Characteristic Properties of Nanoclays and Characterization of Nanoparticulates and Nanocomposites

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Abstract Clays have been one of the more important industrial minerals; and with the recent advent of nanotechnology, they have found multifarious applications and in each application, nanoclays help to improve the quality of product, economize on the cost and saves environment. The chapter describes key characteristics of nanoclays and their classification on the basis of the arrangement of "sheets" in their basic structural unit "layer". Major groups include kaolin–serpentine, pyrophyllite-talc, smectite, vermiculite, mica and Chlorite. The structural, morphological and physicochemical properties of halloystite and montmorillonite nanoclays, representative of the 1:1 and 2:1 layer groups, respectively, are discussed as well. After briefly introducing the surface modification of clay minerals by modifying or functionalizing their surfaces and their incorporation into polymer matrices to develop polymer/clay nanocomposites, techniques that are being employed to characterize these nanoclays, in general, and the sample preparation for these techniques, in particular, are also reviewed in this chapter.

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1   Nanoclays

Nanoclays are ubiquitous nanofiller and belong to a wider group of clay minerals. They are not new to humankind and ceramists have been using them in the development of clay products since prehistoric times. For instance, several clay products had been prepared using Kaolin, with the traditional name China clay, and its use is dated to the 3rd century BC in China. Even though the structure of nanoclays and their nature is being explored for decades and are being used since antiquity, their exact definition is an ongoing subject of debate (Fernandes et al. 2014; Uddin 2008). Clay minerals are hydrous silicates and may simply be described as fine-grained particles with sheet like structure stacked over one another. Owing to this geometry, they are commonly known as phyllosilicates, sheet-structured silicates. Phyllosilicates are mainly composed of fine grained aluminosilicates and are formed as a result of chemical weathering of silicate minerals at the surface of the earth (Majeed et al. 2013; Zhang et al. 2010). Nanoclays are commonly dominated by phyllosilicates and may be separated from the clay fraction or the bulk clay material by different approaches. Methods used for extracting and processing of nanoclays include energetic stirring followed by centrifugation and freeze-drying; centrifugation and cross-flow filtration; and ultracentrifugation (Floody et al. 2009).

Clay minerals are the basic constituents of clay raw materials and platy structure is the dominant morphology. Depending on the clay type, the individual layers could be composed of two, three or four sheets of either $[SiO_4]^{4-}$ tetrahedra or $[AlO_3(OH)_3]^6$ octahedra. The aluminosilicate layers organize themselves over one another like pages of a book, with a regular van der Waals gap between them, called an 'interlayer'. Interlayer possess net negative charge which is due to the ionic substitutions in the sheets of clay minerals. The layer charge is neutralized by cations which occupy the inter-lamellar. These inter-lamellae cations can be easily replaced by other cations or molecules as per required surface chemistry and hence called exchangeable cations. Na^+, K^+, Mg^{2+}, and Ca^{2+}, are among common exchangeable cations present in the interlayer which are exchanged with other required cations. In general practice, to evaluate a material performance and its classification, chemical behavior is paid more importance. On the contrary to this general practice, the physical characteristics of clays are more important in defining various clay groups. Therefore, the clay minerals are broadly classified on the basis of the number and arrangement of sheets in a clay layer. Depending on the number and the way that the tetrahedral and octahedral sheets are packed into layers, the clay minerals can be classified into three classes, i.e., two-sheet layer, three-sheet layer and four-sheet layer (Lee and Tiwari 2012).

Nanoclays are easily available, environment friendly, low cost chemical substances and a large volume of literature has accumulated on various perspectives of

nanoclays' research over the past few decades. Major research domains include (i) synthesis and characterization; (ii) surface properties and stability; (iii) fabrication of nanoclay-filled nanocomposites; and (iv) the use of nanoclays as precursors for the development of novel materials. Nanoclays have found applications in many fields, including medicine (Ambre et al. 2010; Suresh et al. 2010), pharmacy (Carretero and Pozo 2009, 2010), cosmetics (Carretero and Pozo 2010; Patel et al. 2006), catalysis (Garrido-Ramírez et al. 2010; Nagendrappa 2011), food packaging (Azeredo 2009; Majeed et al. 2013) and textile industry (Floody et al. 2009; Shahidi and Ghoranneviss 2014). In addition to these mentioned application, nanoclays are also helpful in environmental protection and remediation. Their potential as adsorbents for volatile organic compounds, and organic/inorganic contaminants in waste water is well documented (Lee and Tiwari 2012; Ouellet-Plamondon et al. 2012; Yuan and Wu 2007). This multifariousness in applications can be attributed to (1) the amazing amenability of nanoclays for change/modification, and (2) the dispersion/delamination of clay layers into individual lamellae. Amenability of nanoclays for modification lies in the fact that inter-lamellae cations can be replaced by desirable cations or other molecules. Simple procedures are required to modify the surface chemistry of nanoclays. This surface modification provides tremendous scope for altering the properties of clays like their polarity, surface area, interlayer spacing, acidity, and pore size and many others that govern their performance in different applications. Nanoclays' tendency to delaminate into individual nanosheets that results in high aspect ratio is their other exploited characteristic behind diverse applications.

