

Recent Advances in Nanoclay/Natural Fibers Hybrid Composites

N. Saba, M. Jawaid and M. Asim

Abstract The growing demand for continual improvement in the engineering applications of thermoplastic and thermoset polymer materials compared with metals in various applications led to the emergence of hybrid nanocomposites by the addition of different nano fillers, with advanced properties. Nano fillers such as carbon black, pyrogenic silica, nano oxides and metal particles are being used as additives in polymers from decades. However, the increasing stringent environmental legislation and consumer awareness highlights the importance of natural, low cost and abundant clay materials such as nanoclays. The hybridization of natural fiber with nanoclay is interestingly positive due to the tendency of nanoclay to upsurge both flexibility and rigidity of the natural fiber in one step. The most promising nanoclay involved in the modification of polymers and natural fibers reinforced polymer composite are montmorillonite, organoclay, saponite and halloysite nanotubes. Nanoclay/natural fibers hybrid nanocomposites have engrossed great attention since their discovery due to their wide variety of properties in food packaging, biomedical devices, automotive industries and other consumer applications with better thermal, physical, mechanical, optical and barrier properties. Present article designed to be a comprehensive source of recent literature and study on nanoclay fillers, its different classes, modification of polymers by nanoclay and their varied applications. This article also intended to covers the recent advances in natural fiber/nanoclay hybrid polymer nanocomposites research study, including their different commercial applications.

Keywords Natural fiber · Nano filler · Mineral clay · Nanoclay · Montmorillonite · Nanocomposite · Hybrid composites

N. Saba (✉) · M. Jawaid · M. Asim
Laboratory of Biocomposite Technology, Institute of Tropical Forestry
and Forest Products (INTROP), Universiti Putra Malaysia,
43400 Serdang, Selangor, Malaysia
e-mail: naheedchem@gmail.com

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1 Introduction

1.1 Hybrid Composites

The word “hybrid” is of Greek-Latin origin. Hybridization is a process of incorporating of two reinforcements (either synthetic fibers/nano fillers/natural/ or metallic fibers) in one polymeric matrix phase or the incorporation of single reinforcements in polymer blends in order to yield better properties such as (high mechanical strength, compressive strength, stiffness, thermal stability and lowered water absorption properties) which cannot be realized in conventional composite materials (Borba et al. 2014; Saba et al. 2014). Hybrid materials are very advanced composites materials consisting of two or more different constituents at the molecular or nanometer level. Properties of hybrid composites is a weighed sum of the individual components, thus it provide combination of properties such as tensile modulus, compressive strength and impact strength (Gururaja and Hari Rao 2012). Hybrid composite materials have extensive engineering application where strength to weight ratio, ease of fabrication and low cost are required. The hybrid composite properties with two different fibers are exclusively governed by the individual fibers length, fibers orientation and fibers content, extent of intermingling of fibers, fibers arrangement and fiber-matrix bonding.

Researchers concluded from their study that the addition of a very small amount of nanoparticle into a matrix can improve both thermal and mechanical properties significantly without compromising the weight or processability of the composite (Hossen et al. 2015). Until now many research works has been made on natural fiber hybrid nanocomposite materials by using nano particles such as nano tube, metal oxides, nanoclays, carbon nanofiber and other nano particles for varied advanced applications.

1.2 Natural Fibers

Currently researchers are concerning more towards the natural fibers as cost effective and light weight reinforced materials. A huge variety of different kinds of natural fibers including cellulosic, wool and animal fibers are abundantly available all around the world (Thakur et al. 2012, 2014). Natural fibers can be classified into different types depending upon their origin such as plant fibers and animal fibers (Eichhorn et al. 2010; Cherian et al. 2011). Natural fibers are of different types based on their source of origin from the plant such as leaf (PALF, sisal, banana etc.), bast (kenaf, jute, hemp etc.), fruit (OPEFB, coir) and seed (cotton, kapok). The mechanical properties of natural fibers (kenaf, jute) are found to be comparable with the commercial synthetic fibers, making the natural fibers highly preferable to synthetic fibers in automotive and other high end applications where weight and stiffness are of primary concerns (Saba et al. 2015b; Thakur et al. 2013). Natural



Fig. 1 Different types of natural fiber used as reinforcement

fibers exhibit a number of advantages in terms of lower densities, specific modulus, cost per weight, cost per unit length besides their renewable and biodegradable nature required for making composite and green composite with bio-resin (Dittenber and GangaRao 2012; Thakur and Thakur 2014). Some of the most common natural fiber that are used as reinforcement in polymer for fabricating hybrid polymer composite especially with nano sized fillers are displayed in Fig. 1.

1.3 Composites

Composite materials have been used by the people of earlier civilization since many centuries. One of finest example include the preparation of bricks for building construction using straw and mud (Akil et al. 2011; Eichhorn et al. 2010). Composite materials are the most adaptable engineering materials having the perfect combination of two different constituents, reinforcing natural/synthetic fibers and plastic polymeric matrix holding the perfect physical or chemical properties of each component (Yan et al. 2014). Moreover, both the constituent of composite

materials remain separate and distinct on a macroscopic level within the finished structure (Bajpai et al. 2012). The term “natural fiber reinforced composite” refers to natural fibers reinforced in some polymeric matrix (thermoplastic or thermoset; natural or synthetic). A number of different polymers are used as matrix materials for composite fabrication depending upon the type of applications (Teacă et al. 2013). The matrix hold and transfer the loads along the reinforced materials (organic to inorganic) in polymer composites (Singh et al. 2013; Saba et al. 2015a) and the reinforcing material (usually fibers) determines the overall properties (Valença et al. 2015). Natural fiber composites are cost effective, possess tool wearing rates, thermal stability, acoustic properties, better formability and confers health safety for manufacturer (Saba et al. 2015b; Batouli et al. 2014).

1.4 Nanoscience and Nanotechnology

Nanoscience is the study of phenomena and manipulation of materials at atomic, macromolecular and at molecular scales, where properties differ significantly from those at a larger scale (Saba et al. 2014). The term “nanotechnology” was invented by Taniguchi in 1974 and is defined as “the science of nano materials (1–100 nm)” and systems with structures and components displaying improved chemical, physical, thermal and biological properties”. Nanotechnology is the advanced technology that deals and describes the design, production, characterization, and application of nano based materials and systems. The field of nanoscience and nanotechnology has blossomed over the last 20 years (Galpaya 2012; Kuilla et al. 2010) and gaining significance in areas of biosensors, biomedical, nanomedicine, computing, aeronautics, polymer modification and many other applications owing to their high surface area with better tendency to amend materials properties. The current applications of nanotechnology in different industrial sectors are shown in Fig. 2.

