement by ion exchange process is not efficient. Therefore, in these clays, the divalent cations should be ion exchanged with easily exchangeable sodium cations prior to modification by onium cations (Ray & Okamoto, 2003). The efficiency of organic modification by ion exchange process in the increasing of basal spacing and consequently the exfoliation of clay and formation of stable nanocomposite systems depends also on the surface charge of clay layers. The surface charge density of clay layers depends on the clay nature and its preparation (growth) conditions. When the charge density of clay layer is high such as about 1 equiv/mol for mica, the electrostatic forces between layers is also high. Therefore the inter layer cations can not to hydrate or swollen and consequently the ion exchange process can not be carried out. The medium charge densities (0.5–0.8 equiv/mol) such as in vermiculite, can make a high potential for partial swelling and hydration of cations. However the divalent cations exist in the inter layer spacing of clays such as vermiculite make the swelling process difficult due to the lower affinity of divalent cations for hydration. The lower charge densities (0.25–0.5 equiv/mol) such as formed in montmorillonite causes to the weak electrostatic forces between layers. Also the presence of

sodium cations, with high affinity for hydration and exchanging, between the MMT layers make this kind of clays more suitable for swelling, organic modification and exfoliation. The structure of the organoclays and their basal spacing also depends on the molecular size of organic onium and its configuration in the inter layer spacing after modification. Figure 4 schematically shows the various configurations of the organic modifiers inserted within the clay layers by ion exchange with sodium cations. It is clear that the charge density of clay layers, the efficiency of ion exchange process and the spatial characteristics of onium cation are effective on the configuration of onium cations in the modified clays.

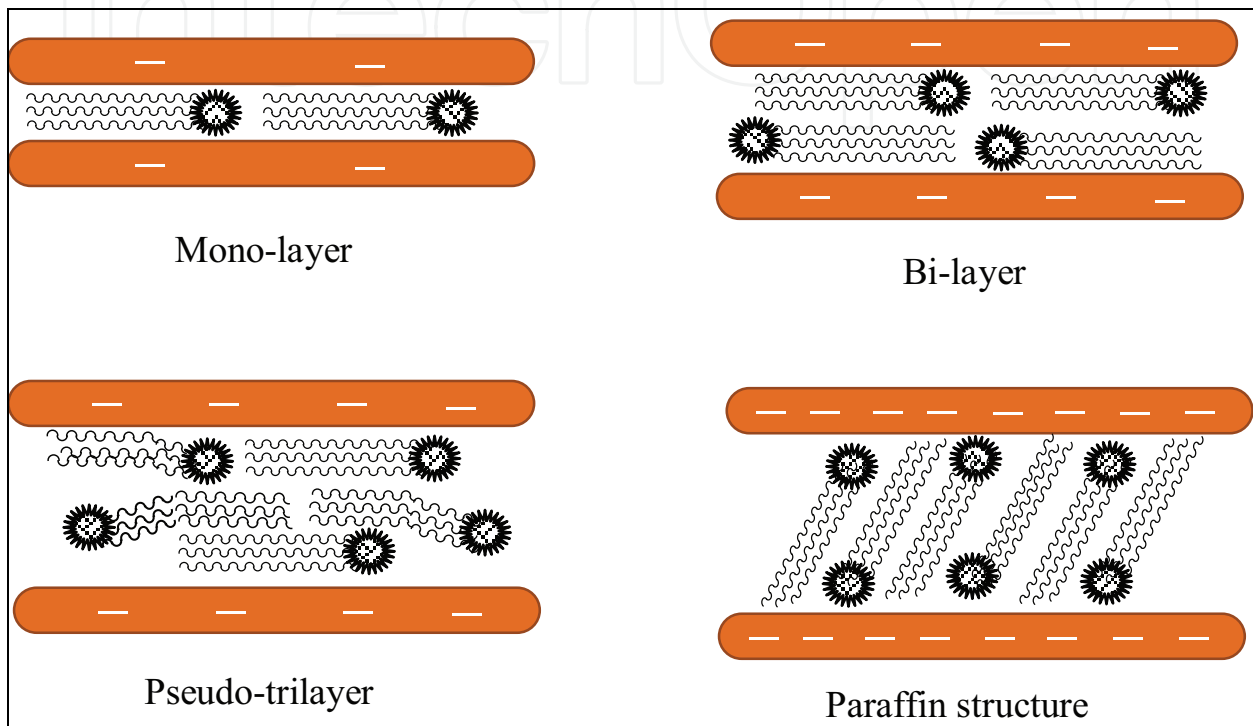


Fig. 4. Various configurations of organic oniums into the clay galleries.

The organic tail of onium laid up parallel to the clay layer can be obtained with lower charge densities. By increasing the charge density of clay layers, bilayer or trilayer structures with more increasing of inter layer spacing can be formed. Finally with the higher charge densities more inter layer spacing is obtained by the formation of paraffin structure. Also increasing of temperature can lead to the structures with more basal spacing by increasing the mobility of onium molecules into the galleries. However in a given temperature two parameters determine the equilibrium layer spacing, the charge density of layers, driving the packing and number of onium chains into the interlayer space, and the size or chain length of organic tail in onium compound.

5. Nanocomposite structure

In general, the structures of polymer/clay nanocomposites are classified according to the level of intercalation and exfoliation of polymer chains into the clay galleries. Various parameters including clay nature, organic modifier, polymer matrix and preparation method are affective on the intercalation and exfoliation level. Therefore depending on the nature and properties of clay and polymer as well as preparation methodology of nanocomposite, different composite micro-structures can be obtained.

5.1 Phase separated structure

When the organic polymer is interacted with inorganic clay (unmodified clay), the polymer is unable to intercalate within the clay layers and the clay is dispersed as aggregates or particles with layers stacked together within the polymer matrix. The obtained composite structure is considered as "phase separated". The properties of phase separated polymer/clay composites are in the range of traditional micro composites.

