

Clays and Their Polymer Nanocomposites



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Abstract Clean drinking water resources are scanty in many regions of the world due to contamination with several organic and inorganic pollutants. Amongst the numerous techniques of contaminant removal, adsorption is the most economic and efficient technique. Though the low cost and readily available clay minerals have been considered as adsorbents of choice, their practical use as adsorbents is limited due to their low adsorption tendency towards organic species, difficulty in regeneration and recovery. Clay–polymer composites combining the advantageous characteristics of clay minerals and polymers have emerged as attractive alternative with high adsorption efficiency, surface area, and renderability. This chapter describes the different classes of clays and polymers used, physicochemical and structural properties of clay–polymer composites, synthetic methodologies, and characterization techniques as well as the main applications in the field of environmental remediation. Finally, the different mechanisms involved in the adsorption phenomena will be discussed.

1 Introduction

Clay refers to the group of materials made up of layered silicates or clay minerals with traces of metal oxides and organic matter. The basic building unit of clay minerals is composed of tetrahedral silicates and octahedral hydroxide sheets arranged in 1:1

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ratio (e.g. kaolinite and serpentine) and 2:1 (e.g. smectite, chlorite, and vermiculite). Depending on the charge the clay particles can be divided into cationic clay minerals and anionic clay minerals [1].

The clay ingredients are split into two categories based on how the alternating sheets of “SiO₂” and “AlO₆” units are arranged. First category is 2:1 clay (smectite, and vermiculite) and second is 1:1 clay (Kaolinite). Usually, 2:1 clay is used rather than 1:1 because they lack the effective intercalation properties, and the separation of layers becomes difficult. This leads to increased charge density which makes the penetration of the layers difficult [2].

Classification of clay

Based on the source, clay is categorized as (1) natural clay and (2) synthetic clay. The clay material comprises SiO₂ and AlO₆ in their composition and arranged in an alternative way. Two-dimensional arrays of Si–O- tetrahedral and 2D arrays of Al or Mg–O–OH octahedral are the main constituents of clay minerals. These sheets of tetrahedral and octahedral structure are stacked in various ways in the majority of clay minerals. They are classified into (a) 2:1 and (b) 1:1 clay type.

a. Tetrahedral sheet structure

The Si atoms are coordinated with four oxygen atoms in Si–O sheets. A typical tetrahedron has the Si atom in its middle, with the O atoms placed on its four corners. Each tetrahedron in the sheet shares three of its four oxygen atoms with three of its neighbours. Each tetrahedron’s fourth oxygen atom faces downward. Tetrahedral sheets or silica sheets are other names for this Si–O sheet [3].

b. Octahedral sheet structure

The Al, Mg–O–OH sheets have a hexagonal close packing because the Al or Mg atoms are coordinated with six oxygen atoms or –OH groups, which are positioned around the Al or Mg atom and with their centres on the corners of a regular octahedron. The octahedral sheet shares the fourth oxygen atom that sticks out of the tetrahedral sheet. As 1:1 layer minerals, this atom sharing may take place between silica and an alumina sheet. In 2:1 layer minerals, two silica sheets on either side of an alumina or magnesia sheet share oxygen atoms. In clay minerals, these layers are layered one on top of the other [4]. Clay in nature is hydrophilic. It is necessary to alter the clay’s surface so that hydrophobic polymers can interact with it. The interlayers of the clay are held via strong covalent bonds which makes dispersion difficult, to avoid all these problems the clay particles are modified before dispersion in the polymer matrices which also increases the interlayer spacing. There is an overall improvement of all the properties such as mechanical, thermal, optical, and barrier properties.

Clays have a special property that allows them to exchange cations between each of their layers and retain them. The cation exchange method is typically used to modify the surface of clay. By treating additional cations in solution, the intercalated cations can be replaced by other cations. The highest number of cations that may be continuously taken up by a particular volume of clay is known as the cation exchange capacity. The adsorption capacity of montmorillonite is governed by its capacity for cation exchange in the interlayer region. Inorganic ions (primarily Na^+ , Ca^{2+} , Mg^{2+} , and K^+), amines, amino acids, cationic surfactants, and non-ionic surfactants are the most exchangeable cations that can be adsorbed on the clay surface via the cation exchange process. The Langmuir-Blodgett reaction between hybrid monolayers of clay mineral and amphiphilic alkyl amino cation can also make the clay surface organophilic. The negatively charged clay platelets in the suspension are adsorbed onto a floating monolayer of the amphiphilic alkyl ammonium cation at an air–clay suspension interface when a solution of the cation is distributed onto the suspension of clay. To create a hybrid multilayer, one can transfer the hybrid monolayers of clay platelets and alkylammonium cations generated at the interface onto a solid surface [3, 5].

Modification can also be achieved by using organic modifiers which leads to high mechanical and thermal properties as well as enhanced liquid barrier properties [6]. Other type of modification includes the formation of composite. When two or more materials, each having their own significant characteristic properties combines to form a new substance with superior properties than the original it is called a composite. Figure 1 summarizes the types of clay composites in which primarily the polymer-based and non-polymer-based materials are used for modification [7]. The layered clays have strong intralayer covalent bonds within the individual sheets which poses a difficulty in dispersion of the clay in polymer matrix during preparation of clay–polymer hybrid composites, thus requiring modification of the clay to form nanocomposites with the polymers. The polymers mentioned are few representative polymers and not exhaustive. Others are mentioned at the appropriate place in the chapters.

As per the work done previously and reported by various authors grafting polar functional groups onto the polymer chains is one of the methods of choice for the polymers which lack functional groups. The best example for this is maleic anhydride which is used for grafting onto PP which then tends to produce clay/PP nanocomposites. Usually, when the clay and the polymer are compatible with each other the intercalation between the two takes place easily without the need of any pretreatment. Most of the polymers available tend to be hydrophobic and generally are not compatible with hydrophilic clays. The clay used has a thickness of 1 nm and the side dimensions which fall between the range of 30 nm to a few micro-metres which totally depends on the clay. The Van der Waals forces and the weak electrostatic forces are the ones responsible between the interlayers and for the stacking of the various layers. Inside the layers the aluminium ions of the layers can be replaced with iron or magnesium or lithium ions so there is charge neutralization.