1.5 Nanocomposites

The discovery of polymer nanocomposites by the Toyota research group has opened a new dimension in the field of materials science (Kuilla et al. 2010; Kojima et al. 2011; Ibeh and Bubacz 2008). A nanocomposite belong to the nanomaterials groups, where nanoparticles have been added to improve a particular property of the material (Saba et al. 2015a, b, c; Marquis et al. 2011). The nanocomposites material encompasses a large variety of systems and frequently regarded as amorphous multiphase solid material (such as the structure of the bone), made of distinctly different components at the nanometer scale having at least one or two or three of the

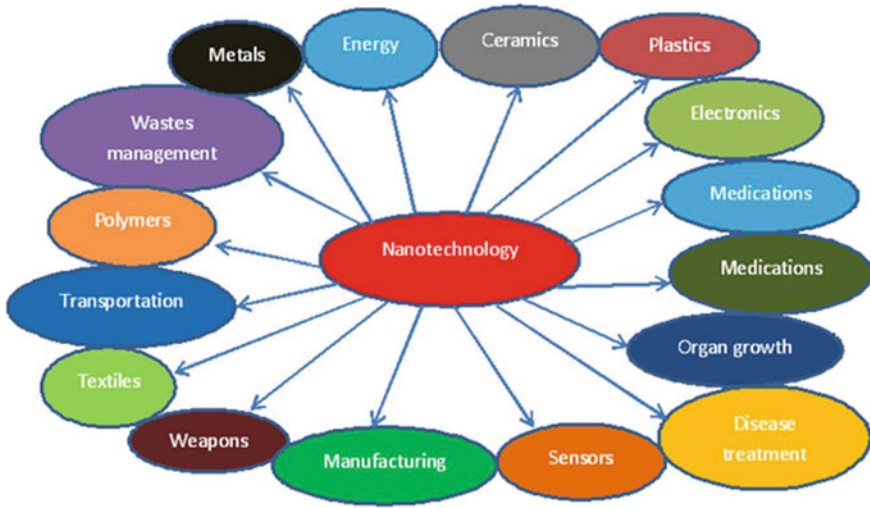


Fig. 2 Diverse applications of nanotechnology

phases dimensions in nano meter range (1–100 nm) (Saba et al. 2014). Moreover, according to the matrix materials, nanocomposites can be classified into three different categories (a) ceramic matrix nanocomposites (CMNC) such as SiO_2/Ni , $\text{Al}_2\text{O}_3/\text{TiO}_2$ (b) metal matrix nanocomposites (MMNC) such as $\text{Ni}/\text{Al}_2\text{O}_3$, Co/Cr and (c) polymer matrix nanocomposites (PMNC) such as thermoplastic/thermoset polymer/layered silicates (Raman et al. 2012). Nanocomposites emerged as appropriate substitutes to overwhelmed the limitations offered by monolithics and microcomposites, owing to the exceptionally high surface to volume ratio or high aspect ratio of the nano sized reinforcing phase (Boufi et al. 2014). Polymer nanocomposites often exhibit better chemical and physical properties dramatically different from the corresponding pure polymers. The polymer nanocomposites properties are governed by the incorporated nanoparticles shape, size, concentration and interactions with the polymer matrix (Karger-Kocsis et al. 2015; Armentano et al. 2010; Abdelrasoul et al. 2015). Nanocomposite however pretend some preparation challenges related with the dispersion and stoichiometry control in the nanocluster phase (Raman et al. 2012).

Currently, nanocomposites have attracted great interest, both in industry and in academia, due to their unique properties and multi-functionality that are well applicable in various fields (Saba et al. 2014) as compared with traditional composites (Babaei et al. 2014). Furthermore, despite of their nano dimensions, most of the processing techniques of nanocomposites remain almost the same as in microcomposites (Saba et al. 2015a, b, c). Several technique are been utilized to characterize or probe the structure and properties of polymer nanocomposites are shown in Fig. 3.

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- Transmission electron microscopy (TEM) (Saba et al. 2015a)
 - Scanning electron microscopy (SEM) (Hakamy et al. 2014)
 - Wide angle (WAXS) and Small angle (SAXS) (Heeley et al. 2014)
 - X-ray diffraction (XRD) (Najafi et al. 2012), (Ahmed et al. 2015)
 - Atomic force microscopy (Fian et al., 2008; Zhu et al., 2002; Liu et al., 2003)
 - X-ray photoelectron spectroscopy (Fian et al., 2008; Liu et al., 2003; Wang et al., 2002)
 - Fluorescence (Jing et al., 2005)
 - Rheology (Kashiwagi et al., 2008; Lee and Han 2003)
 - Infrared spectroscopy (IR)

Fig. 3 Techniques for characterizing nanocomposites

1.6 Nano Particles

Nanometer scale items (10^{-9} m) are defined by the term nano. A nanometer is 80,000 times thinner than a human hair and are equivalent to the billionth of a meter (Saba et al. 2015a, b, c; Raghavan et al. 2012). Nano particle or nano filler are the doping agent that are distributed in the polymer matrix of a composite having at least one of their dimensions in the nanoscale range (Dastjerdi and Montazer 2010). Currently nano fillers either from natural or synthetic source is of great interest and regarded as the most promising materials of the future owing to their unique properties in comparison with bulk counterparts. The most common nano fillers include carbon nanotubes, laminated aluminosilicates (clays), nano fibers, ultra-disperse diamonds (nano diamonds), inorganic nanotubes, fullerenes, nano metal oxides, calcium carbonate, metallic nanoparticles, POSS and graphene (Henrique et al. 2009; Dey et al. 2016). Addition of nano fillers significantly improve or adjust the variable properties of the materials including physical, mechanical, optical, electrical and thermal properties, sometimes in synergy with conventional or traditional fillers (Saba et al. 2014; Shalwan and Yousif 2014). The nano materials can be synthesized by a variety of methods such as chemical, biological and mechanical techniques. The techniques involved in the synthesis are listed in Fig. 4.