5.2 Intercalated structure

When one or more polymer chains are inserted into the inter layer space and cause to the increasing of the inter layer spacing, but the periodic array of the clay layer is still exist, the intercalated nanocomposite is formed. The presence of polymer chains in the galleries causes to the decreasing of electrostatic forces between the layers but it is not totally dissolved. A well-ordered multilayer hybrid morphology with a high interference interactions consisted of polymer chains and clay layer is obtained in this configuration.

5.3 Exfoliated structure

Exfoliated or delaminated structure is obtained when the insertion of polymer chains into the clay galleries causes to the separation of the layers one another and individual layers are dispersed within the polymer matrix. At all, when the polymer chains cause to the increasing of interlayer spacing more than 80-100 Å, the exfoliated structure is obtained. Due to the well dispersion of individual clay layers, high aspect ratio is obtained and lower clay content is needed for exfoliated nanocomposites. Also most significant improvement in polymer properties is obtained due to the large surface interactions between polymer and clay. Various polymer/clay structural configurations have been shown in figure 5.

6. Preparation of polymer/clay nanocomposites

Many efforts have been made for the preparation of intercalated and exfoliated polymer/clay nanocomposites with improved properties. A variety of polymer characteristics including polarity, molecular weight, hydrophobicity, reactive groups as well as clay characteristics such as charge density and its modified structure and polarity are affective on the intercalation of polymer chains within the clay galleries. Therefore different synthetic approaches have been used for the preparation of polymer/clay nanocomposites. In general there are four preparation methods including insitu template synthesis, solution intercalation, insitu intercalative polymerization and melt intercalation.

6.1 Insitu template synthesis

In this method the clay layers are synthesized insitu in the presence of polymer chains. The polymer and clay primary materials are dissolved in an aqueous solution. Typically magnesium hydroxide, silica and lithium fluoride as clay building blocks are mixed with polymer in a solvent. The gel or slurry is refluxed usually at high temperatures followed by washing and drying. The nucleation and growth of clay layers are take place on the polymer chains and the polymer chains are trapped in the clay inter layers. Although the clay layers may be well dispersed within the polymer matrix without the modification of clay by onium cations, however this method has serious disadvantages. The high temperature applied for the synthesis of clay layers causes to the decomposition of polymers. Only hectorite clay is

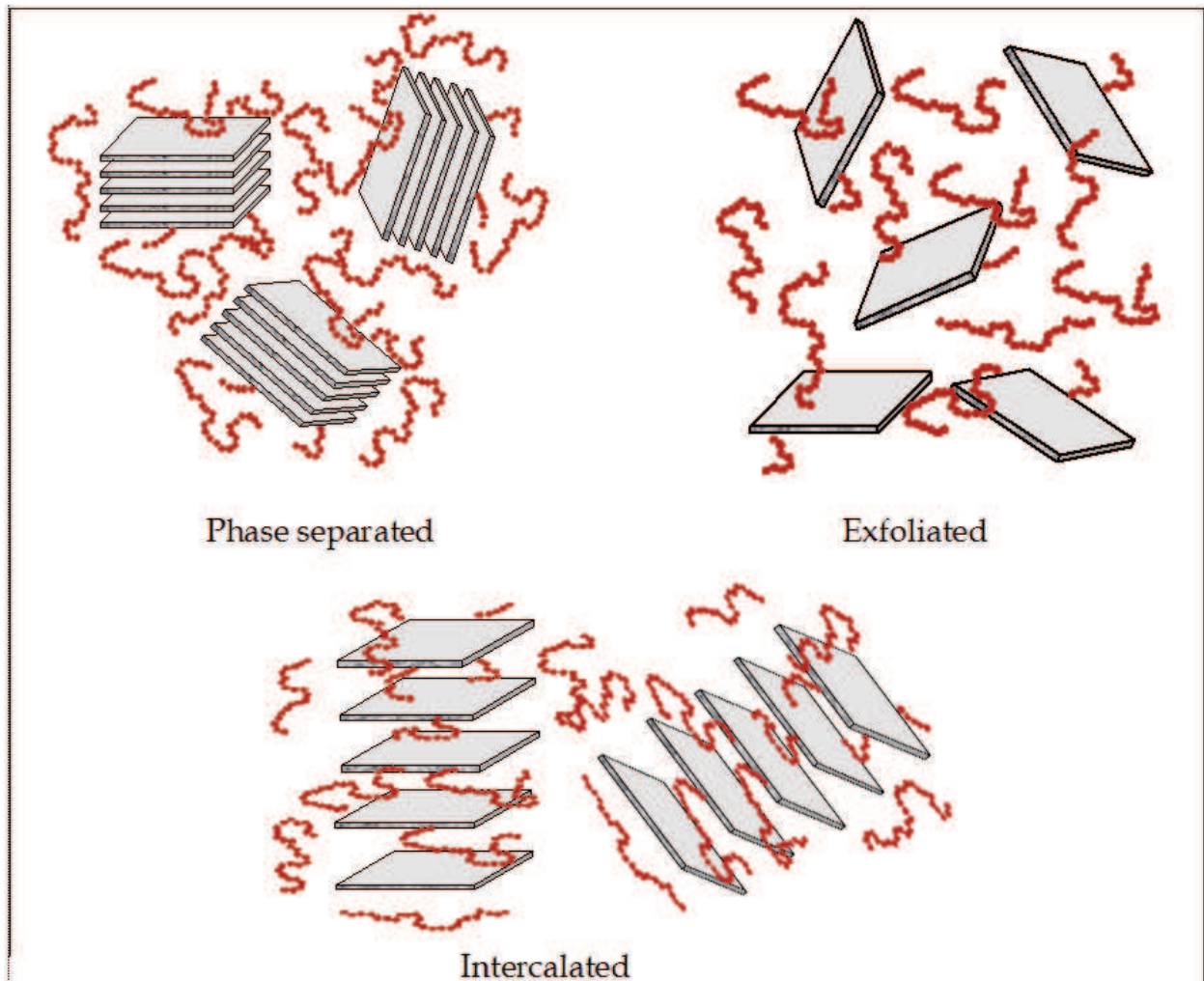


Fig. 5. Various micro-structures of polymer/clay composites.

synthesized at the lower temperatures. Also the synthesized clay crystals, generated by the self-assembly process, have tendency to aggregate. Therefore this method is not widely used and only a few nanocomposites using hectorite clay and poly (vinyl alcohol), polyaniline and polyacrylonitrile have been synthesized by this method (Alexandre & Dubois, 2000; Lagaly, 1999; Zanetti et al., 2000).