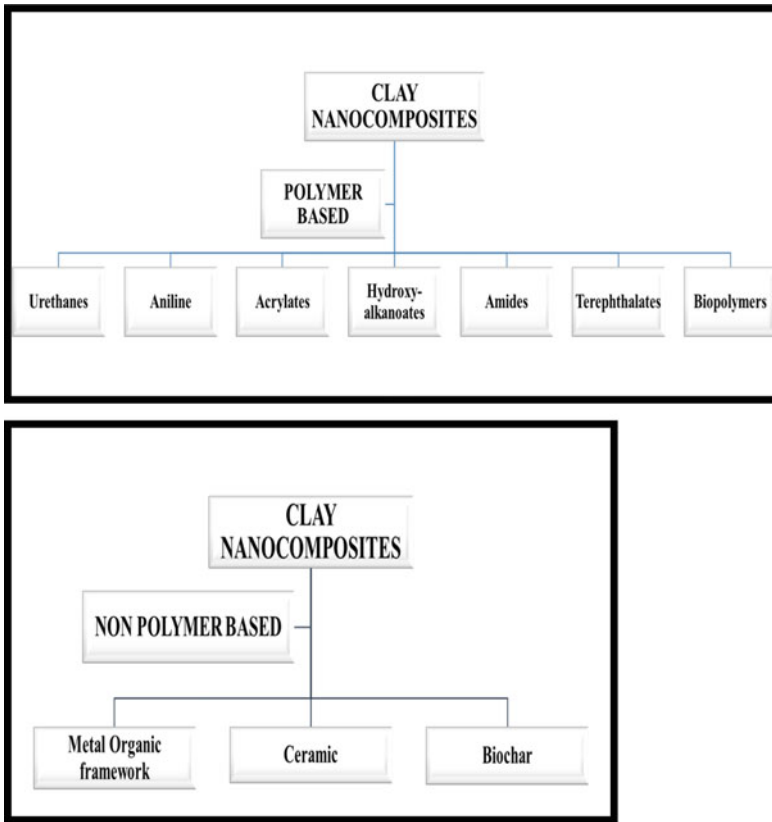


Fig. 1 Types of clay composites based on the materials used for modification

2 Clay and Their Polymer Nanocomposites

The functionality of polymers and clays can be increased by the formation of composites. The composite structure has properties like stiffness, strength, high resistance to fatigue as well as corrosion, low coefficient of expansion, and ease in manufacturing. The polymer-based composites are advantageous in terms of enhancement of the clay properties. Clay possesses some specific physicochemical properties such as high surface reactivity, optimal rheological properties, swelling and colloidal capacity, and high water dispersibility which render them suitable for many environmental remediation applications [8]. The lower clay content and lower weight of clay in the composites add to the advantage of the material. The composites thus exhibit improved biodegradability, tensile strength, modulus, and flexural characteristics that are beneficial for removing pollutants.

When these are scaled down to the nano range, they become nanocomposites. Out of the combining constituents any one of the constituents when has a nanoscale range

then the material is termed to be a nanocomposite. These nanocomposites provide the additional benefit of more surface area, and there is an improvement in the electrical as well as the optical properties. The chemical resistance of these materials is also high and the flame retardancy is also enhanced when compared to simple composite materials [9]. The clay minerals have low price, accessibility, high aspect ratio in the nanoform which offer excellent properties at low loadings, thus keeping the intrinsic benefits of polymer matrix and clay intact.

The modified/intercalated clay–polymer composites have enhanced properties than that of the polymer matrix. Due to the rigid clay structure and high aspect ratio, there is an increase in the stiffness and modulus of polymer matrix, thus increasing its mechanical strength. The increase in the filler volume also contributes to the tensile modulus [2, 10, 11]. The thermal properties of the polymer matrix are enhanced on incorporation of clay particles. All these properties make the clay–polymer composites as compatible adsorbents against the removal of many organic and inorganic species in water bodies. The layered structure of clay has the ability to retain water in the interlayer spacing resulting in heavy metal adsorption and ion exchange. The aspect ratio of clay spread in the polymer matrix also shows an impact on the gas barrier properties [2].

Figure 2 shows the various clays and few representative polymers that have been widely used to form clay–polymer nanocomposites and are summarized in Table 1.

2.1 Types of Polymer Clay Morphologies

The polymer and clay can adopt any of these morphologies—phase-separated, intercalated, and exfoliated [1, 12]. Phase-separated composite structure results when the interaction between the clay and the polymer composite is very weak which does not allow the intercalation of the polymer matrix in the clay composite but results in a structure where the polymer chain surrounds the clay. Due to this, there is not separation between the clay platelets. This may result in large-sized polymer/clay composites which may be of the size of microns. The intercalated clay composites result when some of the polymer chains have penetrated the individual clay platelets. This enhances the interlayer distance between the clay layers. Polymer–clay compatibility is crucial for the success of polymer nanocomposites' qualities when clay is used as reinforcement. An approach for the compatibilization of organic material with an inorganic is claimed via the intercalation of organic components in layered inorganic clays [13].

The exfoliated nanocomposites are completely separated clay nanoplatelets which are homogeneously dispersed in the polymer matrix. The exfoliated composites are the one producing the highest surface area which results in the enhancement of various physicochemical properties of the composites [1]. The exfoliation/intercalation increases the stiffness and modulus of the nanocomposites.