Inorganic and organic nano fillers has gained considerable interest owing to their unique properties and numerous potential applications in the aerospace, automotive, electronics and construction industries (Kuilla et al. 2010; Potts et al. 2011). However, currently the majority of research are focused on polymer nanocomposites based on layered materials of a natural origin, such as a montmorillonite type of layered silicate compounds or synthetic clay (layered double hydroxide) (Li et al. 2009b; Kuilla et al. 2010; Paul and Robeson 2008). The nanoclay reinforced

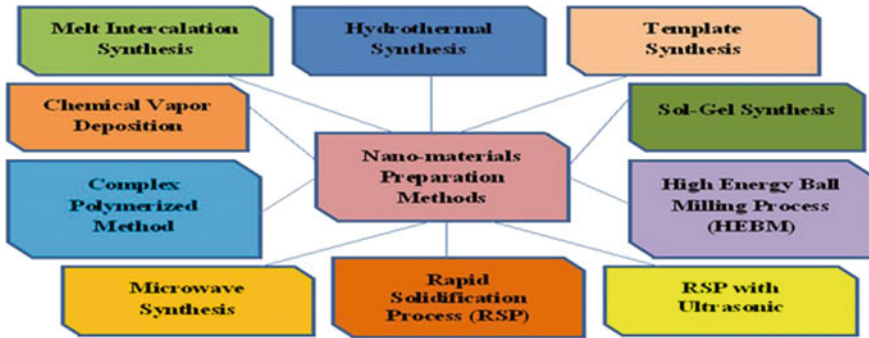


Fig. 4 The various methods for the synthesis of nano materials

polymer composites displays vast potential applications in the variety of areas such as electronics, sensors, information storage, catalysis and structural components (Kushwaha and Kumar 2011; Subramaniyan and Sun 2008). Research study illustrates that the usual content of lamellar nanoclay and organo-modified montmorillonite is in the range of 5–10 wt% due to their high aspect ratio (more than 1000), high surface area (more than 750 m²/g) and higher modulus values (176 GPa) (Uddin 2013). Depending upon the processing conditions and characteristics of both the polymer matrix and organoclay, the in situ dispersion of organoclay inside the host polymer by melt blending can be more or less achieved, leading to intercalated or exfoliated nanocomposites. The general scheme of melt compounding and film casting methods involved in the preparation of nanoclay polymer composites are shown in Fig. 5.

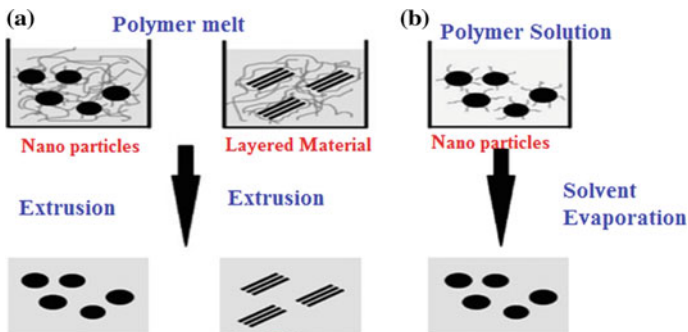


Fig. 5 Preparation methods for nanocomposites: a melt compounding, b film casting (Modified from: Li et al. 2010a, b)

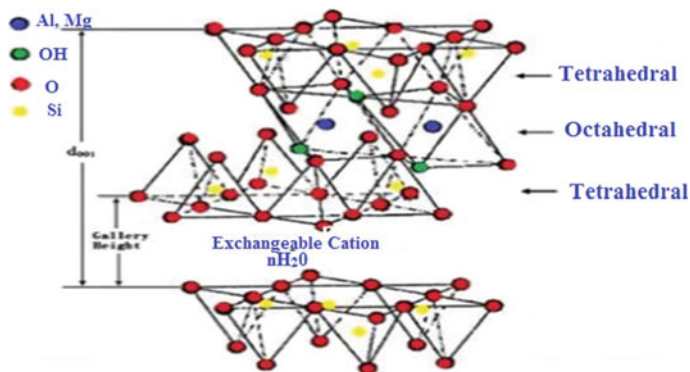


Fig. 6 General structure of clay mineral (Modified from: Nourbakhsh and Ashori 2009)

2 Clay Minerals

Clay deposits composed of clay minerals (phyllosilicate minerals) (Prasanth et al. 2013; Morsy et al. 2011). Clay is a naturally occurring mineral composed primarily of fine grained minerals. These minerals shows plasticity owing to variable water content and on drying or fired can be hardened (Zhang et al. 2015). The most typical structure of clay mineral are displayed in (Fig. 6).

2.1 Nanoclays

Nanoclays is the good example of naturally occurring nanomaterials and are generally used for a clay mineral having a phyllosilicate or sheet structure with a thickness of about 1 nm and surfaces about 50–150 nm in one dimension (Sedaghat 2013; Pavlidou and Papaspyrides 2008). Nanoclays are thus the general term for the layered mineral silicates nanoparticles having high aspect ratio. Depending on morphology of nano particles and chemical composition nanoclays are organized into various classes such as illite, halloysite, bentonite, kaolinite, montmorillonite, hectorite and chlorite (Pavlidou and Papaspyrides 2008). Researchers explored that the nanoclays can be obtained from raw clay minerals through fewer steps (Uddin 2013), instead of the several general synthesis techniques of nano particles. Descriptions of processing stages used in converting raw clay mineral into a nanoclay mineral are displayed in Fig. 7 (Uddin 2013).

The layered structure enables the material to either swell or shrink depending on its water uptake tendency. Moreover, the purity and cation exchange capacity of the nanoclay are one of the critical properties, as it provides the surface activity required for inclusion of modifiers and for surface treatments. The typical structure of the sodium based MMT are shown in Fig. 8 (Paul and Robeson 2008).

