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REVIEW

Nano clays and its composites for food packaging applications

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Abstract

In nature, nano clays can be found in abundance; they are phyllosilicate minerals with a platelet-like shape, flaky, soft structure, low specific gravity, and high aspect ratio. Physical, chemical, mechanical, and barrier properties are all greatly enhanced when clay components are included into a polymer matrix. Today's major nanocomposite food packaging is made from nanomaterials such silver nanoparticles, zeolites, nano zinc oxide, and nano clay. A variety of nano clay modification procedures allow for the incorporation of desirable characteristics into film packaging. Industries and academic institutions alike have been doing extensive research activities to examine the functions and application of nano clay for food packaging. Here, we review the many natural clays currently in use for food packaging. Nano clay safety and risk assessment issues are discussed, as are the features of nano clay composite, the process of oxygen and ethylene scavenging by clay, the use of clay for the engineering of composite film qualities, and so on. The possible toxicity of nano clay to people as a result of prolonged exposure is also discussed.

Keywords Food packaging · Nano clay · Nanocomposites · Nano clay composites · Active packaging · Natural clay · Clay materials

Introduction

Due to the rapid changes in consumer preferences, food packaging has undergone a tremendous transformation over the past few decades. Packaging's essential purpose in transportation and marketing has grown into a valuable role for preservation, identification, and information. Packaging has undergone a significant paradigm shift to improve customer health and safety. An active packaging feature has been designed to prolong the shelf life by incorporating elements that emit or draw substances into or from the packaged food. In contrast, smart packaging methods are those packaging systems that monitor packaged foods' conditions to access packaged food quality information. With all of these purposes, packaging has recently emerged to become the world's third-largest sector, representing around 2% of the gross national product in developed nations [1, 2].

Customer demand for processed and packaged food has led to rapid growth in the packaging business. Recent attempts have fulfilled consumers' expectations while ensuring product quality and safety during distribution through flexible packaging, high barrier material inclusion, sustainable packing, active and intelligent packaging. Changing food packaging and its environmental and socioeconomic consequences will impact the entire food processing sector. "The packaging industry has grown exceptionally at worth USD 700 billion at the global level. The food packaging business is at USD 277.9 billion and is expected to grow to USD 441.3 billion by 2025, at a CAGR of 5%" [3].

Over the course of the last two centuries, packaging has developed from a rudimentary container into an essential part of the design process for many products. Packaging has the objective of serving high-quality, appealing, and inexpensive products to the customers. The packaging industry undertakes significant efforts for industrial and sustainable solutions to optimize packaging material that will minimize the impact on the environment through reducing, reuse, and recycle [4]. Plastic, glass, and metal are primarily non-biodegradable raw materials in packaging applications today,

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which has prompted concerns about environmental pollution, indicating a severe problem for the global environment. Therefore, some biodegradable nanocomposites (c) having different functional characteristics for food packaging can be developed. The biodegradable notion in packaging is known as green packaging, and it includes plant, animal, and metal Nanoparticles. They can replace traditional sources of packaging material, hence reducing the negative impact on the environment [5]. Nanoparticles have been proven to increase packaging features such as mechanical, physical, barrier, and antimicrobial to improve the safe storage period. Low nanoparticle loading in conventional packaging materials can improve the polymer composite's initial properties, manufacturing technique, and process parameters. Nanocomposite packaging materials may be contained a variety of polymers and nanoparticles with the advancement in the features of food packaging. Nanotechnology has proven its potential reliability to improved food packaging functions from basic to advanced level, i.e., containment, storage, preservation, distribution, communication, and marketing of the food packages [6, 7].