1.1 Structural and Physical Properties of Nanoclays

Nanoclays are fine-grained crystalline materials. A layer is the basic structural unit of nanoclays and these layers are prone to arrange themselves over one another like pages of a book. Individual layers are composed of the tetrahedral and/or octahedral sheets and this arrangement of sheets plays a vital role in defining and distinguishing these clay minerals. In tetrahedral sheet, the silicon-oxygen tetrahedra are linked to neighboring tetrahedra by sharing three corners while the fourth corner of each tetrahedron forms a part to adjacent octahedral sheet. The octahedral sheet is usually composed of aluminum or magnesium in six-fold coordination with oxygen from the tetrahedral sheet and with hydroxyl. The sheets form a layer, and several layers may be joined in a clay crystallite. Vander Waals force, electrostatic force, or hydrogen bonding between the layers are the main drivers to clutch these layers with one another and form stacks of parallel lamellae. This stacking results in regular Van der Waal gaps between the adjacent layers. These spaces between the layers are called interlayer or gallery and can be accessed by water, organic cations or polar organic liquids. This intercalation weakens the forces clutching these layers with one another and causes the lattice to expand. The clay minerals' ability to accept changes in surface chemistry and delaminate into individual lamellae are

their pertinent characteristics that have been widely exploited in the development of novel composites.

The tetrahedral and octahedral sheets are building blocks for clay layers and these building blocks are capable of being assembled in a variety of arrangements. Thus the classification of nanoclay structure can be related to the arrangement of these building blocks; and the Table 1 presents grouping of clay minerals on the basis of their sheet arrangement. Clay minerals would have one tetrahedral and one octahedral sheet; one octahedral sheet merged between the two tetrahedral sheets; and one octahedral sheet adjacent to one octahedral sheet merged between the two tetrahedral sheets per layer arrangements and are denoted as 1:1, 2:1 and 2:1:1 sheet arrangement. Examples of 1:1 sheet arrangement include kaolinite, halloysite and serpentine. The 2:1 phyllosilicates are comparatively larger group including Vermiculite, Pyrophyllite, mica etc. as sub groups. Among various expanding and non-expanding 2:1 phyllosilicate groups, smectites, strongly expanding 2:1 phyllosilicates also belong to this layer structure. The term smectite is used to represent a family of expansible 2:1 phyllosilicate silicate minerals having a general formula (Ca, Na, H) (Al, Mg, Fe, Zn)$_2$(Si Al)$_4$O$_{10}$(-OH)$_2$-xH$_2$O, where x represents varying level of water attached to the mineral. Many well known natural and synthetic nanoclays viz. saponite, hectorite, montmorillonite, fluorohactite, and laponite belong to smectite family (Floody et al. 2009; Lee and Tiwari 2012; Majeed et al. 2013; Uddin 2008; D. Zhang et al. 2010). It is worth noting that despite sheet arrangement similarity of the member clays of a particular clay group, the lateral dimensions of all the members are different. In addition, the layer dimensions vary not only for each member clay, but also for the same clay from different origins. Depending upon the number of factors, including source of clay, method of preparation and particulate clay, the thickness of each layer is about 1 nm with lateral dimensions ranging from 300 Å to several microns (Lee and Tiwari 2012; Pavlidou and Papaspyrides 2008).

1.1.1 Halloysite

Halloysites are types of naturally occurring multiwalled aluminosilicates with 1:1 sheet arrangement. The halloysite layer structure is composed of octahedrally coordinated Al^{3+} and tetrahedrally coordinated Si^{4+} in a 1:1 arrangement with water molecules between the layers. A schematic diagram of crystalline structure of halloysite is shown in Fig. 1.

Halloysites were firstly discovered by Berthier as a clay mineral of the kaolin group in 1826, and were named "halloysite" after Omalius d'Halloy who analyzed the mineral first time. These nanoclays are found worldwide and their deposits have been reported in countries such as Australia, China, Belgium, Brazil, France, Spain, New Zealand, Mexico, America and others (Du et al. 2010; Liu et al. 2014; Yuan et al. 2015). Halloysites' aluminosilicate sheets are rolled into tubes and nanosized tubular halloysite, also called halloysite nanotube (HNT) is morphologically similar to multiwalled carbon nanotubes. Even though platy and spheroidal morphologies

Table 1 Classification of clay minerals and their major groups (Floody et al. 2009; Lee and Tiwari 2012; Majeed et al. 2013; Uddin 2008; Zhang et al. 2010)

Layer type	Tetrahedral-octahedral sheet arrangement	Interlayer material	Group	Species	Layer charge per formula unit
1:1	T: O	None or H_2O only	Kaolin–serpentine	Lizardite, berthierine, amesite, cronstedtite, nepouite, kellyite, fraipontite, brindleyite, Kaolinite, dickite, nacrite, halloysite, Odinite	<0.01
2:1	T:O:T	None	Pyrophyllite-Talc	Talc, willemseite, kerolite, pimelite, pyrophyllite, ferripyrophyllite	0
		Hydrated exchangeable cations	Smectite	Saponite, hetorite, sauconite, stevensite, swinefordite, montmorillonite, beidellite, nontronite, volkonskoite	0.2–0.6
		Hydrated exchangeable cations	Vermiculite	Vermiculite	0.6–0.9
		Non-hydrated monovalent cations	True (flexible) mica	Biotite, phlogopite, lepidolite, Muscovite, illite, glauconite, celadonite, paragonite, etc.	0.6–1.0
		Non-hydrated divalent cations	Brittle mica	Clintonite, kinoshitalite, bityite, anandite, Margarite	1.8–2.0
2:1:1	(T:O:T):O	Variable	Chlorite	Amesite, chamosite, cookeite, nimite etc.	Variable