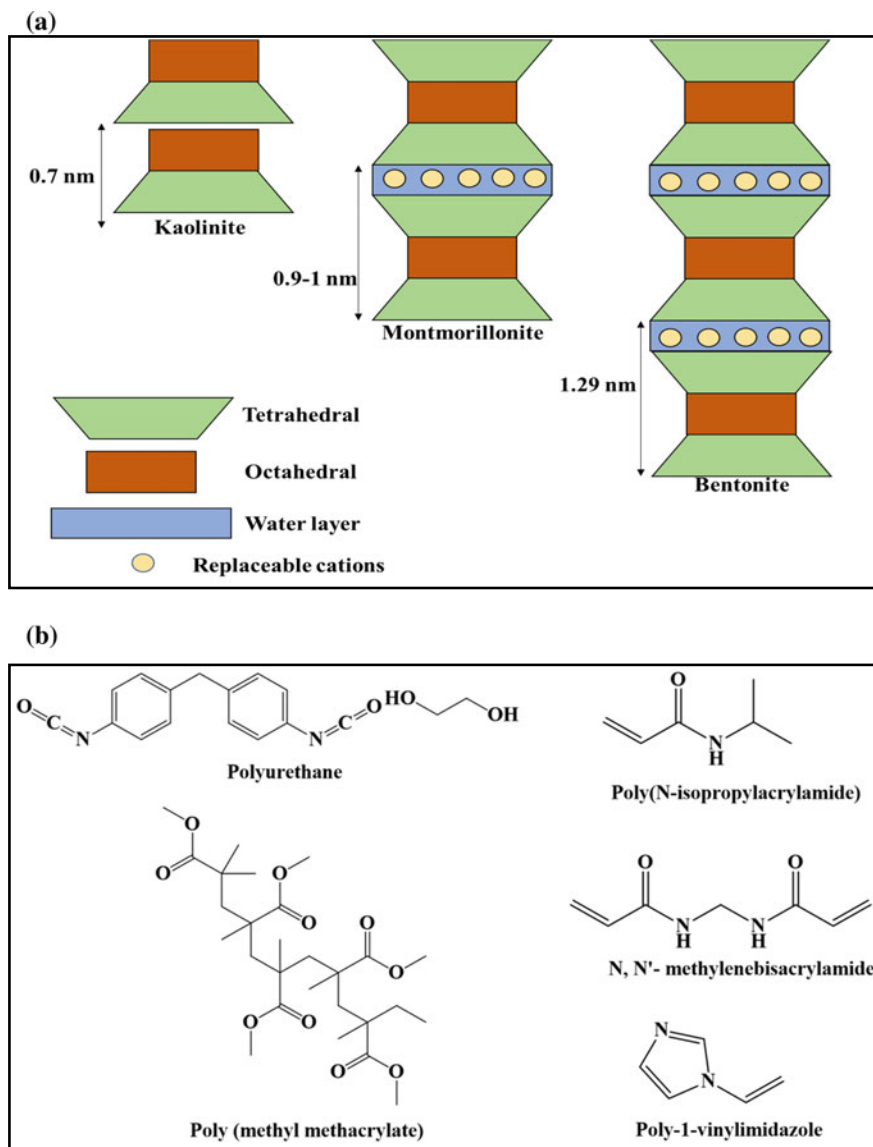
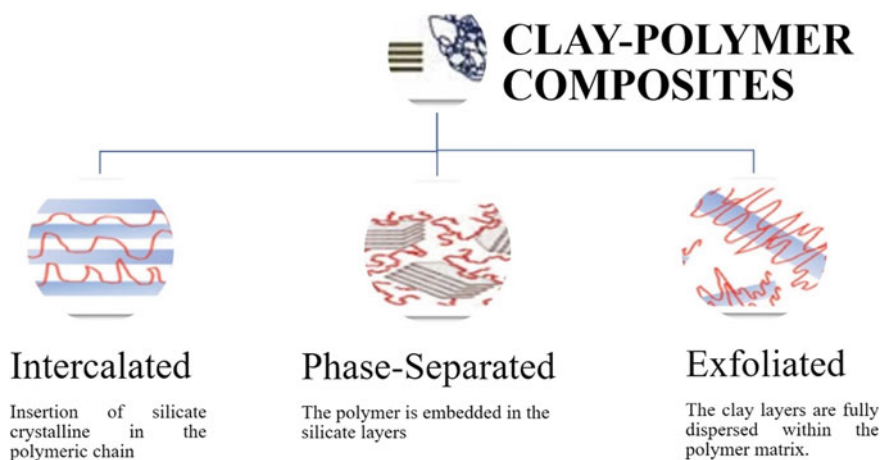


Fig. 2 a) Various types of clays and b) various polymers generally used in the formation of clay-polymer nanocomposites

Table 1 Classes of clay–polymer composites

Classes	Structure	Polymer (General examples)
1 1:1 clays		
Kaolinite	Two-sheet phyllosilicates	Poly(hydroxyl alkanolate).Imidazole, Resorcinol–formaldehyde polymer blends, Chitosan
1 2:1 clays		
Hectorite	Layered silicates	Poly(N-isopropylacrylamide) (PNIPAm)
Montmorillonite	Two tetrahedral sheets	Biopolymer, Chitosan, Polystyrene, Epoxy resin. Natural rubber, Chitosan-polyacrylic acid. Alginate-Aniline, p-cylcodextrine
Bentonite	Lamellar structure	Caprolactam (PA-6), Polystyrene, Phosphatidylcholine, Chitosan, Poly(vinylalcohol)
Vermiculite	Expanding three sheet phyllosilicates	Poly(vinylalcohol), Polyurethane, Poly(Lactic acid), Chitosan
Sepiolite	Sheet-fibrous structure	Polyamides, Polymethylmethacrylate (PMMA), Polyethylene terephthalate, Biobased Polyamide, Caprolactam (PA-6)

Figure 3 shows the schematic in which the clay/polymer hybrid composites are classified on the basis of the interactions between the clay and the polymer layers to adopt different morphologies.