6.2 Solution intercalation

In this method the polymer or prepolymer 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. 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 entropy gained by the exit of solvent molecules from the interlayer spacing, allows the polymer chains to diffuse between the layers and sandwiching. We have used the solution intercalation method for the preparation of epoxy /clay nanocomposites. Diglycidyl ether bisphenol A (DGEBA), (196-208 epoxy equivalent weight, Epiran-05, Khouzestan Petrochemical Company, Iran), was used as the polymer matrix. EPIKURE curing agent 3200, Aminoethylpiperazine (AEP) from Hexion Specialty

Chemicals Inc., was used both as curing agent of epoxy resin and also as intercalating agent for montmorillonite (MMT). The inorganic clay used in this study was K-10 grade MMT obtained from Sigma-Aldrich Co (USA) with a surface area of 130 m²/g. Organically modified clays, Cloisite 30B (d-spacing = 18.5 Å) and Cloisite 15A (d-spacing = 29.88 Å) were provided by the Southern Clay Products. Tetraethylammonium chloride (TEA) salt was also used as intercalating agent of MMT. Acetone was used as solvent.

Depending on the interactions between polymer and clay sheets, intercalated or exfoliated structures may be obtained in this method. This technique is used for the preparation of epoxy/clay nanocomposites. However due to the need for use solvent, this technique can not 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). In our group the emulsion and bulk polymerization methods have been used for the preparation of polystyrene/clay nanocomposites using the Na-MMT, cloisite 30B and cloisite 15A clay materials. The effect of clay swelling method and sonication on the inter layer spacing and intercalation have been investigated. Good dispersion of Na-MMT in the polystyrene (PS) matrix was observed when an emulsion polymerization was employed and good dispersion of cloisite 30B in the PS was observed during bulk polymerization. Cloisite 30B showed better dispersion when this clay was swollen with the monomer during emulsion polymerization. Sonication had good effect on dispersion of the clays in the PS matrix. PS/Cloisite 15A nanocomposites showed minor increase in d-spacing compared to the pure cloisite 15A. TGA analysis showed that the thermal stability of the nanocomposites has been improved compared to the pure polystyrene (table 2).

6.3 Insitu intercalative polymerization

This technique was the first method used for the preparation of polymer/clay nanocomposite by Toyota research group in the preparation of Nylon-6 nanocomposite from caprolactam monomer (Usuki et al., 1993). In this method the organoclay is swollen in monomer liquid or monomer solution. The monomers diffused into the inter layer spacing are polymerized by the heat or radiation, by the diffusion of an initiator or by the organic initiator present on the organic modifier of clay (Hussain et al., 2006). The polymerization is carried out within the clay galleries as well as extra galleries. The growth of polymer chains results to the exfoliation and formation of disordered structure.

This method is suitable for the preparation of thermoset/clay nanocomposites and has been widely used for the epoxies and styrenic polymer nanocomposites (Lan et al., 1995). The polarity of monomer and clay layers determines the diffusion rate and equilibrium concentration of monomer within the clay galleries. Consequently the exfoliation and dispersion of clay layers can be tailored by the clay and monomer chemistry (Pavlidou & Papaspyrides, 2008). Polyaniline/MMT nanocomposites have been prepared by the insitu polymerization of aniline in the presence of MMT (Olad & Rashidzadeh, 2008). Both unmodified and organomodified MMT were used in the preparation of nanocomposites. Due to the using of acidic aqueous solutions for the polymerization of aniline, the polar organic anilinium cations can be interact with both unmodified and modified clays.

6.4 Melt intercalation

Clay is mixed within the polymer matrix in molten temperature. The conventional methods such as extrusion and injection molding are used for dispersion of clay layers within the

polymer matrix. This method is effective technique for the preparation of thermoplastic nanocomposites (Kornmann et al., 2001). The polymer chains are intercalated or exfoliated into the galleries. Clays are organically modified and polymer chains are surface modified with more polar functional groups to enhance their compatibility and therefore promote the exfoliation. In melt intercalation method no solvent is required and it has many advantages for the preparation of nanocomposites and is a popular method for industry (Ray et al., 2003).

7. Structural characterization of polymer/clay nanocomposites

In the preparation of a polymer/clay nanocomposite it is important to know the degree of intercalation/exfoliation and its effect on the nanocomposite moderate properties. In other word there is need to analyze the micro structure of the prepared nanocomposite. Two common techniques including X-ray diffraction (XRD) analysis and transmission electron microscopy (TEM) are widely used to characterize the micro structure of nanocomposite as well as pure clay or pure organoclay. Clays and organoclays show a characteristic peak in XRD analysis due to their regular layered structures. The peak is indicative of the platelet separation or d-spacing in clay structure. Using the peak width at half maximum height and peak position (2θ) in the XRD spectra the inter layer space can be calculated utilizing Bragg's law (eq. 1).

$$\sin \theta = n \lambda / 2d \quad (1)$$

Where λ is wave length of X-ray radiation used in the diffraction experiments, d is the space between layers in the clay lattice and θ is measured diffraction angle. Any change in the inter layer or d-spacing of a clay lattice by organic modification or polymer intercalation causes to the change in the position, broadness and intensity of the characteristic peak in XRD spectra. According to the Bragg law, increasing of d-spacing results to the broadening and shifting of related XRD peak toward lower diffraction angles (2θ). By monitoring the position (2θ), shape and intensity of the characteristic peak for organoclay in nanocomposite structure it is possible to determine the degree of intercalation/exfoliation. For example figure 6 shows the XRD patterns of pristine Na-MMT as well as polystyrene (PS)/Na-MMT nanocomposites prepared by emulsion polymerization method. The characteristic peak of MMT has been appeared at $2\theta = 7.13^\circ$ corresponding to the inter layer space of 1.24 nm. The XRD patterns of polystyrene/Na-MMT nanocomposites containing different clay percents (2-6 wt %) show diffraction peaks all shifted to lower 2θ degrees against the peak of pure Na-MMT, which indicates the increasing of layers spacing due to the intercalation or exfoliation. The experimental conditions, peak position (2θ) and related calculated clay layer spacing obtained from XRD spectra of pure clays and polystyrene/clay nanocomposites have been shown in table 2.