T = tetrahedral, O = octahedral

Fig. 1 Chemical structure of halloysite (Yah et al. 2012)
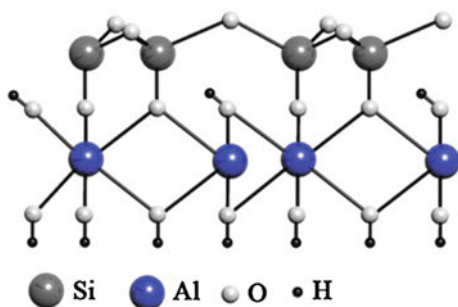
have also been reported in literature, the tubular structure is the dominant morphology of HNTs in nature and has attracted researchers from different scientific fields. HNTs are being used for long and the production of high-quality ceramics such as porcelain or crucible products have been among their traditional applications. However, with the recent advent of nanotechnology, these natural occurring materials with nano-scale lumens are being studied for a large range of new applications such as nano-containers for drug delivery, nano-templates for the fabrication of nanowires and nanoparticles, catalyst carriers, sorbents for contaminants and pollutants and nanofillers for polymers' reinforcement. Among these application of HNTs, their use as an encapsulation vessel for the storage and controlled release of active agents; and load bearing constituents in nanocomposites have been major focus of research in last two decades. In order to evaluate the potential of HNTs for these two aforementioned applications, the general requirements for each of these two potential applications and the halloysite attributes owing to whom it is considered as a potential material are summarized in Table 2.

The structural formula for HNTs is $Al_2(OH)_4Si_2O_5 \cdot nH_2O$ where n represents number of water molecules and could be 2 or 0. HNTs with 2 water molecules are named as hydrated or otherwise dehydrated. When halloysite is mined from

Table 2 Halloysite attributes for its application as encapsulation vessel ad load bearing constituent (Pasbakhsh et al. 2013)

Use:	As additive to polymers	As carriers and templates
Desirable properties:	Tubular	Tubular
	Good dispersion in polymers	Chemical inertness/biocompatibility
	Strong binding with polymers	Easy availability of OH groups
	High aspect ratio	Easy availability of OH groups
		Negatively charged at appropriate pH (or) one positively charged surface
		Large volume in lumen

deposits, there is a layer of water molecules present between the halloystite multilayers (n = 2) and is called HNTs-10 Å (the "10 Å" designation indicates the d_{001}-value of the layers). Dehydrated halloysite (HNT-7 Å when n = 0) or just commercial halloysite may be obtained through the loss of the interlayer water molecules under mild heating and/or a vacuum environment. It is worth noting that the dehydration of HNTs does not affect its morphology, however the removal of inter-layer water results in changes in lattice parameters. Chemical composition of HNTs is same as platy clay kaolinite with water molecules and the unit layers in halloysites are separated by a monolayer of water molecules. Thus the interlayer water in HNTs is one of the main differences distinguishing halloysites from kaolinite. This interlayer water reduces the magnitude of electrostatic forces between adjacent layers of HNTs at the time of formation. Also, there differences in lattice parameters of alumina and silica in both a and b directions (for silica a = 5.02 Å, b = 9.16 Å, and for alumina a = 5.07 Å, b = 8.66 Å). These differences lead to dimensional mismatch of the sheets. In addition to lessen the electrostatic force between the adjacent layers, the presence of inter-layer water facilitates curvature of the layers to accommodate the dimensional mismatch of the octahedral and tetrahedral sheets. Consequently, halloysite crystallizes with the Al–OH sheet forming the inside and the Si–O sheet forming the outside of a unit layer. (Lvov and Abdullayev 2013; Pasbakhsh et al. 2013).

In dehydrated halloysite structure, 15–20 aluminosilicate sheets are rolled over and over; and the structure resembles multi-walled carbon nanotubes. Geometric dimensions of the HNTs are source dependent and ranges from 0.2 to 2 µm in length, 40–100 nm in outer diameter and 10–40 nm in lumen diameter. Typical properties of halloystite nanotubes are compiled in Table 3. In addition to differences in wall-length of HNTs, tubular HNTs with different wall thickness and different spiral structures (power spiral, logarithmic spiral) have also been reported.

Table 3 Typical properties of halloystite nanotubes (Liu et al. 2014)

Property	Value
Length	0.2–2 µm
Outer diameter	40–100 nm
Inner diameter	10–40 nm
Aspect ratio (L/D)	10–50
Elastic modulus (theoretical value)	140 GPa (230–340 GPa)
Mean particle size in aqueous solution	143 nm
Particle size range in aqueous solution	50–400 nm
BET surface area	22.1–81.6 m^2/g
Pore space	14–46.8 %
Lumen space	11–39 %
Density	2.14–2.59 g/cm^3
Average pore size	79.7–100.2 Å
Structural water release temperature	400–600 ˚C

These morphological differences can be due to the formation of HNTs under various crystallization conditions and geological occurrences (Du et al. 2010; Liu et al. 2014; Lvov and Abdullayev 2013; Mitra 2013; Pasbakhsh et al. 2013; Yuan et al. 2008; Yuan et al. 2015).

1.1.2 Montmorillonite

Smectite nanoclays are among heavily researched nanofillers in the field of nanocomposites. Among these smectite nanoclays, montmorillonite (MMT) has got prominence over other member nanoclays owing to its abundance, environmentally friendliness and well-studied chemistry. MMT is a dioctahedral nanoclay with the 2:1 layer linkage. They are the most efficient reinforcement fillers and their reinforcing potential is well documented in literature. The studies revealed that larger surface area and large aspect ratio are the salient attributes responsible for the reinforcement (Arora and Padua 2010; Azeredo 2009). Besides reinforcing effect of MMT, it is also viewed as rigid, impermeable filler. It creates a maze structure when dispersed in polymers, forces the moving gases/vapors to follow a tortuous path, and finally lowers their permeation rate.