**Fig. 3** Classification of clay–polymer composites based on morphologies [2]

2.2 *Different Categories of Clays Used to Synthesize Clay–Polymer Nanocomposites*

(a) **Montmorillonite-based polymer nanocomposites**

Montmorillonite (MMT), a commonly used clay, with general formula $M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$ belongs to the family of 2:1 phyllosilicate. It is a hydrophilic clay which is compatible with polymers like polyaniline (PANI). It has advantages of being naturally abundant and has abundant exchangeable surface charges and has the property of layer exfoliation [11]. Montmorillonite is a potential adsorbent of several cations and organic compounds due to its high cation exchangeability, Bronsted and Lewis type of acidity, huge surface area, chemical and physical stability, and layer structure.

Nanocomposites (NC) comprising MMT and polymer are reported to display greater toughness and strength [3, 13]. Montmorillonites exchanged with chain onium ions having more than 12 carbon atoms demonstrated an interesting benefit. Synthesis of nanocomposites NC with MMT clay phase intercalated in the cross-linked polyurethane network was achieved by the polymerization process of polyol isocyanate precursor and organoclay. The onium ion's structure and length had a significant impact on the intercalation process [14].

Hybrids of cellulose nanofibrils and MMT nanoplatelets are another interesting NCs that are reported to exhibit outstanding mechanical performance along with other features such as minimal oxygen permeability, thermal shielding, and fire retardancy. Optimal properties as compared to their pristine counterparts was achieved due to the aggregation and formation of multi-layered cellulose nanofibrils, MT NC with a weight ratio of 50:50 [15–17].

(b) **Laponite-based polymer nanocomposites**

Laponite is made up of octahedral layers of tetrahedral silica intercalated with layers of Mg^{2+} and Li^+ ions with a composition $Na^{+}_{0.7}(Mg_{5.5}Li_{0.4})Si_8O_{20}(OH)_4$ ^{0.7}. It displays a unit cell that resembles a disc and has a diameter of approximately 25 nm and a thickness of 1 nm. The silanol groups (SiO-), which are negatively charged as well as the groups formed by hydroxyl (MgOH and LiOH), augment the sorption capabilities of laponite-based clay nanocomposites. Depending on the pH of the surrounding solution, they could become positively or negatively charged.

The pH and temperature sensitive “smart” hydrogels such as polymethacrylic acid hydrogel are widely used in agricultural and biomedical fields as delivery methods for controlled release of drugs, fertilizers, and pesticides. Hydrogels do, however, have several drawbacks, such as poor mechanical and adsorption qualities. Incorporation of inorganic components, like clays, into the structure of these hydrogels are reported to alleviate these difficulties [18].

(c) **Sepiolite-based polymer nanocomposites**

Sepiolite, a magnesium phyllosilicate [$Si_{12}Mg_8O_{30}(OH)_4(OH_2)_4 \cdot 8(H_2O)$], has two layers of silica arranged in a tetrahedron and a layer of magnesium ions with octahedral coordination to form threefold strips. The strips are arranged to form channels

with water molecules. The presence of these channels significantly increases the specific surface area of sepiolite by 200–300 m²/g.

Polyamide-6 is a widely used thermoplastics in various industries such as electrical, automobile, and electronic, owing to the excellent mechanical properties. Nevertheless, the crack sensitivity, dimensional instability, and high moisture sorption reduced structural parts applications. Sepiolite had been introduced into the polymer matrix to enhance the mechanical, predominantly tensile and flexural strength and improve thermal properties [19, 20]. The majority of earlier research focused on using macro-size sepiolite as a beneficial filler in thermoplastics to form composites is now being replaced by nano-sized sepiolite. Furthermore, the sepiolite surface may be modified to improve its interaction with the chains of polyamide to improve the composite properties compared to the sepiolite of the unmodified surface. Asensio, *M et al.* investigated the effects of sepiolite orientation and concentration on the morphological, mechanical, and thermal properties of polyamide for structural applications in the automotive sectors [21].

Similarly, polymethyl methacrylate, an acrylic resin has poor thermal and mechanical properties could be improved by formation of composite with sepiolite [19].

(d) **Hectorite-based polymer nanocomposites**

Hectorite ($\text{Na}_{0.3}(\text{Mg},\text{Li})_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) is a trioctahedral smectite clay having an elongated platelet structure with an intrinsic negative charge balanced by exchangeable sodium (Na^+) ions with thickening properties. The hectorite clay provides large surface area and enhances the mechanical properties of the composite in which it is incorporated. A well-known temperature-responsive polymer poly(N-isopropylacrylamide) (PNIPAm) with hectorite as a filler has led to successful reinforcement composite [22].

(e) **Bentonite clay–polymer nanocomposites**

Chemical formula of Bentonite clay is $\text{Al}_2\text{H}_2\text{Na}_2\text{O}_{13}\text{Si}_4$. The surface hydroxyl groups and the structural permanent negative sites of bentonite clay particles each carry a separate type of electrical charge, which contributes to their capacity for cation exchange. The ability of some metal ions to enter their crystal lattice and alter their surface charge with interlayer complexation ability is well recognized.

The applicability of clay can be improved by formation of a composite with polymers such as acrylic acid [23]. To prepare the composite firstly acrylic acid was treated with base to give acrylamide followed by cross-linking with bentonite clay via N, N'-methylenebisacrylamide. The polymerization reaction was carried out at 70 °C in the presence of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ under nitrogen atmosphere to produce the nanoclay–polymer composite. The formation of composite was confirmed by Fourier transform infrared spectroscopy, scanning electron microscopy, and X-ray diffraction that indicated complete dispersion and exfoliation of the bentonite layers

in the composite, leading to an increase of the surface area with applicability in agriculture and environmental remediation.

(f) Kaolinite clay–polymer nanocomposites

Kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), a layer type 1:1 clay mineral, is made up of silicate sheets (Si_2O_5) joined to layers of aluminium oxide/hydroxide ($\text{Al}_2(\text{OH})_4$) through the arrangement of tetrahedral and octahedral sheets. The distance between the silicate layers is 0.72 nm [24]. The cation exchange capacity and specific surface area values of lamellar kaolinite can be significantly increased by exfoliation. To create a novel class of materials with enormous promise as super absorbents, drug delivery systems, tissue scaffolds, rheological modifiers, wound dressings, and biosensors, exfoliated kaolinite nanosheets can be combined with polymer to form nanocomposites.