A nanotechnology is a new approach that includes the characterization, production, and manipulation of structures, devices, or materials with a length of at least 1–100 nm [8–10]. Nanotechnology has diverse applications in food packaging, which has completely transformed the food sector in recent years by facilitating packaging functions such as active and intelligent packaging [4]. Nanotechnology has the potential to serve as the primary factor for food packaging development, such as nanocomposite, nanosensor, nanofiber, a nanoplate, nano antimicrobial, nanoceuticals, and nanocochleate [11]. As a result of these efforts, the search for acceptable materials for food packaging has been intensified. In recent developments, clay materials reinforced polymers known as Polymer–Clay Nanocomposites (PCNs) have demonstrated the potential to supplement the limitations of traditional food packaging solutions, especially cost-effectiveness, environmental sustainability, and consumer safety [12]. Crystallites are a type of nanostructured material composed of organic and inorganic additions with specific geometrical properties. It is immobilized and restrained by its crystal lattice and incorporated into bulk material such as polymers from synthesis and biopolymeric sources such as polyamide (PA), polystyrene (PS), polypropylene (PP), high-density polyethylene (HDPE), linear low-density polyethylene LLDPE, polyethylene (PE), nylons, polyvinyl chloride (PVC), polyurethane, and polyethylene terephthalate (PET), polylactic acid (PLA), poly (glycolic acid) (PGA), poly (caprolactone) (PCL), poly (butylene succinate) (PBS), poly (vinyl alcohol) (PVOH) [6]

Clay-based packaging is one of the sustainable nanotechnology applications in food packaging, where the polymers are reinforced with organic and synthetic nano clay materials. The term clay has several senses that refer to the relevant subject and its application. The clay materials are utilized in different commercial applications. It is used in geology for weather report prediction, petroleum industry, civil construction, agriculture, ceramic goods, plastic, rubber industry, and others, as shown in Fig. 1. Clay has received attention in industries, laboratories, and academics due to its abundance in nature and affordable cost. It also possesses a unique crystal structure, larger surface space, surface electric charge, and cation energy capacity (CEC). CEC promotes hydration, plasticity, swelling, and thixotropy in water [13]. The concept of PCNs emerged in the 1980s. Toyota was the first enterprise to experiment with PCN in the vehicle models for several years [14]. PCN is a hybrid material made from nanoscale particles such as sheets of silicates; for example, the Nanotechnology Product Database collected and analyzed nanotechnology products available in the global market. More than 8694 nanotechnology-based products from 2194 companies in more than 60 countries worldwide were registered in NPD. By August 2020, the NPD has recorded 222 nano clay-based products available in the market from 125 companies in 25 countries. These products are categorized into 70 classes, including electronics medicine, construction, cosmetics, environment, automotive, food and its packaging, agriculture, sporting and toys, paper and printings, soil treatment, water treatment [15]. The United States of America, China, India, Japan, and the United Kingdom contribute 29.7%, 17.6%, 7.7%, 7.7%, and 5.0%, respectively, of the total global production of nano clay-based products [16]. Table 1 shows the commercially available nano clay-based food packaging materials in the current global market.

Clay materials can improve the different properties and characteristics that are essential for the successful application of clay material in polymer composite matrices, such as dispersion tendency, high surface area, hydrophilic nature, and controlled polymer interaction in the matrix [13]. The application of clay materials in food packaging is now getting attention due to their mechanical, chemical, barrier (against oxygen, carbon dioxide, ultraviolet, moisture, and volatiles), thermal properties, and biodegradable nature. There are several benefits of clay-based food packaging over conventional neat polymer packaging. These include improved transparency, toughness, gaseous, moisture, and odor barrier, puncture resistance, abrasion and flex cracking, heat stability, and neutral to fat, grease, and oil. This review focuses on the naturally occurring clay materials for the food packaging application for a sustainable environment and a cost-effective source of biodegradable NCs for the improved food packaging application. It emphasizes the classification, properties, and application of different clay materials used in packaging applications. We also provide insight into the

Fig. 1 Commercial applications of nano clay minerals

safety concerns of the customers overusing nano clay-based food packaging.