Each individual MMT layer having lateral dimensions of 200–600 nm and thickness of a few nanometers is composed of two tetrahedral sheets and an octahedral sheet. The sheets are linked to each other in such a way that the silicon oxide tetrahedron (SiO_4) shares its 3 out of 4 oxygen atoms with the central octahedral sheets as shown in Fig. 2. MMT layers in its pristine from organize themselves over one another where the layered platelets are stacked with different levels of stacking within the clay mineral. Depending upon the stacking level, they could be primary particles or layered aggregates (micro-aggregates and aggregates). During the isomorphic substitution of Al^{+3} by Fe^{+2} or Mg^{+2}; and Mg^{+2} by Li^{+1} in the layer structure, the difference in the valences induces an overall negative charge on each three sheets layer. Different metal cations (Na^{+1}, Ca^{+2}) present between three sheets layers/in the galleries accommodate charge imbalance, thus increasing
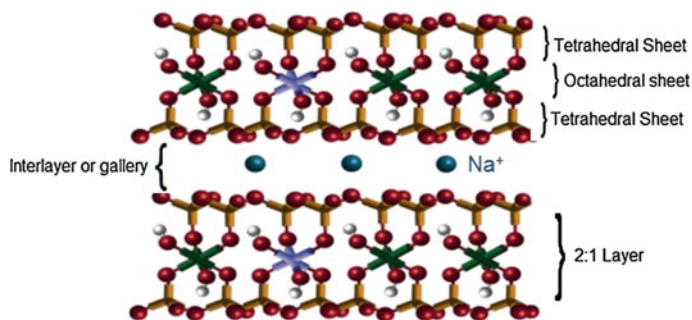

Fig. 2 Structure of Na-MMT (Paul and Robeson 2008)

Table 4 Chemical formula, cation exchange capacity and particle length of commonly used smectites (Ray and Okamoto 2003)

Smectite	Chemical formula	CEC (mequiv/100 g)	Particle length (nm)
Montmorillonite	$M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$	110	100–150
Hectorite	$M_x(Mg_{6-x}Li_x)Si_8O_{20}(OH)_4$	120	200–300
Saponite	$M_xMg_6(Si_{8-x}Al_x)Si_8O_{20}(OH)_4$	86.6	50–60

M: monovalent cation; x: degree of isomorphous substitution (between 0.5 and 1.3); CEC = Cation exchange capacity

the hydrophilic behavior (Bordes et al. 2009; Paul and Robeson 2008; Pavlidou and Papaspyrides 2008). Owing to this hydrophilic behavior, the hydration of MMT causes the galleries to expand and the clay to swell. In addition, the pristine clays are readily dispersed only in hydrophilic polymers (vinyl alcohol, ethylene oxide). To beaten this hydrophilic behavior and to make the clay compatible with hydrophobic polymers, the Na^{+1} present in the clay galleries can also be exchanged with organic cations, such as alkylammonuim or alkyphosphonium/onium ions. Murray (2000) reported that the charge imbalance called as cation exchange capacity (CEC) in smectite is about 0.66 per unit cell due to the isomorphic substitution. The CEC depends on the nature of isomorphic substitutions and varies from layer to layer, hence an average value on the complete crystal is considered (Alexandre and Dubois 2000). It is expressed as mequiv/100 g (meq/100 g) and is reported to range from 80 to 150 mequiv/100 g for smectites (Pavlidou and Papaspyrides 2008). The chemical formula, cation exchange capacity and particle length of commonly used smectites are listed in Table 4.

1.2 Organophilization of Nanoclays

Clay minerals reinforced polymer nanocomposites (CPNs) have received substantial recognition in the field of composites owing to their potential to exhibit remarkable improvements in the mechanical, thermal and barrier properties even at small loadings when compared with their micro-scale counterparts. However, the enhanced performance properties could only be recognized at nanoscale dispersion. To achieve nanoscale dispersion, delamination and, thereby exfoliation of these nanofiller platelets is prerequisite. As discussed in previous section, the clay minerals have strong tendency to form stacks owing to wander walls' forces. Delamination is achieved when there is affinity between the filler and polymer matrix, polymer chains intercalate to clay galleries and delaminate them. However, most of the petroleum based polymers are not compatible with clay minerals owing to the differences in their surface energies; and the exfoliation of clay platelets is one of the main problems encountered while preparing nanocomposites (Kádár et al. 2006). To solve this

problem, the surface energy of clay layers is lowered by their surface modification. In surface modification, surfactants having compatibility with the organic polymers are exchanged with exchangeable cations present in the clay, thereby expanding clay galleries and increasing spacing between the layers (d-spacing). The cations present in MMT galleries are usually exchanged with as alkylammonuim or alkyphosphonium/onium ions (Dadbin et al. 2008; Pavlidou and Papaspyrides 2008; Yoon et al. 2007). The surfactants might also have long hydrocarbon tails. The surface modification is usually accomplished through replacing the alkali cations present in the interlayer (gallery), called exchangeable cations with onium ions connected to hydrocarbon chains (non-polar tail) as shown in Fig. 3 (Majeed et al. 2013). Primary, secondary, tertiary and quaternary alkyl ammonium cations or phosphonium cations having various substituents can be employed as surfactants. The chemical structures of different surfactants that are being commonly used to modify MMT are presented in Fig. 4 (Bhattacharya and Aadhar 2014; Majeed et al. 2013).