The results indicate that the Na-MMT was efficiently dispersed in the polystyrene matrix during the emulsion polymerization due to the hydrophilicity of pure montmorillonite. Also the effect of sonication on the dispersion of Na-MMT layers in the polymer matrix was investigated. The results showed that the polystyrene/Na-MMT nanocomposite prepared by the application of sonication has no noticeable diffraction peak in the XRD spectrum at 2θ values of 2° to 10° (figure 6e). This indicates that the clay plates have been dispersed effectively and may be the exfoliated structure has been obtained.

Sample	Experimental polymerization conditions	2θ (°)	d (Å)
pure Na-MMT	-	7.13	12.38
PS/Na-MMT (2wt%)	Emulsion	2.58	34.16
PS/Na-MMT (4wt%)	Emulsion	2.72	32.46
PS/Na-MMT (6wt%)	Emulsion	2.58	34.16
PS/Na-MMT (2wt%)	Bulk	6.00	14.72
Pure clay 30B	-	4.68	18.86
PS/ clay 30B (2wt%)	Emulsion, swelling with water	3.54	24.93
PS/ clay 30B (2wt%)	Emulsion, swelling with water+ sonication	3.02	29.27
PS/ clay 30B (2wt%)	Emulsion, swelling with monomer	2.79	31.67
PS/ clay 30B (4wt%)	Emulsion, swelling with monomer	2.99	29.51
PS/ clay 30B (6wt%)	Emulsion, swelling with monomer	3.03	29.10
PS/ clay 30B (2wt%)	Bulk	2.71	32.55
pure clay 15A	-	2.95	29.88
PS/ clay 15A (2wt%)	Emulsion, swelling with monomer	2.75	32.16
PS/ clay 15A (2wt%)	Bulk	2.69	32.76

Table 2. XRD data and inter layer space for MMT and PS/MMT nanocomposites.

It may be need to use wide-angle X-ray diffraction (WAXD) patterns in the range $1^\circ < 2\theta < 10^\circ$ to identify the fully exfoliated structures which is correspond to the d-spacing of at least 6 nm. The XRD technique offers a conventional method to determine the d-spacing in the pure clay as well as in nanocomposite structure, within 1-4 nm, using the position, broadness and intensity of characteristic peak in WAXD diffractogram. However the disappearance of such a peak is not a conclusive evidence for a highly exfoliated structure in nanocomposite (Hedayati & Arefazar, 2009).

A direct way to visually observe the nanostructure of nanocomposites and clay d-spacing is to the use of transmission electron microscopy (TEM) technique. TEM micrographs allow a qualitative understanding of the internal structure, exfoliation or spatial distribution of layers within the polymer matrix and their structural defects. In the TEM micrographs, the darker lines in the brighter matrix shows the clay layers because of the presence of heavier elements including Al, Si and O in the composition of clay sheets or layers compared the lighter atoms such as C, H, N and Na present in the polymer matrix or inter layer spacing of clay sheets. Therefore the distance between darker liner sections presented in the TEM micrographs can qualitatively show the d-spacing and dispersion status. Therefore the overall structure of the nanocomposite including intercalation, exfoliation, dispersion and defects of clay layer can be conclusively obtained using TEM technique.