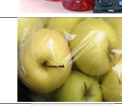
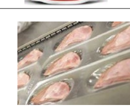
Classification of clays

Clay materials are composed of silicates in a layered structure which is termed (aluminum phyllosilicate). It contains ions of oxides as earth metals, alkali metals, organic metals, etc. The clay materials have been extensively explored as filler material in polymer matrix over the available nanofillers like carbon nanotube, graphene, nanocellulose, and nano-silica due to their reinforcing ability and suitable with polymer matrices [17–22]. The stack of sheets is the primary form of raw clay materials. The sheets are composed of piles of tetrahedral $[SiO_4]_4$- and octahedral $[AlO_3(OH)_3]_6$-structures that render the whole clay materials assembly. The tetrahedral are linked at corners as hexagons, whereas octahedrons are connected by one side [23]. The tetrahedrons and octahedrons are abbreviated as 'T' and 'O', respectively. The classification of clay materials is based on the number and ratio of the layer in fundamental structure, total charge, existing valency in the O and T. According to number and layer ratio, clay materials have three classes as below.

One–one tetra-octa hederal layer

It is a standard two-sheet Tetrahedron and Octahedron structure with an equal distance (inner layer distance) of 0.7 nm.

Table 1 Commercially available polymer nano clay composites available in current global market along with manufacturer, brand name, application and observation

Polymer nano clay composites	Manufacturer	Brand name	Food application	Observation	Film/container
Poly ethylene terephthalate /organoclay	Mitsubishi and Nanocor Ltd., Japan	Imperm®	Alcoholic and non-alcoholic beverage	High barrier and improved oxygen transmission rate	
Nano clay	Debbie Meyer Bread Bags, United States of America	Bread Bags™	Bakery products	High moisture barrier	
Poly ethylene terephthalate /Organoclay	Honeywell, United States of America	Aegis™ OX	Beer	Improved clarity and transparency	
Montmorillonite based polymer	FUJIGEL SANGYO LTD, Japan	NaturaSorb ® SN series	Food package barrier film	Chemical inert, economic	
Poly ethylene terephthalate /nano clay particles N-coat	Multifilm Packaging Corporation, United States of America	FOOTHILL FARMS ™	Cereal based Snacks and Ready to eat food	High gas barrier	
Kaolin	Imerys SA, France	BARRISURF™ FX	Fast foods	gas barrier, i.e., Oxygen, Nitrogen, Carbon dioxide, or microorganism barrier	
Polyethylene, Ethylene vinyl alcohol, Polyamide, Polypropylene and organoclay	Mondi Uralplastic, Russia	Poliplen ®	Meat, fish, and dairy products (tea, coffee)	The barrier to gases and odor	
Polyethylene / Polypropylene /Organoclay	TERM Mondi Uralplastic, Russia	Polyelf®	Meat and cheese package	Reduced moisture migration	
Nylon resin/Organoclay	Honeywell, United States of America	Aegis BarrierPro2™	Beverages	Excellent barrier to CO_2 and O_2 clarity and recyclability	
Organoclay	Laviosa Chimica Mineraria, Italy	DELLITE™	Fruits and vegetables	Less weight, greater barrier to gases	
Polyethylene/Polyamide/organoclay	BYBK Materials Technology, China	Suhou™	Soups	Antibacterial activity	
Kaolinite	NanoBioMatters Industries S.L, Spain	O_2Block™	Meat	O_2 scavenging activity	

All of the elements are distributed in such a way that the total electric charge between the two sheets is neutral (quasi-neutral). These are also known as the serpentine and kaolinite groups. Sheets are layered so that oxygen is present in front of the OH group of the adjacent layer, resulting in an interlayer hydrogen network. Pile of sheets is rich platelets with a few hundred nanometers of lateral extension and tens of nanometers of thickness. Clays such as serpentine, halloysite, and kaolinite are prominent examples in this group.

One-octahedral in between two tetrahedral layers

Two tetrahedral layers (side-wise) linked to one octahedral sheet form a three-layer materials type, designated as 2:1 or TOT type of clay materials such as mica, smectite, and vermiculite groups. This materials group has an exchangeable cation, which can be substituted easily with other available cations that form absorption capacity on the surface of the sheets.