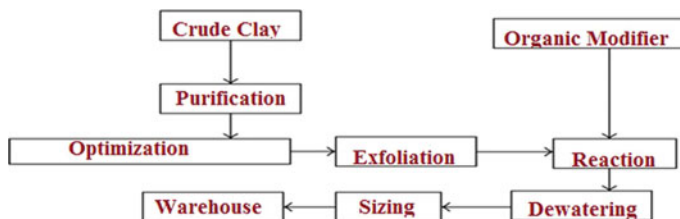


Fig. 7 Stages involved in the conversion of crude clay into nanoclays (Modified from: Uddin 2013)

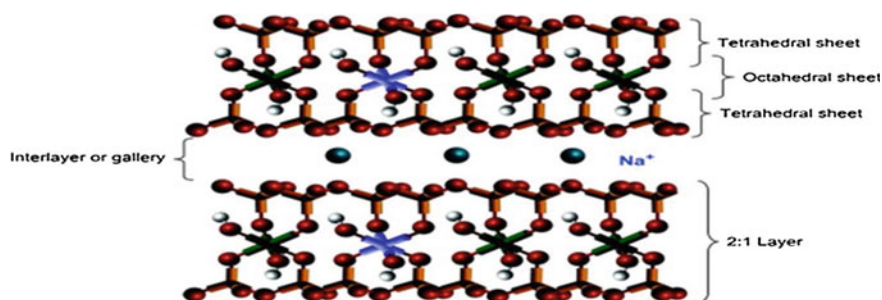


Fig. 8 Structure of sodium montmorillonite (Modified from: Paul and Robeson 2008)

Nanoclays products are typically modified with ammonium salts and are often called “Organically modified nanoclays or organoclays” (Zhang et al. 2015). Organoclays are one of the attractive and promising hybrid organic inorganic nanomaterials generally used for polymers and polymer based composites modification. The synthesis of organoclay is shown in Fig. 9. The clay surfaces modification render them organophilic to make them compatible with hydrophobic organic polymers (Jahanmardi et al. 2013).

Researchers stated that the structure of nanoclays or its dispersion in resins are of various types and can be characterized as phase separated, intercalated, or exfoliated displayed in Fig. 10 (Nabil et al. 2015).

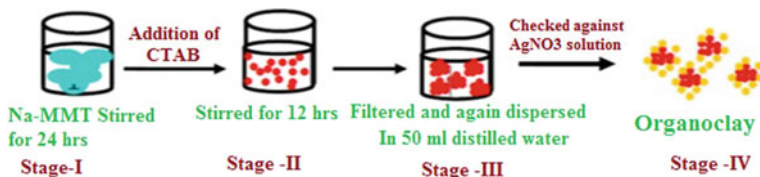


Fig. 9 Scheme for the preparation of nanoclay

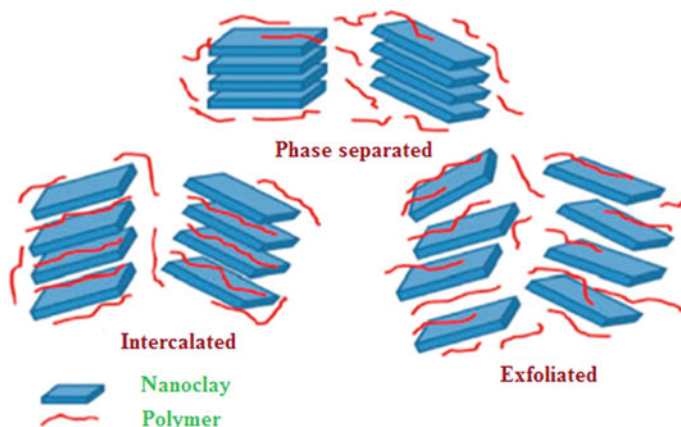


Fig. 10 Dispersion mechanism of nanoclay in resin (Modified from: Nabil et al. 2015)

2.2 *Platy Nanoclays*

The 2:1 phyllosilicates family of nanoclay is the most commonly used layered silicate in polymer nanocomposites (Jahanmardi et al. 2013). Their two-dimensional layers are made up of two tetrahedral coordinated silicon atoms fused to an edge-shared octahedral sheet of either aluminium or magnesium hydroxide. MMT, talc, hectorite, pyrophyllite, nontronite and saponite are the members of the layered smectite clay group (Sedaghat 2013; Henrique et al. 2009).

2.3 *MMT Nanoclays*

MMT nanoclays since 1847 have gained much research interests over the past decade. MMT was first labelled for its occurrence in montmorillon mineral in department of Vienne (France) more than 50 years before the discovery of bentonite in the US (Özcan et al. 2004; Ursache and Rodrigues 2014). However, chemically, it is hydrated sodium calcium aluminium magnesium silicate hydroxide $(\text{Na, Ca})_{0.33}(\text{Al, Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$ (Shirini et al. 2012; Sedaghat 2013). Most generally it is merged with muscovite, chlorite, illite, kaolinite and cookeite (Ehlmann et al. 2007). Iron, potassium and other cations are the common substitutes, but their ratios however varies greatly with source (Uddin 2008). MMT nanoclays are similar like saponite clay, belongs to extremely soft phyllosilicate group of minerals having extremely small nano sized particles, with fine layered grained structure (Shirini et al. 2012). MMT typically form in microscopic crystals and are derived from bentonite ore, forming anisotropic platy clay structure.

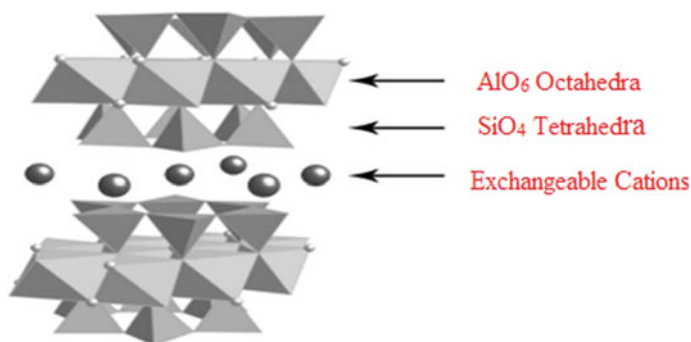


Fig. 11 Crystal structure of dioctahedral smectite type clay, MMT (Modified from: Nakato and Miyamoto 2009)

MMT is a subclass or member of the natural smectite group (2:1 clay), having 2 tetrahedral sheets sandwiching a central octahedral sheet. Crystal structure of 2:1 layered smectite nanosheet (MMT) are illustrated in Fig. 11 (Nakato and Miyamoto 2009). Thus MMT consist of aluminosilicate layers surface-substituted with metal cations stacked in ~ 10 μm -sized multilayer stacks. The particles are plate-shaped with an average diameter around 1 μm with the surface dimensions generally 300 to more than 600 nm, resulting in an unusually high aspect ratio (Nakato and Miyamoto 2009). MMT featured by having better cation exchange capacity and 50 % octahedral charge (due to isomorphous substitution of Mg for Al) (Srasra et al. 1994; Chan et al. 2011a, b).