The methods used for the synthesis of clay–polymer hybrid composites, the mechanism involved during the synthesis, the physicochemical properties of the composites prepared using different polymer matrices, and finally the application of these clay–polymer composites in removal of dye and heavy pollutants from waste water are discussed below.

3 Methods of Synthesis

Clay–polymer hybrid composites can be classified on the basis of method of synthesis. Figure 4 outlines the general methods of synthesis of nanocomposites.

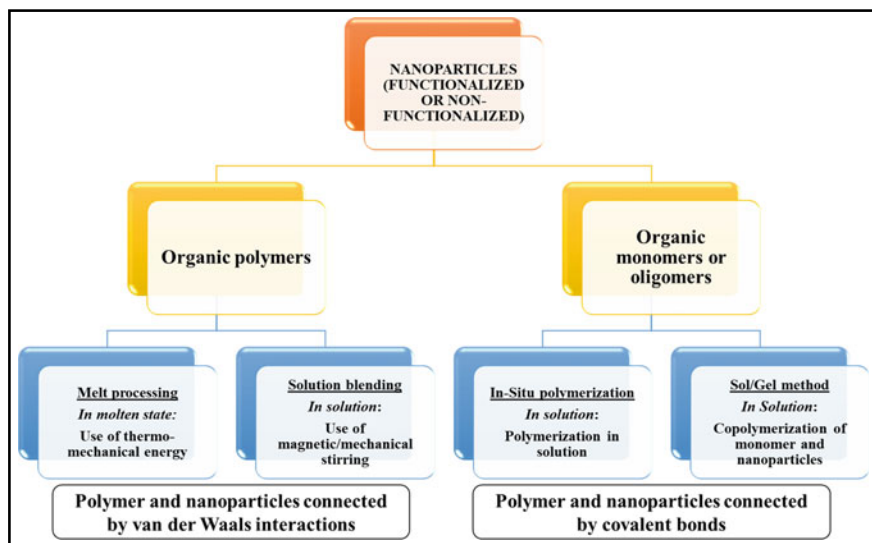


Fig. 4 Outline of the techniques used in the preparation of nanocomposites [2]

3.1 In Situ Polymerization Method

This method is mostly used to obtain well exfoliated clay platelets in the polymer matrix [9]. In this method, an initiation step takes place which results in the development of a hybrid between the polymer molecules and the organoclay. The organo-modified clay is swelled within a liquid monomer solution, which ultimately leads to the monomer dispersion in between the clay spacing. Thereafter, the polymerization process takes place to form the polymer. The polymerization step can be triggered by applying radiation or thermal energy along with a catalyst or an initiator which is added prior hand before the clay layers get expanded by ion exchange method [2]. The in situ polymerization method (i) tolerates resourceful molecular strategies of the polymer matrix, (ii) is an effective approach for the synthesis of polymer nanocomposites having extended property range, and (iii) is a technique which helps in developing an interface between the filler and the polymer matrix by modifying the matrix structure and its composition as well. This technique is generally used for formation of composite with thermosetting polymers.

3.2 Solution Blending Method

This technique is one of the easiest methods amongst the three methods available. This technique is also called solution-induced intercalation. The polymer is dissolved in a solvent initially along with clay dissolved in the same solvent separately. The clay solution is then poured in the polymer solution and homogenized for a uniform amount of time followed by evaporation of solvent [2]. However, use of organic solvents makes the method environmentally unsafe [25]. The major driving force in the intercalation process in this technique is the increase in total disorderliness of the system which is also called as desorption process of the solvent molecules. Solution blending method gives rise to uniform nanoclay dispersion.

3.3 Melt Blending Method

The melt blending technique is an industrially viable method which is eco-friendly and has high economic potential [1]. This method provides a better compatibility between the clay and the polymer as the polymer is directly reinforced in the polymer matrix. The mixture is then annealed over the polymer's melting point [2]. The melt-mixing generally results in three different polymer-clay morphologies. When the polymer is not able to diffuse in the interlayer spacing and the clay instead of getting dispersed stays in an agglomerate state, microcomposites are obtained. The intercalated nanocomposite is obtained when the multilayer morphology is seen with the polymer chains diffuse into the interlayer and the spacing is approximately

2–4 nm [10]. The third type of morphology obtained is exfoliated one where the individual clay platelets get suspended in a polymer melt with the interlayer distance of 8–10 nm [10]. The most preferred is exfoliated morphology which gives the largest matrix-filler contact area. The melt intercalation method provides an advantage that the technique is very specific as there is intercalation in systems where solvent is not involved. This technique is widely used for the fabrication of poly lactic acid/clay nanocomposites [25].

3.4 Sol–Gel Method

The technique involves dissolving the desired oligomer or polymer in sol–gel solution followed by hydrolysis and condensation of clay. The polymer involved in the composite can be cross-linked for better interaction with clay. Cross-linking by organo-functional silanes is widely adopted wherein the organo silyl groups can be hydrolyzed and co-condensed to form clay–polymer composite. Cross-linking leads to an improvement in thermal stability, resistance to solvents, and deformation.

Dual layer nanocomposite can be formed by sol–gel technique [26]. The advantage of this method is that a more uniform and well-oriented material is obtained. The surface area of the material is also high and nano-sized particles can be achieved with ease. The processing temperature here is low which results in homogeneity and the reaction can be controlled stoichiometrically to render pure products. The technique yields product which has high strength and high specific modulus [27].

Other types of modification include the formation of clay–polymer magnetic composites wherein the polymer matrix is filled with magnetic clay nanoparticles. Even clay–biopolymer nanocomposites have been formed to improve the properties such as surface functionality and reactivity. One of the best examples for this is the composite formed from chitosan which have proven to be excellent adsorbents for the removal of pollutants from water [28].