Two tetrahedral with two octahedral

Each octahedral layer in the 2:1:1 structure is connected to another tetrahedral layer, and the net electric charge between these four sheets ranges from 1.1 to 3.3. This clay contains mica-like sheets with a negative charge that is balanced by a positively charged octahedron. This group of clay materials must include chlorites, donbassite, and chamosite. Clay's classification is ambiguous due to its diverse microcrystalline structured species, which are prone to variation in arrangement with numerous replacement possibilities. As a result, clay material classification has advanced in a different perspective and commercial application. "The nomenclature committee of the International Association for the study of clays (AIPEA) relies on the crucial structural data which depict there are different possible classifications of clay materials" based on various characteristics and properties. Following are some categories:

- The combination of layers "(T/O or 1/1; T/O/T or 2/1; T/O/T/O or 2/1/1)";
- The position of cation in the octahedron;
- The cationic filler interlayer;
- The interlayer components, such as cations and water molecules, are present.

Preparation of natural clay-based nanocomposites

Clay material preparation begins with mining and collecting raw clay, followed by crushing, drying, and screening of materials. Later, clay materials are classified based on the degree of dispersion/intercalation of the polymer, followed by various nanocomposite preparation methods and their applications in food packaging, as shown in Fig. 2. Clay dispersion is required in polymer matrices for the development of polymer composite packaging material. Covalent bonds, which cause clay dispersion in polymer matrices, are a source of concern between clay layers. Clay particles are modified before dispersion in the polymer matrix to address this issue. Changing clay materials involves expanding the space between clay sheets with functional moieties surfactant or hydrophobic grafting. This variation leads to ease in clay incorporation into the polymer composites, even in

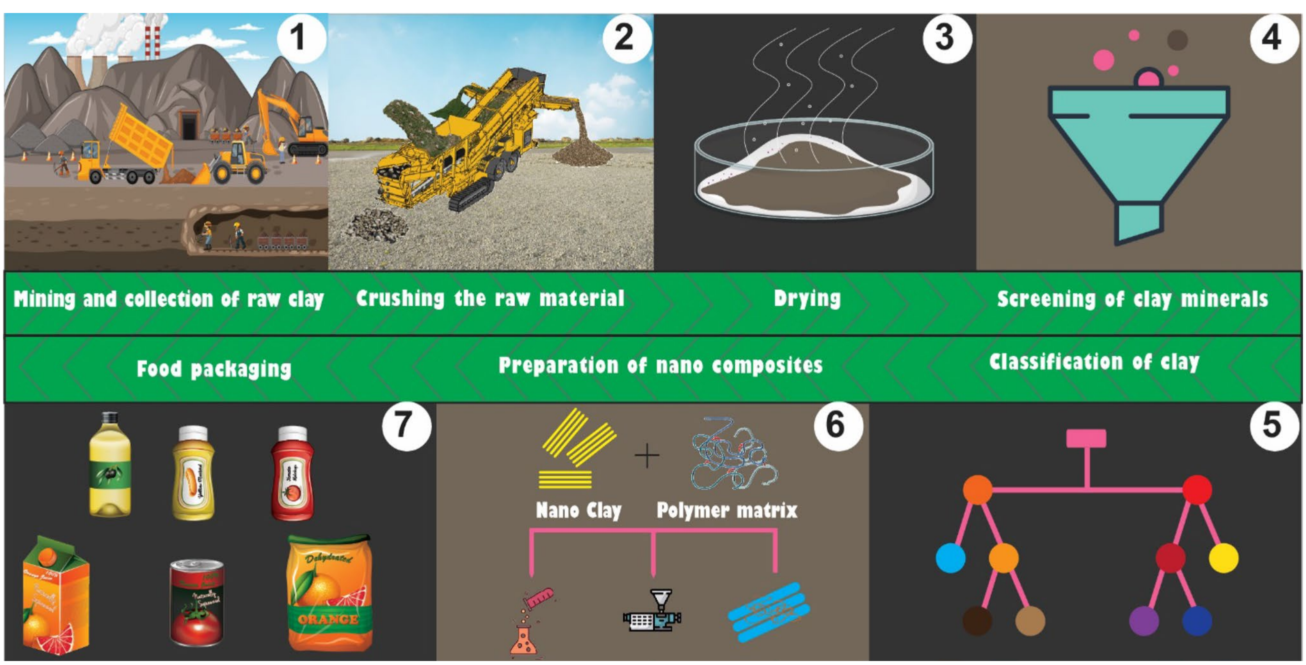


Fig. 2 Schematic representation of nano clay material life cycle beginning with the raw material collection, processing, preparation of nanocomposites and their applications in food packaging

the hydrophobic polymer nanocomposites (PNCs) [24]. Several studies have been conducted in the late 1990s on manufacturing characterization for food packaging applications. The polymer nanocomposite development involves different clay materials such as MMT, kaolinite, hectorite, and sepiolite. A wide range of synthetic (PE, PVC, nylon) and biobased polymers (starch, cellulose, PLA) have been investigated for the development with varying amounts of nano clay, i.e., usually 1–5 wt% [25].