Naturally occurring MMT is highly hydrophilic. The MMT water content tendency varies greatly and it increases greatly in volume when it absorbs water. Researchers also synthesized modified MMT through clay surface modification, since polymers are generally organophilic, the unmodified nanoclay disperses with great effort in polymers. After modification (“surface compatibilization or intercalation”) the MMT can become compatible (organophilic) to the conventional petroleum polymers and dispersed readily in polymers for better properties in nanocomposites (Nakato and Miyamoto 2009).

2.4 Halloysite Nanotubes (HNTs)

Halloysite nanotubes were firstly reported by Berthier as a di-octahedral 1:1 clay mineral of the kaolin group in 1826, and its deposits are extensively found widely in the soils of countries such as France, China, Belgium, New Zealand and Australia (Du et al. 2010). HNTs are unique and versatile white and slight red nanomaterials (Fig. 12a), formed naturally within the earth over millions of years,

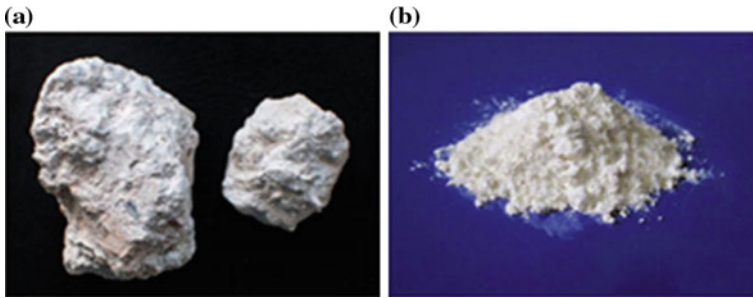


Fig. 12 Showing raw halloysite (a) and ground halloysite (b) (Liu et al. 2014)

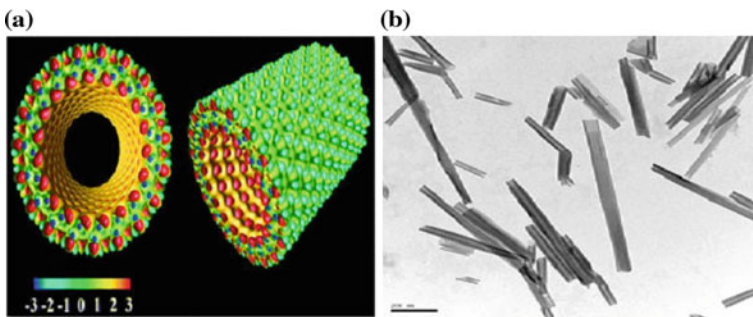


Fig. 13 Showing HNT model (a) and the TEM image of HNTs (b). **a** Kamble et al. (2012) **b** Du et al. (2010)

due to strain caused by lattice mismatch between adjacent silicon dioxide and aluminium oxide layers (Kamble et al. 2012). The stone-like raw halloysite is easily ground into powder (Fig. 12b) (Liu et al. 2014).

HNT is the naturally occurring double layered aluminosilicate ($\text{Al}_2 \text{Si}_2 \text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$), ultra-tiny hollow tubular structure with diameters typically lesser than 100 nm and with lengths typically ranging from about 500 nm to over 1.2 μm (Kamble et al. 2012). HNT model and its SEM micrograph are shown in Fig. 13a, b. The HNTs rapidly emerged as a raw material for the future because of being relatively cheaper, abundant and sustainable nature compared to commercial and expensive CNTs. They are chemically similar to kaolin clay with several interesting applications in the construction industry (Yunsheng et al. 2008; Montes et al. 2015). Recently researchers developed two types of halloysite nanotubes (single walled and multi walled) models to amplify effectively its nanotechnology applications (Zhang et al. 2015).

3 Nanoclay Polymer Composites

Nowadays the growing concern towards the utilization of renewable materials as filler in the matrix highlights greatly the importance of layered silicates clay minerals as nano filler owing to its availability and versatility (Ray and Okamoto 2003). MMT and organoclays are widely used for dispersion in polymers due to the high aspect ratio and the large interface of the polymer nanoclay interaction in the polymer composites (Fareed and Stamboulis 2014). Toyota research group in the early 90s, declared the first use of nanoclays reinforcement in the manufacturing of nylon-6-based nanoclay composites. They concluded that addition of nanoclays perfectly influence the crystallization process and the structural changes (Sandler et al. 2004). Untill now a variety of polymers except a few hydrophilic polymers such as poly (vinyl alcohol) and poly(ethylene oxide) which are modified by organoclay are well reported in literature.

Depending on the process conditions and polymer/nanofillers bonding the layered silicates dispersed into the polymer matrix in different states of intercalation and/or exfoliation (Baniassadi et al. 2011). Polymer nanoclay composites involve the interaction of polymer matrix with the nano-plates of clay, formed by the dispersion of low weight percentages of nanoclay into polymers (Fareed and Stamboulis 2014). The three different types of nanocomposite usually results by the dispersion of nanoclay to the polymer matrix are shown in Fig. 14 (Baniassadi et al. 2011).

However, the exfoliated structures displayed far better properties compared to other two nanocomposites (Pollet et al. 2004). Nanoclay reinforced polymer composites and their laminates have excellent properties including enhanced physical (optical, dielectric, permeability, transparency and lower shrinkage), thermal (decomposition temperature, flammability, coefficient of thermal expansion and higher thermal stability) and mechanical properties (tensile toughness, tensile strength and tensile modulus) even at a very low filler loading with respect to pure polymers (Babaei et al. 2014; Hossen et al. 2015; Najafi et al. 2012). Untill now many research study were made, to investigate the effect of nanoclay loadings on the properties of different polymers. The nanoclays addition in very low weight

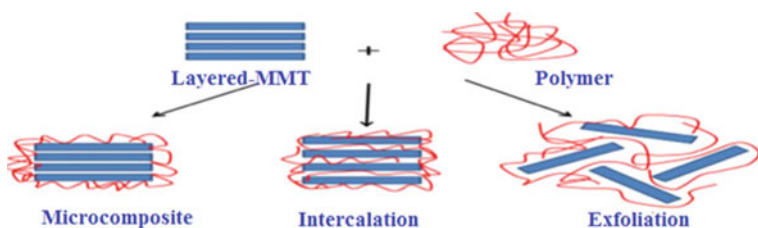


Fig. 14 Structural morphologies in polymer/MMT (nanoclay) nanocomposite (Modified from: Baniassadi et al. 2011)