4 Characterization of Clay–Polymer Nanocomposites

Various techniques have been employed to characterize the composites. Techniques like Fourier transform infrared spectroscopy, scanning electron microscopy, field emission scanning electron microscopy, X-ray diffraction, Brunauer–Emmett–Teller (BET) analysis, UV–Vis spectroscopy, and high-resolution transmission electron microscopy (HRTEM) have been used [11].

XRD and TEM are two complementary techniques to analyse the structure of nanocomposites [2]. XRD is a useful technique for the determination of the interlayer space between layered silicates and the changes in the interlayer space during the formation of a nanocomposite. A decrease in the 2θ value that is the increase in d-value, due to expansion is indicative of formation of intercalated structures. This

expansion gives us an understanding that the polymer has penetrated the separation but there is preservation of the repeated layer structure. The structure of the silicate is unaffected in phase-separated polymer-organoclay mixes so the organoclay basal reflection remains the same. The exfoliated structures have a lot of layer separation due to which the layer stacking is interrupted, and hence, there are no observable peaks. This disappearance of the peaks is due to extreme separation or due to the lack of the order in the nanocomposite. However, XRD has some limitations, as it is imperfect for measuring delaminated and exfoliated polymer-clay nanocomposites as no peaks are visible in this case [2]. The degree of crystallinity offered by polymers and their composites impacts the application of that composite [14]. Exfoliation means disorderliness which sometimes also leads to amorphous peaks [6].

XRD of pure montmorillonite (the most common clay used for the formation of polymer-clay nanocomposites) can be seen at $2\theta = 7, 14, 19$ and 26° . And according to Scherer equation, the nano-montmorillonite shows crystallite size of 38.4 nm [15]. The peak of SiO_2 emerges at $2\theta = 26.96^\circ$, whereas the peak at $2\theta = 20.12^\circ$ is attributed to the aluminium silicate (Al_2SiO_5) [29]. Similarly, the kaolinite peak is seen at $2\theta = 9.58^\circ$ and 29.06° which shows some amount of crystallinity [30].

TEM provides better information about the structure and gives elaborate information about the morphology and defects present on the surface. The TEM images enable us to recognize the heavy atoms such as Al, Si, and O of the clay as well as the lighter atoms like C and H of the polymer. Even the filler atoms such as Na and Mg can be seen in the TEM images. The dark lines in TEM represent the layered silicates and the polymer appear brighter. So, this spacing between the dark and the bright lines gives the idea between the intercalation and the way the clay has been dispersed in the polymer [2]. For example, a well-known and common composite is between montmorillonite (MMT) and polyaniline (PANI), which has been well characterized using low angle XRD from an angle of 3° to 70° . Polyaniline exhibits peaks at about $2\theta = 15^\circ, 20^\circ$, and 25° while the MT used to synthesize the composite showed a typical peak at $2\theta = 6.08^\circ$, which corresponded to a d-spacing of 14.52 Å. If the peaks are sharp, it indicated crystallinity of the polymer [30].

Similarly, SEM images also help in knowing the structures of the composites. For example, a biopolymer-clay nanocomposite derived from biopolymer of *M. olifera* seed showed SEM images where a rough profile was obtained due to the insertion of biopolymer in between the layers of the clay structures. It showed that the biopolymer was well seated in the clay layers and the exfoliation of the polymer achieved was good. The SEM images thus helped in identification of the nanostructure composite formed in between the clay and polymer layers [14]. The signal intensity at each pixel usually corresponds to a number which is proportional to the number of electrons that are emitted from the surface and is represented as a greyscale value. Usually, as reported previously it has been seen that the fillers in general have been identified and characterized as white bands (upper grey values) while the polymer matrix can be identified as black bands (lower grey values) [10].

In case of FTIR, the pure components and the nanocomposites can be distinguished by the vibrational spectral bands obtained before and after nanocomposite formation. For example, in the polyaniline montmorillonite composite the typical

Si–O bands have been identified at 1016 and 1101 cm^{-1} which also were present in the individual components confirming the intercalation of the two components. FTIR helps to distinguish between the pure clay and the organo-modified clay too. MMT and the organo-MMT is one such example. The peaks obtained at 3600–3000 cm^{-1} were attributed to the OH and NH stretching which were obtained as broad peaks in the organo-modified MMT. The Si–O in-plane stretching was found in the range of 1003–1087 cm^{-1} which after the formation of the organically modified MMT shifted to lower energy by 10–12 cm^{-1} [6].

The Karaya gum-graft-poly (2-methacryloxy ethyl) trimethyl ammonium chloride/montmorillonite clay composite (KG-g-PMETAC/MMT) is another example where FTIR has been used to characterize the functional groups present in the composite. Here, the band at 1727 cm^{-1} has been attributed to the C = O stretching vibration, and the band at 1447 cm^{-1} is given to the bending vibration of quaternary ammonium groups present in the matrix. The bands at 1030 cm^{-1} , 910 cm^{-1} , and 852 cm^{-1} have been attributed to the presence of Si–O in-plane stretching, Al–O and Mg–O bending vibrations of the clay [31].

Techniques based on X-ray spectroscopy such as X-ray photoelectron spectroscopy, energy-dispersive X-ray spectroscopy, and near edge X-ray absorption fine structure spectroscopic techniques help in understanding the chemical compositions of the clay–polymer nanocomposites materials. Usually, the elements of interest in organic polymer nanocomposites that can be identified by XPS are C(1 s) at 285 eV, N(1 s) at 398 eV, O(1 s) at 531 eV, F(1 s) at 685 eV, Si(2p) at 99 eV, S(2p) at 164 eV, S(2 s) at 228 eV, P(2p) at 130 eV, P(2 s) at 188 eV, Cl(2p) at 200 eV, Cl(2 s) at 271 eV, and Br(3d) at 69 eV binding energies.