The physical and chemical methods are the two most common methods for modifying clay particles. The physical alteration technique involves the adsorption of modifying materials on the clay surface. There is no change in the clay structure, which results in a minor improvement in the final polymer composites.

On the other hand, the chemical procedure is that the polymer is coupled with specific functional groups or organo-silane molecules onto the surface of the clay materials [22]. Furthermore, alteration is performed through an ion exchange mechanism caused by cationic and anionic functional groups. As a result, improved intercalation between the clay particles and modifying agents was achieved with chemical modification. Modifying agents improvised the dispersion of clay particles in polymer composite matrix when clay materials are spread in polymer matrices having a higher aspect ratio (length/width) and wide surface area, resulting in better performance features such as increased mechanical, barrier, thermal, and optical properties of composite matrix [22]. There are several methods for modifying clay materials for better incorporation in a polymer composite; however, in situ polymerization, solution-induced intercalation, and melt processing are widely accepted procedures.

In situ polymerization method

The polymerization method involves polymer insertion between the clay layers then expanding and dispersing the layers into the uniform fine matrix. This process enhances the suitability of polymer and clay particles. Then clay particles are infused with a fine layer to the bulk matrix, which later undergoes various processes like extrusion, compression, and casting [24].

Solution-induced intercalation

Solution-induced intercalation involves dissolving clays in a polymer solution to expand and distribute them. Initially, the clay material is mixed separately in a similar solvent/solution. Then, this mixture is allowed to combine with polymer–solvent/solution and homogenize for a short duration before casting it on a flat surface and removing the solvent/solution by evaporation [24]. Due to the high cost of solvents, this process was not economically viable for commercial NCs for polymers. There are specific health and safety concerns with this approach. However, this process is suited for water-soluble polymers. It is economical for the commercial manufacture of NCs because of the low cost of employing water as a solvent and the minimum health and safety issues [22].

Melt processing of nano clay-based nanocomposites

In this method, clay and polymers are intercalated during the melting process. When compared to the solution blending method, this method provides better polymer and clay material mixing. Clay particles are directly reinforced in polymer matrices using the melt-integration method. This method's efficiency may not be as high as in situ polymerization, and the composites formed by this method frequently have a partially exfoliated layered structure. On the other hand, the polymer processing industry can use the methodology to create NCs using the traditional method. This approach has a critical role in increasing the commercial production of clay/polymer NCs [22].

Effect of nano clay on engineering properties of packaging material

Nano clay is used to develop nanocomposite reinforced polymer due to its high mechanical, thermal, barrier, high benignity, and stability, low cost, availability, and sustainability [26–28]. The type of polymer, nano clay, and degree of dispersion are vital aspects in improving nanocomposite properties [29].