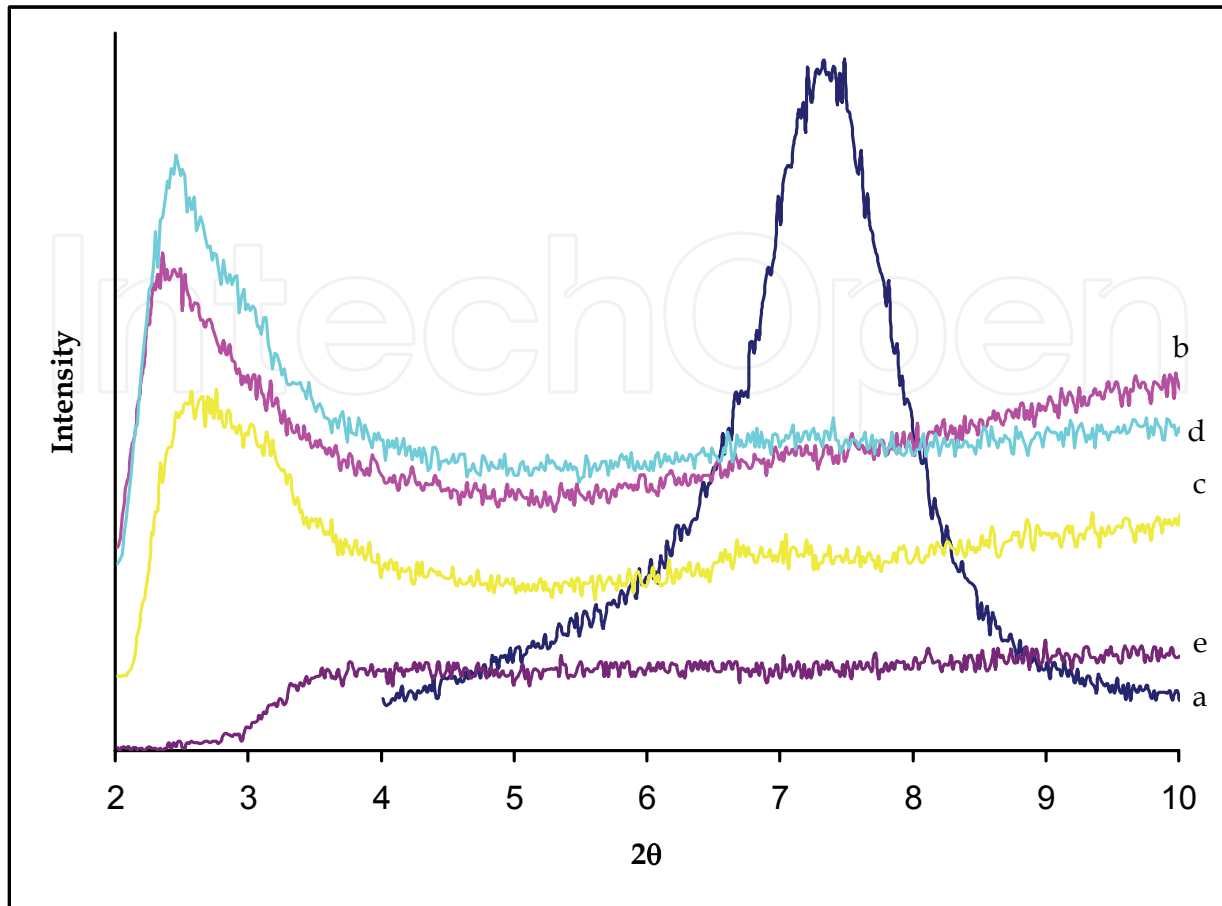


Fig. 6. XRD patterns of pure Na-MMT (a) and PS/Na-MMT nanocomposites prepared by emulsion polymerization method with clay content of 2 wt % (b), 4 wt % (c) and 6 wt % (d) and PS/Na-MMT (2 wt %) with sonication (e).

However both XRD and TEM techniques are essential tools for evaluation of the nanocomposite structure and complementary show the structural features of polymer/clay nanocomposite microstructure. XRD provides almost quantitative and TEM provides qualitative informations about the exfoliation and d-spacing of clay layers in the polymer matrix compared to that of in pure clay material. Also other techniques such as those based on thermal analysis, can be used to evaluate the interfacial interactions between clay layers and polymer chains.

8. Properties of polymer/clay nanocomposites

The aim for the addition of clay minerals to the polymers is to improve the polymer properties and to produce the polymer/clay nanocomposites with demand characteristics for desired applications. Almost it is wanted to obtain a nanocomposite with demand properties and characters or overcome the drawbacks of polymers while remaining the intrinsic advantages of primary polymer matrix.

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 which help to the more remaining of polymer original useful

properties. 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 mechanism and effective parameters are discussed.

8.1 Mechanical properties

The first and important goal in the application of fillers to the polymer is improvement in the mechanical properties and therefore fillers are commonly called as reinforcement agents (Jiang et al., 2005). The mechanism of the reinforcement is based on the higher resistance of rigid filler materials against straining due to their higher module. When a 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, if the interfacial interactions between filler and matrix is adequate (Tortora et al., 2002; Gorrasi et al., 2003).

Therefore the larger the interface between filler and matrix, and also more strong interfacial interactions, the great the reinforcement effect will be. Also the modulus increases by increasing the filler ratio in the composite or 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. In fact due to the very higher aspect ratio of nano-clay fillers compared to that of regular fillers such as glass fibers, dramatic improvements in the mechanical properties of nanocomposites are achieved even at very lower nanoclay additions (LeBaron et al., 1999). In another approach, polymer chains, adhesived by strong physisorption forces onto the rigid clay mono layers, become equally a portion of rigid material and dramatically exhibit high modulus. Considering the very large interfacial area in well dispersed nanocomposite structures, significant improvement in the modulus can be expected. However any enhancement in the polymer-clay interfacial contact leads to the better stress transfer in the nanocomposite. It has been well demonstrated that the enhancement in the interfacial adhesion properties between clay and polymer by surface modification of polymer chains using a suitable polar compatibilizer causes to the increasing in the mechanical properties of nanocomposite (Osman et al., 2005; Mittal, 2008). It should be noticed that in higher loadings of compatibilizers, they may cause to the some degree of plasticization due to their lower molecular weight, which negatively affect on the modulus of nanocomposite (Mittal, 2008). Also the using of organically modified clay filler increases both the modulus and stiffness of nanocomposite because of the more intercalation/exfoliation achieved. At all, any parameter which helps to the intercalation of polymer molecules within the clay galleries and consequently causes to the more exfoliation and interfacial interactions, results to the greater improvement in the modulus. However it is difficult to achieve the complete exfoliation of clay layers and there are variety of platelet structures with different thicknesses (depending on the number of layers stacked together) in polymer matrix. Fornes and Paul (2003) have analytically formulated the effect of incomplete exfoliation on the nanocomposite properties.

Also it has been reported that the tensile modulus increases by increasing the filler volume fraction in nanocomposite (Mittal, 2007). However clay loading more than threshold limit value, causes to leveling-off in the increasing period of Young's modulus, which is due to the formation of partially exfoliated/intercalated structure after that fully exfoliated structure formation (Ray & Okamoto, 2003; Alexandre & Dubois, 2000).

Also the incorporation of clay minerals usually improves the tensile strength of polymers (Fornes et al., 2001; Shelley et al., 2002; Kojima et al., 1993). However the tensile strength is influenced by the final morphology of nanocomposite. There are a number of reports on the reduction of tensile strength by the addition of clay minerals (Alexandre & Dubois, 2000; Finnigan et al., 2004). 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. The stronger interfacial interaction causes to the increasing of stress at break and the weak interfacial forces may lead to some decreasing of stress at break for nanocomposite. The polymers with more polarity such as nylon and rubber based polymers have more strong interfacial interactions with polar clay layers and their nanocomposites represent improved stress at break values compared to that of pure polymer (Wang et al., 1998). Polyamide/clay nanocomposites have shown highly improved stress at break values, because of their higher degree of exfoliated structures based on the presence of strong ionic bonds between polymer chains and clay layers (Alexandre & Dubois, 2000). The nanocomposites of non-polar polymers such as polyolefines with clays exhibit weak interfacial interactions and low degree of exfoliation and consequently show decreased or slightly improved stress at break values. However the modification of polymer chains or clay layers may be causes to improved stress at break characteristics for non-polar polymers.