Many intact and modified types of clays are commercially provided by a lot of suppliers. A list of commercially available nano clays along with their organo modifier and other characteristics are provided in Table 5 (Bordes et al. 2009; Cui and Paul 2011; Hemati and Garmabi 2011; Morawiec et al. 2005; Su et al. 2011; Tjong 2006). Structure of organo-modifier plays a vital role in delaminating and dispersing a nanoclay in a particular matrix. Thus, the selection criterion of organoclay depends majorly on the type of polymer matrix used. The effect of structure of organomodifier on the dispersion of MMT in a series of EVA based copolymers have been considered by the researchers. Cui and Paul (2011) studied the effect of modifier structure in dispersing MMT in EVA matrix and reported that the clay modified with surfactants having two alkyl tails was more dispersed than that having one alkyl tail. The researchers also observed that there should be a long chain carbon of 12 or more atoms to organophilize the natural clay mineral for exfoliation. Exfoliation of the clay in polyolefin is upgraded by increase in the number of long alkyl chains on the surfactant. On the other side, the nanocomposites formed by polyamides show an opposite trend. As for the polyamides, the surfactants having a single long alkyl tail gives the excellent exfoliation, and increase in alkyls gives undesirable polyamide alkyl interaction, as a result of which
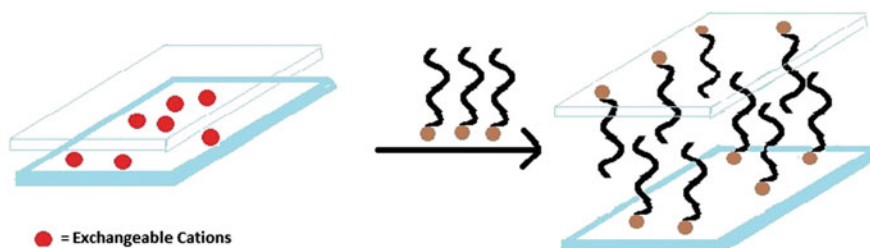

= Exchangeable Cations

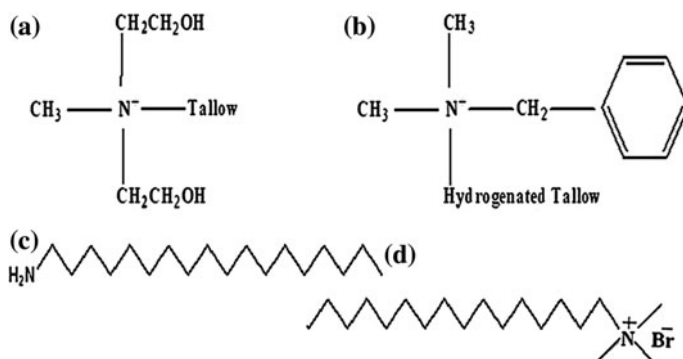**Fig. 3** Organophilization of montmorillonite (Majeed et al. 2013)

Fig. 4 Chemical structure of commonly used organomodifiers: **a** methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium, **b** dimethyl, benzyl, hydrogenatedtallow, quaternary ammonium, **c** octadecylamine, and **d** Cetyl trimethyl ammonium bromide (Bhattacharya and Aadhar 2014; Majeed et al. 2013)

exfoliation decreases (Hotta and Paul 2004). In short, increment in d-spacing depends on the cation exchange capacity of layers, content and structure of surfactant and on the way the surfactants arrange themselves in the clay.

1.3 Nanoclays as Nano Fillers for Polymer-Clay Nanocomposites

Nanocomposites are a fairly new class of composite materials where a filler having at least one dimension in the nanometer (10^{-9} m) range is dispersed in a continuous matrix. They got recognition after the first successful development of Nylon nanocomposites having enhanced mechanical properties by the Toyota researchers. Since then, nanocomposites have been major area of research. The nanocomposites have shown improved mechanical and thermal properties; decreased flammability and barrier properties than both micro and macro composite materials. The filler loading; their shape, aspect ratio and their affinity towards matrix material are among distinctive parameters that play a vital role in modifying the properties (Goettler et al. 2007). The nanocomposites could be prepared by different methods including in situ polymerization, melt intercalation and direct mixing. The dispersed filler can be of the shape of sphere, tube, fiber or lamellae. The correlation of properties of materials with filler size has gained a great deal of importance with the recent advancement in the field of nanotechnology. Owing to their exceptional potential to exhibit peculiar characteristics that could not have been achieved with their traditional micro-scale counter parts, they have attracted a great deal of interest to exhibit enhanced and novel properties. There have been studies on the incorporation of nanoparticles having differences in shape, size, aspect ratio, structure

Table 5 Commercially available clay minerals along with surface modifiers (Bordes et al. 2009; Cui and Paul 2011; Hemati and Garmabi 2011; Morawiec et al. 2005; Su et al. 2011; Tjong 2006)

Supplier/ commercial designation	Clay	Surface-modifier	Modifier concentration (meq/100 g clay)	d_{001} (Å)
Southern clay products (USA)				
Cloisite®Na+	MMT	–	–	11.7
Cloisite®10A	MMT	dimethyl, benzyl, hydrogenatedtallow, quaternary ammonium	125	19.2
Cloisite®15A	MMT	dimethyl, dihydrogenatedtallow, quaternary ammonium	125	31.5
Cloisite®20A	MMT	dimethyl, dihydrogenatedtallow, quaternary ammonium	95	24.2
Cloisite®25A	MMT	dimethyl, dehydrogenated tallow, 2-ethylhexyl quaternary ammonium	95	18.6
Cloisite®93A	MMT	methyl, dihydrogenatedtallow ammonium	95	23.6
Cloisite®30B	MMT	methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium	90	18.5
Nanofil®15	MMT	dimethyl, dihydrogenated tallow alkyl quaternary ammonium	93	28
Nanofil®SE3000	Bentonite	dimethyl, dihydrogenated tallow alkyl quaternary ammonium	–	–
NanocorInc. (USA)				
Nanomer®1.30P	MMT	Octadecylamine (ODA)	120	22
Nanomer®1.44P	MMT	dimethyl dialkyl ammonium halide	–	–
Laviosa Chimica Mineraria (Italy)				
Dellite®43B	MMT	dimethyl benzylhydrogenated tallow ammonium	32−35	18.6
Dellite®72T	MMT	dimethyl dihydrogenated tallow ammonium	–	–