The carbon-based bonds as well as the main chain elements can be characterized by XPS. A more effective method which gives us more surface-sensitive information is angle-resolved XPS. Here, the detection limits are considerably reducing and the XPS signal from an area closer to the surface is obtained. If the thickness of the polymer film is less than 3λ , then the non-destructive vertical chemical composition and the distribution of the elements can also be analysed.

Energy Dispersive X-ray Spectroscopy is another widely used non-destructive technique for both qualitative and quantitative analysis. Here, the energy of the emitted X-rays is characteristic of the types of elements present in the material. This technique when combined with SEM helps us to closely examine the chemical composition of the three-dimensional structure.

Another emerging technique is the X-ray Absorption Spectroscopy which involves the near-edge absorption fine structure (NEXAFS) The edge where the X-ray is absorbed by the target is characteristic of the element in the sample as the signal is generated by the resonance of the electron waves and the backscattered electron waves of the other electrons surrounding the atom. K-edge spectrum of the carbon is examined when it comes to identification of C(1 s) electron in organic/polymeric materials and composites. The techniques provide both quantitative and qualitative analysis giving us an idea of orientation and composition of the material [32].

The thermal stability of the composite can be analysed by thermogravimetric analysis (TGA). The volatile matter that is liberated as the composite degrades as a

function of temperature is studied. The addition of clay in the polymer matrix adds to thermal stability. The TGA weight loss stages are generally divided into three main steps (a) the loss of water content, hydroxyl groups, and volatile compounds of the polymer, (b) decomposition of aliphatic chains and dehydration of the cellulosic rings or other components present, and (c) degradation of matrix remaining if any [15]. One of the examples for this is PMMA-MMT nanocomposites which has 40–50 °C greater decomposition temperature than the individual components [2]. Another example is the comparison of pure polystyrene (PS) and polystyrene nanoclay composite which again shows a 30–40 °C stability over the pure polystyrene.

The tensile properties can also be analysed. It is generally seen that the tensile strength in organically modified polymers increased with increase in clay content from 0 to 6 wt %, but the increase then ceased beyond 6 wt% and instead a decrease was found. The addition of organoclay increases the tensile strength and is due to the agglomeration of the organo-clay particles and intercalation between the organoclay and the polymer matrix [6]. The organically modified sodium montmorillonite by octadecyl ammonium-zinc oxide nanoparticles which has been incorporated in the chitosan matrix and used for food packaging has also exhibited similar behaviour [31].

BET analysis gives an idea about the surface area and the pore size of the polymer. For example, in the MMT/PANI composite [33], the PANI showed a porous morphology, whereas the MMT clay had a less porous morphology and therefore had a lesser specific surface area. The formed composite had a lesser surface area than pure PANI possibly due to the intercalation; however, the adsorption properties were found to be better than the pure PANI.

5 Application

Contamination and degradation of the aquatic environment are the major global concern of our society. The limitation of clean drinking water sources urges a necessity to either treat the waste before discarding it to the water bodies or treat the polluted water in rivers, lakes, and other aquatic bodies. A lot of industrial effluent including organic and inorganic wastes, heavy metals, dyes, and aromatic compounds is discharged in the water bodies untreated which pose a considerable risk to the clean drinking water sources. These are harmful to both humans and aquatic life in the water bodies. Thus, the removal of these pollutants is absolute necessity. Clay–polymer composites act as efficient adsorbents in the uptake of these pollutants and treatment of the water bodies.

With the growth of textile industries, the pollution of water bodies with the untreated discharged dyes is increasing. Dyes usually are synthetic in origin, have complex aromatic molecular structures which are more stable and difficult to biodegrade. They can be cancerous and mutagenic to humans. They also prevent the penetration of light from the surface of water thus hampering the photosynthesis process of aquatic life.

Heavy metals contained in industrial effluents constitute a major environmental concern as they are persistent, cannot be degraded/destroyed, and can be biomagnified by organisms. Presence of these metals above the permissible limits in drinking water can alter the metabolic body processes and induces impairment and dysfunction in blood and cardiovascular system in human adults and particularly in children.

The removal of these heavy metals and dyes using adsorption by clay–polymer nanocomposites remains an interesting area of research. Table 2 shows the recent application of clay–polymer hybrid composites in the removal/uptake of dyes and heavy metals.

The adsorption efficiency of dyes and heavy metals can be attributed to the electrostatic attraction between the pollutant and the adsorbent. The various interactions between the surface functional groups of the clay–polymer hybrid composite and the dye/heavy metal leads its adsorption on the surface of the adsorbent. For instance, Chitosan-Glyoxal/Kaolin used for the removal of Remazol Brilliant Blue R (at pH 4) has $-NH_2$, $-OH$ and $Si-OH$ groups on the surface. At the acidic pH value, the amino group as $-NH_3^+$ along with the positively charged surface of the composite material resulted in electrostatic attraction of the sulfonic acid groups of the dye. Hydrogen bonding and $n-\pi$ interactions between the clay composite and the aromatic ring of the dye further augment the adsorption process [32]. The electrostatic interactions and hydrogen bonding between adsorbent and adsorbate were confirmed from FTIR and XPS analysis. The appearance of characteristic peaks of functional groups of adsorbates in FTIR of composite and the shifts observed in XPS proved the interaction between them [11]. The interaction between Methyl Orange and clay–polymer composite were discussed on similar grounds by Kang et.al. [35]. Quin et al. discussed the interaction between Cu^{2+} and the clay composite based on the appearance of Cu^{2+} peak in XPS after adsorption and disappearance of the peak of sodium due to cation exchange between sodium ions and copper ions [36].

Thus, electrostatic interaction between the surface of the clay–polymer hybrid composite and the dye/heavy metal plays a role in the removal of the pollutant. Also, hydrogen bonding between the surface functional groups and those of the adsorbate contribute to the removal. If the molecular structure of the pollutant has the presence of aromatic rings, then $n-\pi$ interactions also contribute to the adsorption phenomenon.