Mechanical properties

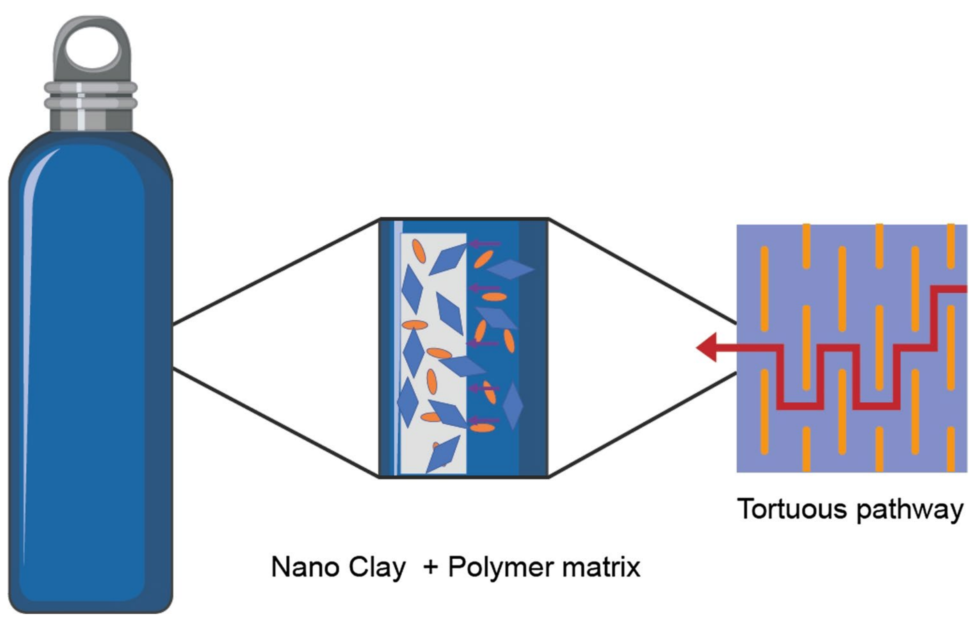
Mechanical property is one of the utmost requirements to develop a packaging material to sustain wear and tear during different operations throughout the complete food processing chain until the product reaches the customers. Tensile strength (TS), elongation at break (EB), and young's modulus are significant mechanical properties in food packaging. A polymer such as Nylon-6 demonstrates substantial improvement in mechanical properties, such as a 103% and 49% increase in Young's modulus and tensile strength, respectively, when using nano clay as a filler even at low loading (1–5 wt%) [30]. An improvement was observed in the tensile strength (TS) of gelatine-based biofilm with the increase in the halloysite nano clay, with low filler loading of 5% nano clay. TS is an essential requirement for food packaging materials as it allows them to withstand the applied stress during food processing, storage, and shipping [31]. A decreasing value of EB was noticed; however, it was not significant with three percentages of nano clay addition. The researchers noticed that decreasing value of EB is correlated with the potential of biodegradability of the film [32]. The elastic/young's modulus is associated with the content of nano clay in the polymer. Earlier, at 3% addition of nano clay, the young's modulus was not noticeable, however with increasing the concentration of nano clay, the value of young's modulus improved by ~ 60%, which can significantly improve the food packaging application [32]. One of the studies depicted that the enhancement of tensile strength of starch/montmorillonite (MMT) film with decreasing EB corresponding with increasing concentration of MMT [33].

A recent study was involved a potato starch mixed with nano clay MMT and a comparison of mechanical properties were made to control film, where they found that elevation in the level of nano clay leads to improved young's modulus (1.32–2.99 MPa%) and reduced elongation at break (EB) (80.80–55.72%). Reduced EB value attributed to intercalation of silicate sheets which cause a decrease in the flexibility and rigidity of film [34]. Similar results have been recited of mechanical properties like EB and TS in an earlier study where the nano clay halloysite was added as a plasticizer in different volumes (0, 2, 4, 6, and 8 wt%). The halloysite at concentration two percent significantly affects the mechanical properties as the lower filler loading level shows maximum TS and EB. When the filler is more than 2 wt%, both values TS and EB are reduced. This improvement is due to the accumulation of the nano clay; however, when glycerol was added without any nano clay, it exhibited maximum TS, and the film shows maximum EB value with eight percentage of halloysite nano clay addition to the film [35]. In a recent study with plasticizers and 2:1 Phyllosilicate smectite, hectorite was found to be applied in the preparation of film using a casting process. The mechanical parameters of the produced film support prior research that shows that nano clay increases the film's mechanical properties, such as TS, EB, and young's modulus. The young's modulus and toughness of the packaging film improved with increasing nanofiller hectorite content, but it increases dramatically beyond 10% weight hectorite [36].