and geometry; and several nanoparticles have been recognized as possible additives to enhance performance properties (Arora and Padua 2010). Nanoclays are rigid fillers and improvement in the moduli of matrix material with the incorporation of these nanoclays is generally attributed to their high stiffness. Polymeric matrices are soft materials and their reinforcement with rigid nanoclays impede the free movement of polymer chains neighboring to the filler and if the interfacial adhesion

between the filler and the chains is satisfactory, the filler behaves as load bearing constituent. Improvement in the mechanical properties of polymer matrices with the addition of nanoclays have been published in many reviews (Patel et al. 2006; Paul and Robeson 2008; Pavlidou and Papaspyrides 2008). Beside improvement in the mechanical properties of polymers, nanoclays also have potential to reduce the permeability of gases, like oxygen and carbon dioxide; organic vapors and moisture through the nanocomposite films (Duncan 2011; Silvestre et al. 2011). Uniform dispersion of rigid impermeable nanoclays impede the diffusion of permeating molecules by forcing them to follow a tortuous path (Grunlan et al. 2004; Khaliq Majeed et al. 2015; Majeed et al. 2014; Nazarenko et al. 2007; Sanchez-Garcia et al. 2007). Increased flammability resistance (Tabuani et al. 2011; Zanetti and Costa 2004; J. Zhang et al. 2009) and enhanced thermal stability (Bertini et al. 2006; Durmuş et al. 2007; Giannakas et al. 2008; Santos et al. 2009) of nanocomposites are among the various other benefits attributed to the nanoclays.

2 Characterization

The appropriate characterization of nanoparticles exhibit a wide range of challenges and the selection of suitable technique is considerably substantial. Nanoparticles characterization is carried out to determine the surface area, porosity, solubility, particle size distribution, aggregation, hydrated surface analysis, zeta potential, wettability, adsorption potential, shape, size of the interactive surface, crystallinity, fractal dimensions, orientation, intercalation and dispersion of nanoparticles and nanotubes in nanocomposite materials. Some of the significant characterization techniques carried out for functional group identification (FT-IR); and the morphology and particle size determination (SEM & TEM) are discussed in the subsequent sections.

2.1 *Fourier Transfer Infrared Spectroscopy (FTIR)*

FTIR analysis of a chemical substance shows marked selective absorption in the infrared (IR) region. After absorption of IR radiation, the molecules of a chemical substance vibrates giving rise to close packed absorption bands called IR absorption spectrum which will correspond to the characteristic functional group and bands present in a chemical substance. Thus an IR spectrum of a chemical substance is a finger print for its identification. FTIR technique used to identify the different silicon bonds in clay structure. Specific bond produces characteristics vibrational peaks. Sample is prepared by adding 1–2 mg clay in equal amount of KBr and ground to fine powder. This mixture is placed in 13 mm casting dye and pressed about 9000 kg to make the fine shape of pellet. Solid casted pellet is placed in the path of light source at wave number ranges from 400 to 4000 cm^{-1} with scan rate of 40

Table 6 Characteristics peaks of the clays (Abdullah et al. 2015; Muthu et al. 2016)

Clay	Characteristics peak (cm^{-1})
Bentonite	3415 -OH Peaks, 471 Si-O-Al and 523 Si-O-Mg
Halloysite	1033 Si-O-Si, 3695 Al-OH
Montnorillonite	3422 (Water), 3624 (Al-OH)
Kaolinite	3696, 3671, 3650
Illite	3600
Smectite	3622
Saponite	3740 (Si-OH), 3670 (Mg(OH)$_2$)
Sepiolite	3719 (Si-OH) 3689 (Mg$_3$OH)
Nacrite	3701 and 3647 (out-of-plane), 3647 (in-plane)
Dickite	3708, 3654, 36228 (inner surface OH)
Lizardite	3686 (Mg-OH)

depending upon the desired resolution. As KBr and clay both are hygroscopic material, it may swell after absorbing moisture from air. To minimize the moisture effect samples are placed in oven at 130 °C overnight. Then samples are placed in the desiccator for further analysis. As the moisture is there, it may cause to change the chemical nature of clay by shifting K$^+$ ions from KBr to clay [15] and affect the clay spectra. It has been reported that peak intensity at 3415 and 1638 cm^{-1} may be due to presence of water molecules from moisture. Si-O-Si bond is confirmed from 1053 cm^{-1} (Abdullah et al. 2015). The peaks at 471 and 523 cm^{-1} ascribe the presence of bonds such as Si-O-Al and Si-O-Mg. The limitation of photo-acoustic mode for clay characterizations is overcome by using attenuated total reflection (ATR) mode. In ATR-FTIR analysis clay is spread completely over the diamond crystal for functional group investigation. Strong absorbance of moisture from the sample could be resolved by heating sample at 80°C and covered the sample with parafilm (Echegoyen et al. 2016). Clays and its characteristics peaks are presented in Table 6.

2.2 Scanning Electron Microscopy (SEM)

SEM technique does not affect the chemical nature of clay samples. It is very informative technique to identify the structure and chemical composition of any material including raw clay, pure clay materials and its derivatives.