6 Conclusion

This book chapter provides a comprehensive overview on the properties of clay–polymer hybrid composites, different polymers used for the surface modification which contribute to an enhancement in various physicochemical properties of clay, various methods of synthesis and finally the environmental applications of clay–polymer hybrid composites focussing on the adsorption of dyes and removal of heavy metals. The intercalated clay/polymer composites show high mechanical

Table 2 Recent application of clay–polymer hybrid composites in the removal/uptake of dyes and heavy metals

Adsorbent	Adsorbate	pH	Removal efficiency (%) or Adsorption capacity (mg/g)	Isotherm model	Kinetic model	Ref
Polyaniline/Montmorillonite clay nanocomposites	Green 25	6	100%	Langmuir	Pseudo Second order	30
Montmorillonite nanosheet/poly (acrylamide-co-acrylic acid)/sodium alginate hydrogel beads	Methylene blue	6.83	530.7 mg/g	Freundlich	Pseudo Second order	11
Polyacrylate/Bentonite	Pb (II)	–	1554 mg/g	Langmuir	Pseudo Second order	34
Chitosan/Montmorillonite	Methyl Orange in presence of Methylene Blue	3	1060 mg/g	Langmuir	Pseudo First order	35
Chitosan hydrogels/Montmorillonite nanosheets	Cu (II)	4	119.42 mg/g	Langmuir	Pseudo Second order	36
Chitosan/Montmorillonite	Methylene Blue	8	276.03 mg/g	Freundlich, Dubinin-Radushkevish	Pseudo Second order	14
Chitosan/Montmorillonite/Polyaniline	Methylene Blue	–	111 mg/g	Temkin	Pseudo Second order	37
Polypropylene-g-Maleic Anhydride-Chitosan/Montmorillonite	Pb (II)	8	90.9%	Langmuir	Pseudo Second order	38
Chitosan/Polyacrylic acid/ bentonite	Malachite Green	6	454.55 mg/g	Langmuir	Pseudo Second order	39
Cross-linked Chitosan/Bentonite beads	Crystal Violet	5	169.49 mg/g	Langmuir	Pseudo Second order	40
Chitosan-Glyoxal/Kaolin	Remazol Brilliant Blue R	4	447.1 mg/g	Langmuir and Freundlich	Pseudo Second order	32

(continued)

Table 2 (continued)

Adsorbent	Adsorbate	pH	Removal efficiency (%) or Adsorption capacity (mg/g)	Isotherm model	Kinetic model	Ref
Chitosan-Azadirachta indica/Kaolinite	Congo Red, Methylene Blue	6,7	104.66 mg/g, 99.01 mg/g	Langmuir	Pseudo Second order	29
Cellulose/Clay composite	Rhodamine B	2	95.6%	Redlich-Peterson	Pseudo Second order	15
Cellulose/Clay bio composites	Pb (II), Cd (II)	7	265.67 mg/g, 50.38 mg/g	Langmuir	Pseudo Second order	41
Carboxymethyl/Chitosan/Montmorillonite	Pb (II), Congo Red	5,7	87.95 mg/g, 91.77 mg/g	Langmuir	Pseudo Second order	42
Carboxymethyl cellulose-g poly (acrylamide)/montmorillonite nanocomposite	Malachite Green	7	172.4 mg/g	Langmuir	Pseudo Second order	43
Zr (IV) encapsulated carboxymethyl cellulose/montmorillonite	Reactive Red 2, Acid Orange 7	3	100%	Freundlich	—	44
Graphene oxide-montmorillonite/sodium alginate aerogel beads	Methylene Blue	5.99	150.66 mg/g	Freundlich	Pseudo Second order	45
Karaya gum-graft-poly (2-methacryloyloxy ethyl) trimethyl ammonium chloride/montmorillonite clay composite	Methylene Blue, Toluidine Blue, Crystal Violet, Azure B	—	155.85 mg/g, 149.64 mg/g, 137.77 mg/g, 128.78 mg/g	Freundlich	Pseudo First order	46
Tetraethoxysilane functionalized Na-bentonite polysulfone/polyethylenimine composites	Methylene Blue	—	99%	—	—	47

(continued)

Table 2 (continued)

Adsorbent	Adsorbate	pH	Removal efficiency (%) or Adsorption capacity (mg/g)	Isotherm model	Kinetic model	Ref
M. Oleifera/Bentonite	Cd (II), Cr (VI), Pb (II)	6–8, 2–4, 5–7	99.99%	Langmuir, Langmuir, Freundlich	–	14

strength, filler volume, tensile strength, and thermal properties which are beneficial from the point of view of environmental application of pollutants and remediation of waste water. Though the low cost and readily available clay minerals have been considered as adsorbents of choice, their practical use as adsorbents is limited due to their low adsorption tendency towards organic species, difficulty in regeneration and recovery. Clay-polymer composites combining the advantageous characteristics of clay minerals and polymers have emerged as attractive alternative with high adsorption efficiency, surface area and renderability. The different classes of polymers that have been used in formation of composites include chitosan, polystyrene, polypropylene, polyesters, polyurethanes, epoxies, and polyvinyl chloride. The synthesized composites are known to exhibit enhancement in the adsorption potential for effective removal of the pollutants. Methods such as in situ polymerization, solution-induced intercalation, and melt processing have been described in detail. The unique characteristics and properties of the synthesized material using the above techniques have been noted and described in brief. Various characterization techniques applied allows us to distinguish between intercalated, exfoliated, and phase-separated polymer clay nanocomposites. Through the tensile property studies, one can conclude the tensile strength especially in organically modified materials and increase with the percentage load of the clay up to 6% of weight after which a decrease in the tensile strength was seen. The later part of the chapter highlights the application of the clay composites in the environmental area such as removal/uptake of dyes and heavy metals from water resources. Hence, clay-polymer hybrid nanocomposites are highly promising material for waste water treatment along with robust and rugged material property for environmental application is now prominent for sustainable future.

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