Table 1 Reported study on nanoclay based polymer nanocomposites

Reinforcements/polymer	Properties improvement	References
Nanoclay/polyamide	Nanocomposites shows effective thermal conductivity, elastic modulus and mechanical properties	Baniassadi et al. (2011)
MMT aerogels/NR	Improved mechanical, rheological, swelling properties and viscoelastic response	Pojanavaraphan et al. (2010)
PLA/nanoclay	Improved mechanical properties (Peak stress, elongation at break, young modulus and degradation rate)	Nieddu et al. (2009)
Nanoclay/PEU	Nanoclays acts as effective flame retardants coatings for polyester urethanes. It also improves the physical, mechanical and thermal stability of the composite	Patel and Patel (2014)

Notes Polyester urethanes (PEU), Natural rubber (NR), Montmorillonite (MMT), Polylactic acid (PLA)

percent (1–5 %) can significantly improves the properties of the polymer base. Some of the important research work on nanoclay based polymer composites were tabulated in Table 1.

4 Nanoclay Hybrid Polymer Composites

Many researchers have used MMT nanoclay as filler in hybrid polymeric composites and their laminates due to its well-known exfoliation/intercalation chemistry, surface reactivity, high surface area, cost effectiveness and easy availability (Hossen et al. 2015; Dewan et al. 2013). Some of the important research work on nanoclay based polymer composites were tabulated in Table 2. A variety of natural fibers (from jute to oil palm fibers, either in short fiber, nonwoven mat or in woven fabrics) are modified by the nanoclays.

5 Applications of Nanoclays and Polymer Nanoclay Composites

Clay materials are relatively commercially available, inexpensive, easily can be modified, non-corrosive and recyclable in nature (Shirini et al. 2012; Jahanmardi et al. 2013; Najafi et al. 2012). They have been explored from decades as they shows huge importance in various fields of agriculture, ceramics, construction and other industrial or domestic applications. Nanoclays (layered silicates) and organoclay are of considerable interest for bulk applications from many decades as they have high aspect ratio, large specific surface areas associated with platy layered

Table 2 Reported study on natural fiber/nanoclay hybrid nanocomposites

Reinforcements/polymer	Properties improvement	References
WSF/nanoclay/foamed HDPE	The addition of nanoclay up to 2 % improved the mechanical resistance. The water absorption and thickness swelling properties of HPDE/WSF composites also witnessed reduction by the addition of nanoclay	Babaei et al. (2014)
Glass fiber/nanoclay/polypropylene	Incorporation of nanoclay improves the thermal stability, flexural strength, flexural modulus and tensile strength of the hybrid material	Rahman et al. (2013)
Almond shell flour/OMMT/polypropylene	3 wt% OMMT filler addition decreases the water absorption and thickness swelling. It also improves the physicomechanical (tensile and flexural properties) properties of the developed hybrid composites	Zahedi et al. (2015)
Bamboo fiber/nanoclay/HDPE	Nanoclays addition significantly enhanced the modulus properties of the HDPE–clay hybrids	Han et al. (2008)
Wild cane grass fiber/MMT nanoclay/polyester	The addition of nanoclays improves the tensile strength, modulus and impact strength of the wild cane grass fiber composites. The weight loss of nanoclay filled wild cane grass fiber/polyester composites found to be 30 and 22 % less compared to composites without nanoclay at maximum percentage volume of fiber	Prasad et al. (2015)
Flax fiber/nanoclay/soy protein resin	Nanoclay addition considerably enhanced the mechanical (tensile and flexural) properties of the hybrid composite	Huang and Netravali (2007)
Jute/nanoclay/polyester	Enhancement of mechanical (compression, flexural, ILSS) and dynamic mechanical properties by the addition of nanoclay. It also reduces water absorption properties of JPC	Dewan et al. (2013)
Wood fiber/nanoclay/polypropylene	Nanoclay addition improves both the mechanical and physical properties. It also lowers the water absorption properties with relative to pure composite	Nafchi et al. (2015)
OPEFB/nanoclay/PU foam	The addition of nanoclays improves both, the thermal and barrier properties of BHPU composite	Ali and Ahmad (2012)

(continued)

Table 2 (continued)

Reinforcements/polymer	Properties improvement	References
WF/MMT/PLA	Intercalation of MMT in the PLA matrix enhances the tensile modulus and water resistance properties of the bio-composite.	Kumar et al. (2010)
WPI/Modified nanoclay (Cloisite Na ⁺ , Cloisite 20A, and Cloisite 30B)	Nanoclay significantly improves the tensile and the water resistant properties of the developed composite films. The WPI/Cloisite 30B composite films showed a strong resistance towards bacteriostatic effect of <i>Listeria monocytogenes</i> and Gram-positive bacteria	Sothornvit et al. (2009)
Flexible PU/organoclay	Organoclay incorporation in PU foams leads to reduction in cell size. It also upsurge cell density and tensile modulus of the developed foams	Jahanmardi et al. (2013)
Sepiolite clay/epoxy-DGEBA	Sepiolite reduces the whole degradation process on the temperature scale. It improves the thermal stability and flame retardant effects of the hosting epoxy by fasten the char layer formation during the burning process on both condensate and vapor phase	Zotti et al. (2015)
HF/nanoclay/Portland cement	Improved the thermal stability, lowered the water absorption, porosity. The density, fracture toughness, flexural strength and impact strength get improved by the addition of nanoclays	Hakamy et al. (2014)
Treated and untreated Jute fibers/nanoclay/polyethylene	Nanoclays incorporation improves both physical and mechanical properties of the hybrid composite. Tensile strength and modulus improves by approximately 8 and 15 % respectively with respect to the composites without nanoclays	Hossen et al. (2015)
Poplar (<i>Populus nigra</i> L) sawdust/nanoclay/polypropylene	Nanoclay considerably inhibited the growth of wood-deteriorating fungi in the wood polymer composite	Bari et al. (2015)
Wood flour/nanoclay/polypropylene	Both mechanical (flexural and tensile strengths) and physical properties improved by the incorporation of nanoclay. The water absorption properties significantly reduced in nanoclays filled composite	Yusoh (2015)
Wood flour/glass fiber nanoclay/polypropylene	Tensile modulus and tensile strength increases, while the water absorption tendency decreases considerably by the addition of nanoclay	Kord and Kiakojoouri (2011)

(continued)

Table 2 (continued)