Barrier properties

Barrier property is generally defined by the water vapor permeability and oxygen permeability of nanocomposite polymer or film. Clay-based NCs have shown excellent barrier properties compared to neat polymers. The diffusing molecules are restricted by well-dispersed, randomly orientated sheets of clay materials. The distribution of clay materials in the composite improves the aspect ratio and delay/hamper in the shortest pathway (tortuous pathway) for the migration of diffusive molecules such as gases, water vapor, and volatile compounds, as illustrated in Fig. 3. This arrangement of clay particles restricts the passage of gas and liquid molecules through the polymer matrix, resulting in a decrease in permeability. Barrier improvement in the clay/polymer composites suggested an attractive application of these materials' infiltration for different industrial solutions [37]. Various models have been developed earlier, assuming that random dispersion of diffusing molecules depends on the adjacent parallel layers of clay materials placed vertically to the diffusion orientation [38, 39]. The aspect ratio of the clay particle is responsible for reducing the permeability of the diffusing molecule through the polymer composites. They found that organoclay/nano clay alone cannot support the developed NCs. It has a limited driving force in the PET

Fig. 3 Improvement of the tortuous pathway with nano clay composite



polymerization, and degradation occurred at polymerization temperature. These disadvantages of organoclay can be overcome using clay-supported catalysts. The intercalation of stimulus into the clay layer improves the barrier property of the surface. The interlayer also creates a tortuous path that delays the migration of molecules from packaging material to food [40].

PET is extensively utilized for food packaging development. The exfoliation was stimulated at one percent OC (*N*-methyl diamine ester with adipic acid), which causes a twofold reduction in the permeability [41]. When a catalyst such as Chlorotitanium (tri-isopropoxide) was provided on the MMT, the oxygen permeability of film was reduced by 10–15 times with 1–5 wt% clay [40]. The addition of two percent dodecyl ammonium-MMT lowered the water vapor permeability coefficient by 50% [42]. Clay materials with low levels decreased significant absorption of O_2, H_2O, N_2, and other diffusing substances. Several findings suggest that incorporating catalysts improves barrier properties of the clay-based nanocomposite polymer for different applications. The clay materials and natural rubber (NR) latex NCs show excellent barrier properties for film or lamination in packaging film. The addition of 1–3 phr (per hundred resin) reduced O_2 permeability by 66% [43], use of 20 phr of Na + -MMT led to a reduction of 50% of N_2 permeation as compared to neat polymer matrix [44], 40% toluene, and 50% oxygen reduction observed with 3 phr of dodecyl ammonium-MMT in the NR-clay-based NCs matrix [45]. Different industrial companies, such as Nanocor and Mitsubishi Gas chemicals (New York), have produced nanocomposite nylon Imperim® with better barrier properties in film and bottle manufacture for food packaging industries. Barrier property is essential for liquid food packaging such as fruit juices, dairy products, carbonated drinks, etc. [46].

Thermal stability of clay-based polymer composites

Clay materials improve the dimensional stability (linear dimensional) of the nanocomposite polymer. The coefficient of thermal expansion (CTE) is high for the neat polymers, which is responsible for the elongation of the material on heating. Clay materials enable these polymers to sustain in high temperatures during the different processes with the preparation of PCNs. Higher CTE is responsible for dimensional changes during molding and hampers in the automotive process in food and pharmaceutical packaging [47]. High-temperature processing cause degradation of neat polymer-based packaging in different industrial application. So, it is imperative to understand the degradation mechanism of the polymer at high temperature, which will lead to modification with clay reinforcing into the neat polymer that provides heat stability to the clay/polymer NCs [48, 49]. It has been reported that some NCs combining with clay materials with the polymers HDPE [50], LDPE [51], LLDPE [52], PA [53], PS [54], PET [55], PVC [56], PBT [57], PPT [58], nylon 6 [59] epoxy resins [60] showed significant improvement in thermal stability as well as structure of the clay/polymer nanocomposite. The researchers depict that the clay layer's degree of dispersion and intercalation into polymers matrix led to high thermal stability.