Sample preparation is most important step to observe the morphology and to explore the relative composition of metals present in the sample. Solid sample is placed onto the carbon tap which is fixed at copper grid. Air is puffed on the surface of sample for uniform distributions. Clay material is non-conductor which is made conductor after platinum (Pt) coating for ten min in sputter coater. Coating may reduce the charging of sample. In solution migration technique the clay suspension

is prepared and a drop is spread onto the silicon chip where it is allowed to dry in air. Usually 5 kV accelerating potential is used to study the morphology and elemental composition of clay sample. Relative chemical composition of clay could be obtained by using energy dispersive X-ray (EDX) analysis. Nanoclay shows diversity of size and diameter of the particles. It has been reported that diameter may sometimes below or at 1–10 µm or even higher. Defining criteria for nanoparticle has been set by European Commission on October 2011; nanomaterial must have at least one dimension in range of 1–100 nm (Echegoyen et al. 2016).

SEM technique helps to explore the clay/PP nanocomposite structure. These samples are molded using injection molding technique. Layer structure of the composite material could be identified as: upper layer, middle layer and inner most layer. Thickness of layer depends on cooling while mold filling. Layer structure has been reported in Fig. 5a–f (Yu et al. 2015). In multilayer composite structure, different components are appeared as parallel layers to the flow direction of injected material into the mold. A uniform thickness of layers is observed at 70–400 nm with a little deposition of nanoclay agglomerates.

For energy dispersive X-ray studies live image is selected using SEM software. The part of image is selected and focused; where one wants to know the relative chemical composition of the material. The relative abundance of elements is mapped and these elements are segregated on the basis of energy requirements for Kα emission. EXD profile is obtained by selecting energy requirement (in KeV) at x-axis and relative abundance on y-axis. Kα emission of element is the specific characteristic which corresponds to the absorption of energy as difference of

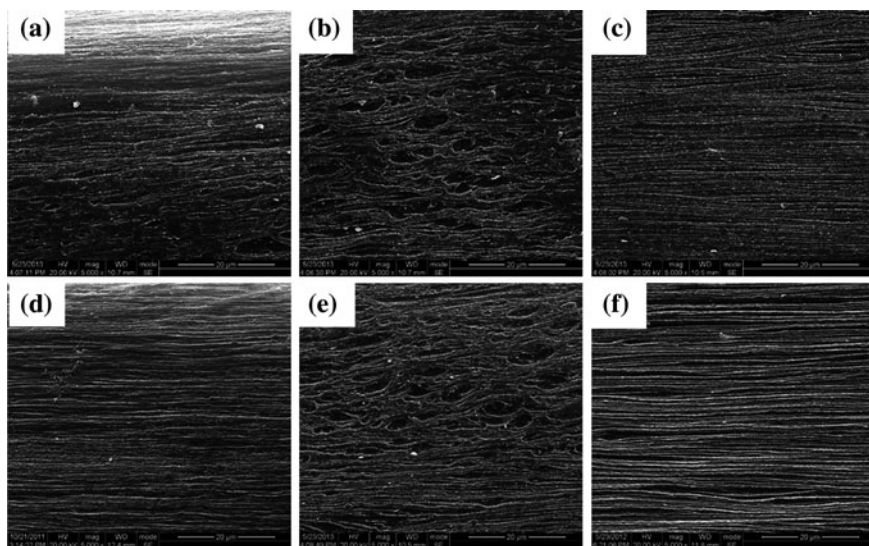**Fig. 5** Shows morphology of composite structure **a**, **d** outer layers, **b**, **e** middle layer, **c**, **f** inner layer (Yu et al. 2015)
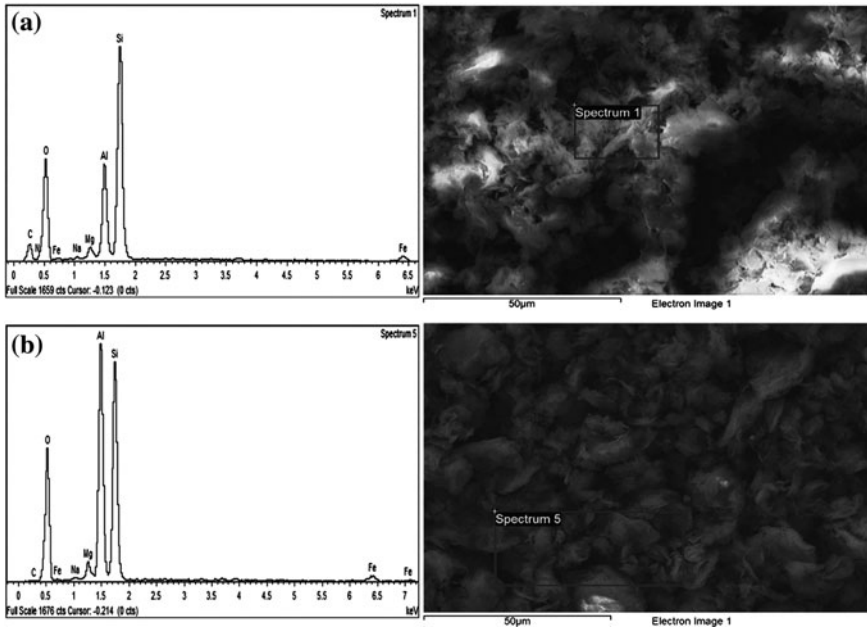
Fig. 6 **a** EDX spectra of nanoclay, **b** selected live image (Hakamy et al. 2015)

K-energy level is used to identify the element. While the peak height corresponds to the abundance of the element. Hakamy et al. (2015) studied EDX profile of nanoclays while characterizing nanoclays and calcined nanoclays/cement nanocomposites and the spectra is shown in Fig. 6. The figure attributes the selection of spot for analysis and furthermore image process is applied. EDX profile concludes that skeleton of nanoclay is composed of elements: first mostly of silicon, second most oxygen, third most aluminum and other includes are: carbon, magnesium, iron and sodium.