Elongation at break for polymer/clay nanocomposites is similarly dependent to the interfacial interactions of polymer/clay system. There are both increasing and decreasing reports of elongation at break for polymer/clay nanocomposites in literature (Finnigan et al., 2004; Yao et al., 2002). The impact strength of polymer/clay nanocomposites was also studied and compared with that of pure polymer systems. The reports are usually emphasis on the increasing of impact strength by the addition of very low fraction of clay loadings such as 0.1 wt% (Zhang et al., 2000; Oya et al., 2000). In these studies organic modified clay fillers were added to the compatibilized polyolefines. There are also reports on the decreasing of impact resistance by the addition of clay materials (Phang et al., 2005). Dynamic mechanical analysis studies on polymer/clay nanocomposites have shown that usually storage modulus and glass transition temperature (T_g) are improved by the addition of clay nanofillers (Nam et al., 2001; Laus et al., 1997; Krikorian & Pochan, 2003; Ray et al., 2002).

8.2 Thermal properties

Thermal stability of polymer/clay nanocomposites have been analyzed and compared with that of pure polymer under various oxidative (air) or non-oxidative (inert gases) conditions. Thermogravimetric analysis (TGA) has been usually used to evaluate the thermal stability of polymer and their nanocomposites. In this technique, the weight loss of the material due to the formation of volatile compounds under degradation because of the heating and temperature rising is monitored.

In general, it has been reported that the polymer/clay nanocomposites are thermally more stable than pure polymers (Ray & Bousima, 2005; Becker et al., 2004; Zanetti et al., 2004; Wang et al., 2002). That is the incorporation of clay fillers into the polymer matrices results to the improvement of their thermal stability. The effect of clay layers has been more explained as superior insulation and mass transport barrier against the volatile compounds

generated during the decomposition of polymer under thermal conditions (Zhu et al., 2001). Also it has been reported that clays assist 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).

Blumstein (1965) first reported the improved thermal stability of PMMA/MMT nanocomposite. TGA showed that PMMA intercalated into the Na-MMT has 40-50 °C higher decomposition temperature. Vyazovkin et al. (2004) reported the thermal stability of polystyrene/clay nano-composite compared to pure PS. They have showed that PS/clay nanocomposites have 30-40 °C higher degradation temperature compared to pure PS under nitrogen and air heating degradation conditions. Other studies have been showed that the nature of the clay modifier can affect on the thermal stability of modified clay and related nanocomposites (Mittal, 2007).

In some other studies the thermal decomposition behavior of nanocomposites and pure polymers under air (oxidative decomposition) and inert gas (non-oxidative decomposition) have been compared (Berta et al., 2006; Zhao et al., 2005; Beyer et al., 2002). Results showed that the formation of insulator layered char in oxidative degradation is achieved better than non-oxidative degradation heating program using some inert gases such as helium (Zhao et al., 2005; Beyer et al., 2002). Therefore under inert gas thermogravimetric experiments the nanocomposites may have the same degradation temperature as pure polymer.

We have analyzed the thermal degradation behavior of PS/MMT nanocomposites as well as pure PS. According to the results, thermal stability of nanocomposite has been improved compared to the pure polystyrene. Thermogravimetric analysis (TGA) of neat PS and PS/clay nanocomposites was obtained by heating program of 10 °C /min. Figure 7 shows the TGA curves for PS and PS/MMT nanocomposites. According to the results, the degradation temperature of the PS in nanocomposites has been shifted to higher temperatures compared to neat PS. The temperature of the 50% degradation of PS/clay nanocomposites has been increased compared to the pure PS. The 50% degradation temperature of pure PS was 411 °C, but that of the PS/Na-MMT nanocomposite was 422 °C and for PS/Cloisite 30B was 416 °C which is indicating respectively 11 °C and 5 °C improvement with 4 wt% of the clay loadings. For PS/Cloisite 30B nanocomposite two stages of weight loss under heating program took place. The first stage of weight loss at temperatures of about 220-312 °C represents the decomposition of modifying agent of Cloisite 30B. The second stage of weight loss at temperatures of about 312-450 °C is related to the decomposition of PS. The TGA data are summarized in table 3.

The effect of polymer compatibilizer on the thermal degradation behavior of compatibilized polymer/clay nanocomposites has also been investigated. Results showed that the incorporation of compatibilizers even with low molecular weight has not a significant unwanted effect on the thermal degradation of nanocomposites (Mittal, 2008).

8.3 Flame retardancy

Because of the large use of polymers especially in domestic applications, there is need to reduce their potential for ignition or burn in order to make them more safer in applications. Conventionally chemical additives as flame retardants are used to retardant the ignition and control burn.