Reinforcements/polymer	Properties improvement	References
Nanoclay/low molecular weight PF	Addition of nanoclay into a phenolic matrix significantly increased the surface hardness, MOE, dimensional stability, water repellency and abrasion resistance	Nabil et al. (2015)
Nanoclay/glass fiber/polyester	Nanoclay improves mechanical properties and also accelerates the tool wear.	Prabhu et al. (2013)
OPMF/nanoclay/PLA/PCL	Nanoclay successfully improves the flexural properties, impact resistance, water resistance and compatibilizes the OPMF/matrix adhesion.	Eng et al. (2014)
Nanoclay/sisal fiber/epoxy	Tensile, dynamic properties and wear properties improves with nanoclay incorporation	Mohan and Kanny (2011)
Pine cone fibers/nanoclay/polypropylene	Improvement in mechanical and thermal properties by the addition of nanoclay	Arrakhiz et al. (2013)
Poly(ester-urethane)/OMMT	Nanoclay addition increases the T _g , increased non-flammability (V-0 rating). It also improves morphology, mechanical and thermal properties	Kausar (2015)
Wood flour/nanoclay/polypropylene	Improvements in thermal stability and resistivity towards water absorption by nanoclay addition	Tabari et al. (2011)
Reed fiber-MAPP/nanoclay/polypropylene	Tensile modulus and strength of hybrid composites significantly increased. The water absorption property decreases with nanoclay loading.	Najafi et al. (2012)
Bamboo fiber/nanoclay/epoxy/polyester	Addition of nanoclay enhances the elastic modulus, thermal stability, water absorption resistivity and wear resistance properties of hybrid composites	Kushwaha and Kumar (2011)
Bagasse/nanoclay/polypropylene	Nanoclay improves the physical and mechanical properties, lowered the water absorption tendency compared with conventional composites	Nourbakhsh and Ashori (2009)
Untreated and silane treated NaOH/woven coconut sheath/MMT/polyester	Dynamic factors and T _g value slightly increases with the incorporation of nanoclay in the composite system	Rajini et al. (2013)
Wood fiber/nanoclay/HDPE	Nanoclay enhance the mechanical properties and the flame retardancy of WPCs	Lee et al. (2010)
MMT/wood flour/HDPE	Mechanical properties of HDPE/wood-flour composites get considerably improved by MMT incorporation	Faruk and Matuana (2008)

(continued)

Table 2 (continued)

Reinforcements/polymer	Properties improvement	References
Industrial hemp/nanoclay/UPe-EMS	Nanoclays addition retains stiffness without sacrificing toughness. It also improves the thermal barrier properties	Haq et al. (2008)
Coir fiber/wood fiber/MMT/polypropylene	Physicomechanical and biodegradable properties subsequently increases by the incorporation of nanoclays	Islam et al. (2015)
HF/nanoclay/cement	Nanoclay addition increases the microstructure density, thermal stability, flexural strength, fracture toughness, and its impact strength. Beside this it reduced the porosity and water absorption tendency as compared to nanoclay unfilled HF cement composite	Hakamy et al. (2014)
Sisal fiber/nanoclay/metakaolin/Portland cement	The interfacial bond between cement matrix and fiber and flexural properties get improved significantly by the addition of nanoclay	Wei and Meyer (2014)
Carbon fibers/E-glass fiber/OMMT/epoxy	Mechanical properties get considerably improved by the incorporation of OMMT	Liu et al. (2004)
Carbon fibers/glass fibers/MMT/wood flour/polypropylene	The MMT addition enhanced the tensile modulus by 34 % and lowers the water absorption tendency of the hybrid composite	Turku and Kärki (2014)

Notes Wheat straw flour (WSF), Organically modified montmorillonite (OMMT), High density polyethylene (HDPE), Inter-laminar shear strength (ILSS), Unsaturated polyester (UPE), Epoxidized soybean oil (EMS), Hemp fabric (HF), Modified montmorillonite (OMMT), Phenol formaldehyde (PF), Polycaprolactone (PCL), Oil palm mesocarp fiber (OPMF), Natural rubber (NR), Whey protein isolate (WPI), Woven flax (WF), Polyurethane (PU), Oil palm empty fruit bunch (OPEFB), Melting temperature increases (Tm), Storage modulus (E'), Jute fabric reinforced polyester composites (JPC), Bio-nanocomposite hybrid polyurethane (BHPU), Modulus of elasticity (MOE), Glass transition temperature (Tg), wood fiber/plastic composites (WPCs), Polyester urethanes (PEU)

morphology, to results an improvement in the mechanical properties of polymers. Nanoclays also being used as flame retardants in the plastics industry to improve fire safety of their products. Integrating nanoclays into the plastic reduces drastically the amount of combustible material through a protective layer preventing the spreading of the fire. The transparency of nanoclay are also being used in films for achieving maximum mechanical properties and optimum clarity, as the presence of impurities act as stress concentrators, resulting in poor impact and tensile properties (Zhang et al. 2015). Nanoclays also conveys some practical potential biomedical applications such as in anti-bacterial efficacy, sterilizing phenomenon, toxins adsorption and in membrane coating (Dastjerdi and Montazer 2010; Wilson 2003).

Currently, one of the major applications of nanoclays is in the fabrication of polymer clay nanocomposites. These natural nanomaterials also acts as a rheological modifiers and additives in paints, inks, greases and cosmetics, pollution control bio-systems carriers, delivery systems for the controlled release of drugs (Floody et al. 2009). The incorporation of small amount (0.5–5.0 wt%) of MMT in the polymer matrix modified the polymer leading to a remarkable improvement of the physical, mechanical, fracture, wear resistance, thermal stability, peak heat release rate, flame retardancy, biocompatibility and chemical properties of the resulting composite as compared to conventional materials (Li et al. 2010a, b; Kushwaha and Kumar 2011; Uddin 2013). Currently the most particularly polymers that are modified includes epoxy, polyester, polyethylene, polypropylene, polystyrene and nylon using platy nanoclay mineral (Uddin 2013). MMT clays and acid treated MMT also been extensively used in catalytic cracking, acid-based catalysis processes and in materials applications from past 60 years. Organoclays are potentially being used as gas absorbents, rheological modifiers, polymer nanocomposites and as drug delivery carriers (Matsuda et al. 2013; Shirini et al. 2012).