2.3 Transmission Electron Microscopy (TEM)

TEM is non-destructive technique used to study the morphology and diffraction pattern of nanoclay. TEM samples are prepared using solution dispersion and extrusion method. In solution dispersion method; nanoclay sample could be dispersed in ether, ethanol or isopropyl alcohol (IPA). Less than 2 mg of sample is suspended in 5–10 mL of dispersion medium which is placed in the beaker and allowed to sonicate for 15 to 30 min to ensure the complete dispersion of nanoclay. A drop of sample solution is placed onto the copper grid and allowed to dry in

vacuum oven to avoid any particulate contamination. After 24 h copper grid mounted with sample is placed on the sample holder and fixed with screw. Sample holder is carefully and gently placed in the TEM column and waited for pressure adjustment. This sample preparation method could be used for pure, raw and modified nanoclay. Extrusion and casting method is used for sample preparation of nanoclay composites. Furthermore this sample is cut into 130 nm slice using ultra-microtome and fixed on the holder. Morphology of samples is recorded using different magnification and potential where image gives the significant information.

Morphology of different clay materials has been reported by Jeong et al. and is shown in Fig. 7a–c (Jeong and Achterberg 2014). The figure shows the compact arrangement in clay layers of illite, chlorite, kaolinite etc. with deposition of different particle sizes. These particles are compactly and tightly packed in layers structure as suggested from TEM micrograph.

Transmission electron microscope at high resolution mode called HRTEM describes the diffraction pattern and layer orientation in structure. Different layers structure and deposition of different material could be distinguished apparently from micrograph. This approach has been reported in Fig. 8a–c (Jeong and Achterberg 2014), diffraction pattern shows the alignment of lattice fringes. Parallel lattice spacing suggested the presence of similar particle with regular geometrical orientation and darker spots may suggest the deposition of different particle in under layers of thin slice of clay particle.
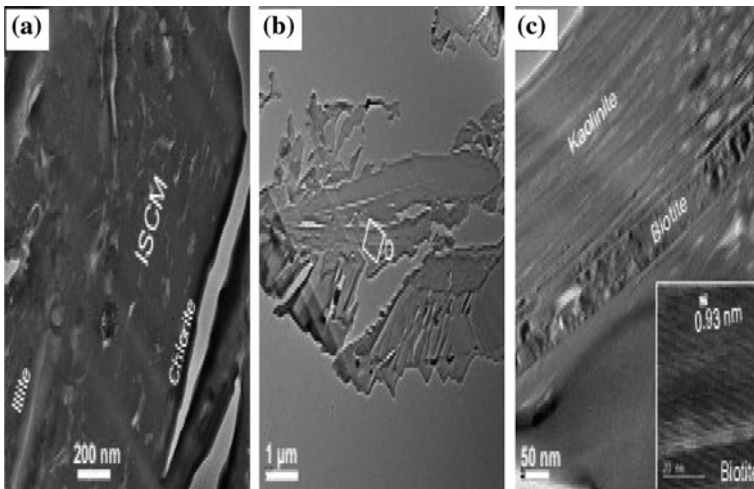

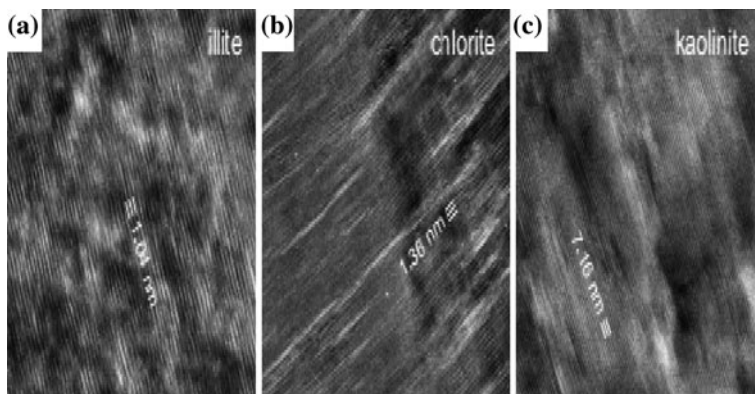**Fig. 7** Clay shows the deposition different particle sizes (Jeong and Achterberg 2014)

Fig. 8 HRTEM of clay particles which shows the lattice fringe (Jeong and Achterberg 2014)

3   Conclusion and Future Perspective

The study of nanoclays is a large field and shows an immense potential to be explored. Nanoclays have long been used in several applications and their uses are based on their structural and physical characteristics that are discussed in detail in this chapter. Introduction of nanoclays as fillers or additives in polymers for various desired effects has been of enormous interest for research and development studies. An interesting concern, along with the studies addressing how nanoclays change the behavior of polymeric materials, is to discover more about nanoclays. Various techniques that are used to characterize nanoclays are described in detail in this chapter and further studies could pay more attention to deep analysis with new advanced techniques. Despite clay minerals are ubiquitous in nature, several interesting nanoclays are not available in sufficient quantities therefore their synthesis will be a highlighted field of clay science and may lead to a breakthrough in the field of nanocomposites. Finding new applications of such synthetic clay minerals, including pillared clay minerals, porous clay hetero-structures, and nanocomposites, will be another promising work. Information on occupational exposure to nanoclays during extraction, development, and application is limited and is highly desirable. An additional demanding area is the potential of nanoparticles (from packaging material) to migrate to packaged food and their eventual toxicological effects, if any.

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