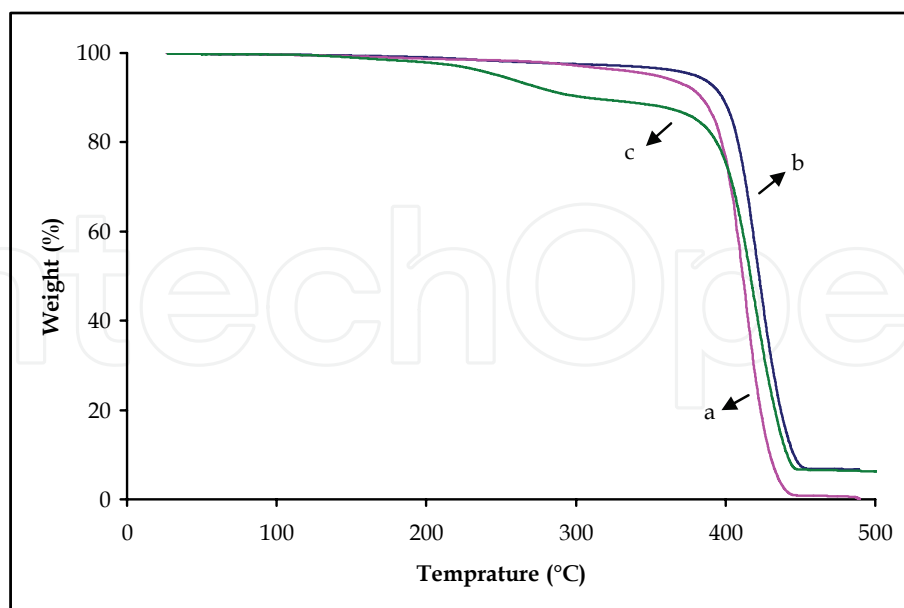


Fig. 7. TGA curves for PS (a), PS/Na-MMT (b) and PS/Cloisite 30B (c).

Traditionally a number of halogen-based as well as phosphorous and some other compounds have the flame retardancy effect in polymers without the reducing of their other properties and quality. 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). Some of inorganic candidates require high level of loading which cause to un-wanted effects on the costs, process ability and quality of the product (Zhao et al., 2005; Laoutid et al., 2009).

Sample	$T_{0.15}^a$ (°C)	$T_{0.5}^b$ (°C)	End Degradation temperature (°C)
Pure PS	392°C	411°C	447°C
PS/Na-MMT (4 wt %)	404°C	422°C	455°C
PS/Cloisite 30B (4 wt %)	380°C	416°C	450°C

Table 3. Thermal degradation data of the PS and PS/clay nanocomposites, based on the TGA results. ^a : 15% Degradation temperature ($T_{0.15}$) and ^b : 50% Degradation temperature ($T_{0.5}$).

Also in other work the thermal properties of epoxy and epoxy/clay nanocomposites were investigated. Figure 8 shows the TGA thermograms of the neat epoxy and epoxy/cloisite 30B nanocomposite with 3% and 5% wt of cloisite 30B. In general, major weight losses are observed in the range of ~300-400 °C for epoxy and nanocomposites, which may be corresponding to the structural decomposition of the polymers. It can be seen in figure 8 that the Td (the temperature of degradation at which weight loss is 20 wt %) for epoxy/cloisite 30B (3 wt %) nanocomposite has shifted toward the higher temperature range against to the pure epoxy in a way that, the Td of the nanocomposite is 319 °C, which is superior to that of the pure epoxy (Td = 313 °C). However the Td of epoxy/cloisite 30B (5 wt

%) nanocomposite is lower than that of neat epoxy due to the catalytic effect of nanoclay on the cross-linking reaction of the epoxy resin with curing agent. After ~ 500 °C, all of the curves became flat and mainly the inorganic residue remains. The char yields of the nanocomposites are higher than that of the neat epoxy.

Investigations on the polymer/clay nanocomposites have been demonstrated that clay minerals represent some degree of flame retardancy along with the improvement in the physical and mechanical properties for polymers (Kiliaris & Papaspyrides, 2010; Giannelis, 1998). However detailed explanations implies that clay materials are beneficial for retarding the flame spread in developing fires and they not improve the ignition retardancy or control the fully developed fires (Livchik & Weil, 2000; Zanetti et al., 2002; Zanetti, 2006). Therefore the clay minerals are used together with a low fraction of conventional flame retardants (Wang et al., 2004). However the clay minerals and traditional flame retardants have considerable synergistic effect in the reduction of ignitability of polymers and various reports of organically modified clay nanocomposites combined with halogenated flame retardants (Weil et al., 1992; Wang et al., 2005) and phosphorous flame retardants (Zhang & Horrocks, 2003; Hao et al., 2006) were presented in literature. The synergic effect of clays on the flame retardancy of halogenated and phosphorous compounds causes to the reduction of their volume fraction needed in the polymer/clay nanocomposite systems.

In a series of other works attempts have been made to intercalate the various phosphorous flame retardants into the clay galleries. The clays modified with such phosphorous compounds have been used in the preparation of nanocomposites with various polymers. In this approach the phosphorous flame retardants are shielded by the clay sheets which prevent their evaporation during preparation of nanocomposite especially by the melt compounding method and it's remaining for more efficient flame retardancy in the final product (Chigwada & Wilkie, 2003).

Schartel et al. (2006) have used tetra-phenyl phosphonium modified clay for the preparation of nanocomposites based on DGEBA resin. Toldy et al. (2006) have also used phosphorous compounds both as curing agent and flame retardant in the preparation of epoxy/clay nanocomposites.

8.4 Barrier properties

One of the most considerable effects of clays in the polymer matrix properties is the dramatic improvement of barrier properties of polymers. Clay sheets 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 9) (Pavlidou & Papaspyrides, 2008; Yano et al., 1993).

The degree of enhancement in the barrier properties depends on the degree of tortuosity created by clay layers in the diffusion way of molecules trough 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 vapors (Tortora et al., 2002; Ray et al., 2003; Lange & Wyser, 2003; Giannelis, 1996; Koh et al., 2008).