In recent time, HNTs are the economically available and relatively cheaper nano sized raw material as compared to morphologically similar MWCNTs to apply in conjunction with various polymers such as nitrile rubber, natural rubber and polypropylene to form polymer-halloysite composite nanotubes (Rawtani and Agrawal 2012). Halloysite is a nontoxic and biocompatible material, which makes it a potential candidate for medical applications and household products (Zhang et al. 2015).

HNTs displays vast non-biological and biological applications such as drug and DNA carrier, tissue engineering scaffold, for cellular response, for osteoblasts and fibroblasts response (Rawtani and Agrawal 2012; Liu et al. 2014). HNTs are the main active ingredient in the “living nature deep cleansing mask” (New Zealand) which deeply purifies and refines the facial pores. The hollow HNTs tube can be filled with various active ingredients to meet the requirements for household, cosmetics, personal care and extended release products (Liu et al. 2014). HNT also being used for atom transfer radical polymerization, layer-by-layer coatings on wood microfibers, polyurethane coatings, scratch resistance coatings, also acts as a sorbents for various contaminants and pollutants (Li et al. 2013). Nowadays they are also being used for catalytic conversions, differentiation studies, hydrocarbon processing, molecular hydrogen storing, dispersion improvement and as an enzymatic nano reactor (Rawtani and Agrawal 2012).

Polymer nanoclay composites are one of the most promising alternatives to steel and wood based polymer composite, initially developed for the aerospace industry. Table 3 summarizes the different applications of nanoclays and their polymeric nanocomposites.

Table 3 Tabulates the different applications of nanoclays and their polymeric nanocomposites

Applications of nanoclay and its types				Applications of nanoclay polymer composite
Nanoclays	MMT	Organoclays (Cloisite® 30B)	HNT	Nanoclay based nanocomposites
Enhance properties of many polymers (thermoset and thermoplastics)	Fabrication of polymer nanocomposites with superior thermal, mechanical, gas-barrier and water resistant properties	Fabrication of polymer clay nanocomposites	Fabricating high performance polymer nanocomposites and green composites with natural rubber	MMT and HNTs nanocomposite application in optical, electronic, magnetic, thermosensitive and as biopolymer composites devices
Properties improvement of polypropylene spun bond fabrics	Catalytic cracking catalysts from past 60 years	Dimensional stability of flexible polyurethane foams	Bio-nanomaterial and formation of bio-nanocomposite film	MMT and HNTs perfectly modified the properties of epoxy resin, polypropylene, polyamide, natural rubber
Wide-spectrum mycotoxin binder	Modification of the polymeric materials	Rheological modifiers in paints, inks, grease and cosmetics	For corrosion prevention and fire retardant for nylon 6 and polymers as insulating coatings	Anti-microbial and green nanocomposites from HNTs. Formation of bio-nanomaterial and formation of bio-nanocomposite film
Wastewater treatment as a potential and cheaper adsorbent for cationic dyes	Materials applications	Color, shining retention and coverage for cosmetics (lipsticks, nail lacquers and eye shadows)	As adsorbent for cationic dyes such as neutral red (NR), methylene blue, malachite green from dye contaminated wastewater or aqueous solutions	Civil infrastructure
Drug delivery applications	Synthesis of commercial glass ionomer cement	Thicken the lubricating oils, greases	Cosmetics formulation, tissue engineering, macro molecular delivery systems and cancer cell isolation applications	Commercial packaging

(continued)

Table 3 (continued)

Applications of nanoclay and its types				Applications of nanoclay polymer composite
Nanoclays	MMT	Organoclays (Cloisite® 30B)	HNT	Nanoclay based nanocomposites
Rheological modifiers in inks, grease, paints, varnishes and cosmetics	Adsorb bacterial toxins associated with gastrointestinal disturbance and hydrogen ions produced in acidosis and steroidal metabolites related with pregnancy	Formulation of ink to amend the evenness of printing inks	Host for the polymerization host for several conductive and non-conductive polymers	Medicine
Bio-medical applications (sterilizing effect, adsorption of toxins membrane coating)	Carrier and in drug delivery applications	Removes humic acid from potable water	For immobilization of metalloporphyrins and silver nanoparticle	Domestic household appliances
Modification of textiles, UV-absorber	Pollution control and water treatment	Pollution control and waste water treatment	Manufacture of high quality white and ceramic ware	Mostly in Aerospace and industries automobiles. nanoclay composites in sensor technology for making sensor coating materials and in QCM sensors

Source Nakato and Miyamoto (2009), Sedaghat (2013), Floody et al. (2009), Jahanmardi et al. (2013), Jahanmardi et al. (2013), Li et al. (2009a), Floody et al. (2009), Fareed and Stamboulis (2014), Subramanian and Sun (2008), Rawtani and Agrawal (2012), Du et al. (2010), Marney et al. (2008), Dastjerdi and Montazer (2010), Mittal (2009)

They are now feature in almost every area of modern industrial production and enterprise, like automobiles, household appliances, medicine, weaponry, civil infrastructure and packaging (Floody et al. 2009). Polymer nanocomposites reinforced with HNTs possess highly increased tensile and flexural strength, toughness, elastic moduli, higher thermal stability, flame retardancy and unique crystallization behavior (Liu et al. 2014; Yuan et al. 2015).

6 Conclusion

Research activities in the area of nano-materials have been increased dramatically from past decades. Currently nanoclays are the most valuable nano fillers displaying great reinforcing effects due to their high thermal stability, improved mechanical strength, biocompatibility and great abundance. Natural tubules HNTs are unique, versatile and important class of nanoclays extensively used in modifying polymer in polymer composites formed by surface weathering of aluminosilicate minerals. We concluded that nanoclays minerals are the most promising alternative to expensive nano fillers such CNT's, POSS and graphene in improving or modifying the polymer and polymer composite properties with exciting potential applications. The incorporation of naturally existing nano materials as filler in nanocomposites exhibit distinctly improved properties such as improved thermal stability, higher flame retardancy, reduced CTE, better mechanical performance and improved clarity for optical applications. Organoclay, MMT and HNTs are of considerable interest in the field of polymer nanocomposites both for structural and functional applications. In this review article, we provided an overview of the recent research regarding nanoclay including MMT, HNT, organically modified nanoclays, nanoclays based polymer nanocomposites and an insight into their different potential applications. This review paper expected to delivers valuable evidence or literature information for further research and in the elaborative study of novel nanoclay based macro-micro hybrid nano polymeric composites as compared to other nanocomposites derived from commercially synthetic nano fillers.

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