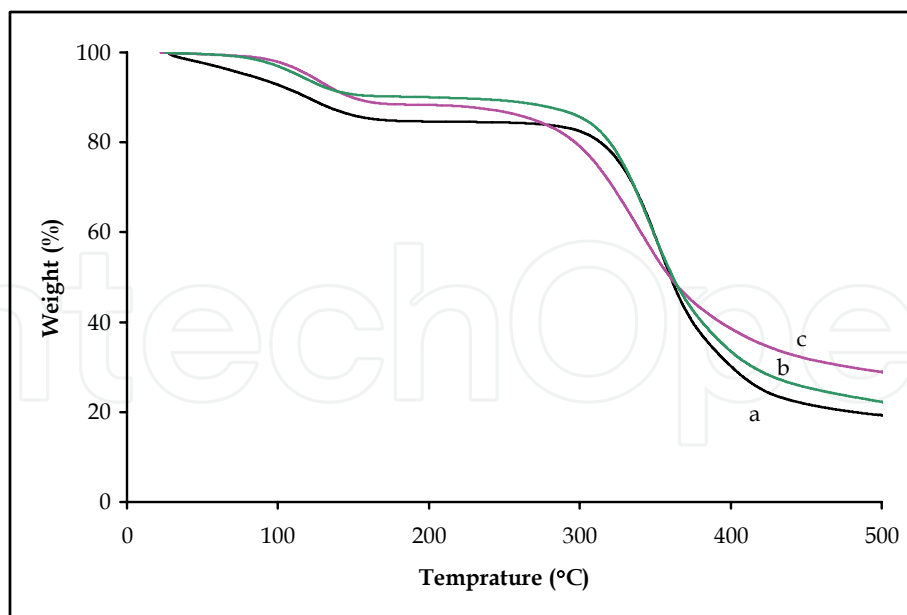


Fig. 8. TGA thermograms of neat epoxy (a) and epoxy/cloisite 30B nanocomposites with 3 wt % (b) and 5 wt % (c) cloisite 30B contents.

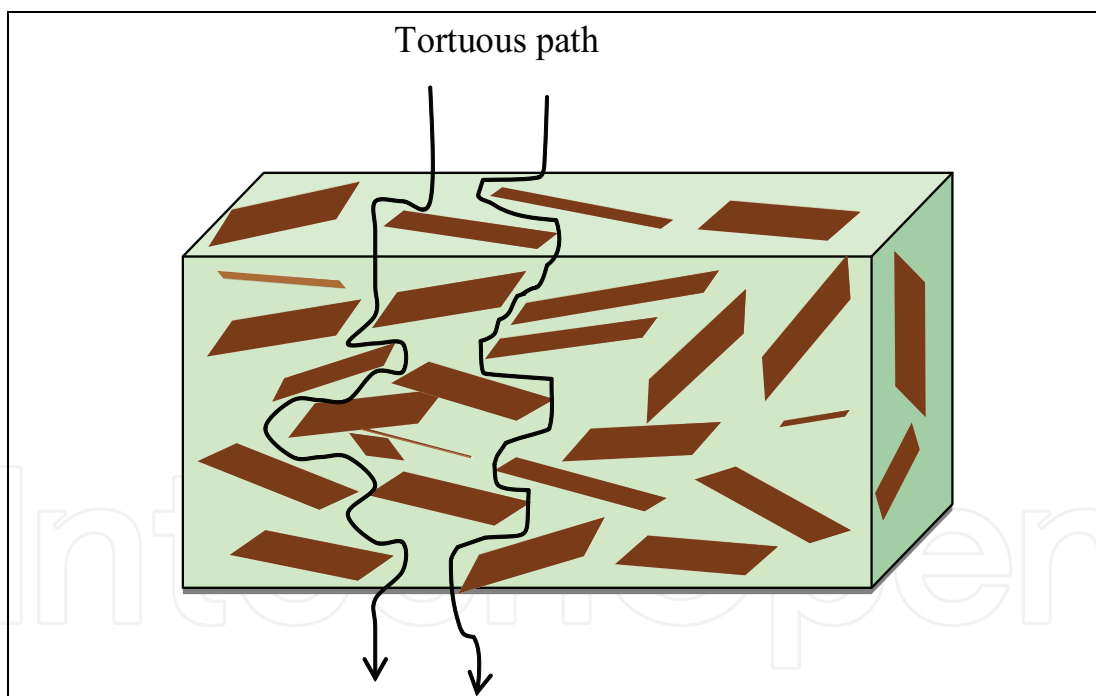


Fig. 9. Scheme of the mechanism of barrier improvement by the addition of clay platelets.

8.5 Anticorrosive properties

Polymers are widely used as anticorrosive coatings on metals to prevent the corrosion. Primarily polymeric coatings act as physical barrier against the diffusion of aggressive species to the metal surface. However most polymer coatings show some degree of permeations especially in long time period of contact with aggressive species. Various techniques have been applied to improve the barrier effect of polymeric coatings. One of the

effective methods is based on the preparation of polymer based composite or nanocomposite coatings by the addition of proper fillers to the polymer coating matrix. It has been shown that the addition of platelet fillers like as 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 figure 9.

The nanocomposite of various polymeric materials such as polystyrene, poly (styrene-co-acrylonitrile), polyaniline, polypyrrole, polysulfone, polyacrylates, polyimide and epoxy with unmodified and organically modified clays have been investigated as anticorrosive coatings on metals (Yeh et al., 2008; Olad & Rashidzadeh, 2008). According to our results obtained by electrochemical tafel slope analysis, the corrosion current of iron samples coated by the 100 μm thickness of polyaniline/MMT coating is more lower than that of samples coated by pure polyaniline coating with the same thickness in various corrosive environments (Olad & Rashidzadeh, 2008).

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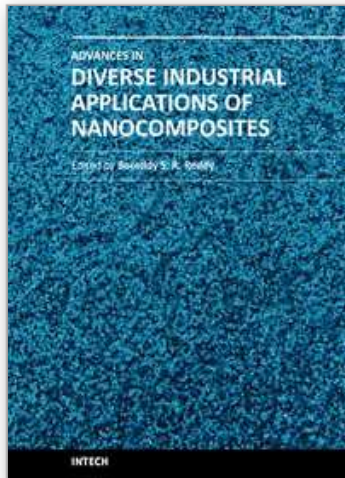
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Nanocomposites are attractive to researchers both from practical and theoretical point of view because of combination of special properties. Many efforts have been made in the last two decades using novel nanotechnology and nanoscience knowledge in order to get nanomaterials with determined functionality. This book focuses on polymer nanocomposites and their possible divergent applications. There has been enormous interest in the commercialization of nanocomposites for a variety of applications, and a number of these applications can already be found in industry. This book comprehensively deals with the divergent applications of nanocomposites comprising of 22 chapters.

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