Ethylene scavenging activity of nano clay

Nano clay is now an emerging innovative way to scavenge the ethylene from the food package. Porous clay heterostructure (PCH) is widely applied to prepare material having intercalation of a surfactant within the galleries of the clay layers. The aim of adding a functional group on the surface of the clay is to improve ethylene adsorption. PCH is modified with MTS to bind the methyl group for increasing ethylene adsorption in ethylene scavenger packaging. Two layers of phyllosilicate where tetrahedral sheets contain areas of Si^{4+} or Al^{3+} and octahedral layers consist of Mg^{2+} or Al^{3+}. Ethylene may be removed with surface adsorption active edges on the material such as kaolinite, cristobalite, clinoptilolite.

These clays can be incorporated into ethylene permeable sachet by extrusion process [61]. Ethylene removal using zeolite as an adsorbent material has received significant attention in pharmaceutical and food industry applications. It is mentioned that advantageous properties of the hollow porous area with cation exchange, adsorption, and molecular separating attributes. So, it is utilized as ethylene scavenging material into packaging films. There are several publications available in which authors have demonstrated zeolite application for ethylene scavenging activity [62–64]. A sachet containing a $KMnO_4$-loaded sepiolite was evaluated for ethylene scavenging activity and found helpful in reducing the release of ethylene content in the produce [65]. Ethylene scavenger system was developed with $KMnO_4$-sepiolite and combined with the modified atmosphere packaging (MAP). Results showed a significant reduction in product weight loss and delayed titratable acidity (TA) loss [66]. Halloysite nanotubes (HNT) are widely available green material from natural deposits. A high aspect ratio permits them to be utilized as nanocarrier in polymeric structure which is used as a discharge of active agents in NCs [67].

The ethylene scavenger activity of HNT has been examined and found that the material significantly improved the ethylene scavenging activity by 1 g of alkali-HNT from the product within 24 h of 49 Microliter from packed produce. HNTs are categorized as generally recognized as safe (GRAS) for application in food packaging [61]. HDPE film was modified with clay kaolinite to create oxygen scavenging film, and they observed the improved O_2 scavenging activity of 43 mL O_2/g at 100% relative humidity (RH) and

37 mL O_2/g at 50% RH [68]. A polymeric film with organo-modified montmorillonite (OMMT) and iron nanoparticles affects the physicochemical properties of the film with 2% of OMMT to PP film, the oxygen scavenging ability of the film increased by 77% [69]. Oxygen and ethylene scavenging properties of clay-based NCs promise excellent features in food packaging, enabling safe storage of fresh and packed foods. The application of clay-based composite for oxygen and ethylene scavenging activity depends on the approval and cost-effectiveness of the food grower and processing units. Thus, extra efforts should be taken to tackle the limitations and reduce the production cost of these technologies.

Applications of natural clay in food packaging film

Clay materials are widely available in nature, so it is inexpensive and rational to be utilized as a functional agent for food packaging. It significantly enhances the physicochemical and degradable properties of composite even at a lower filler load (< 10 wt%). Different surface modification of nano clay offers desirable divergent properties, making it a suitable choice for the numerous commercial applications [70]. Extensive research on nano clay has valuable functions in food packaging applications, such as active and intelligent activity. Other factors are responsible for incorporating nano clay into polymer matrices like polymer types, nano clay, filler loading percentage, processing techniques, desirable properties, and end-product applications. In all inorganic nano additives, nano clay materials are one of the most extensive studies in recent times.

Although phyllosilicates are commonly found in clay, they may also contain additional elements that give it strength and flexibility [71]. The majority of phyllosilicates used as nano clays in food packaging are layered because they are made up of layers that can be separated into individuals when needed. These layers range in thickness from 0.7 nm to several nanometers in length, resulting in nanoparticles with a high aspect ratio. The previous investigations on polymer-layered NCs (biodegradable and synthetic polymer), both in general and in the context of packaging, are shown in Tables 2 and 3 had some excellent assessments in the field have been published in recent years [72, 73]. MMT, hectorite, saponite, bentonite, vermiculite, rectorite, asbestos (chrysolite) are primary clay materials, which are most suitable for food packaging application with some others clay-like halloysite, sepiolite, and palygorskite [74–77].

Montmorillonite (MMT) clay-based nanocomposite

Among these clays, MMT is the most widely utilized in NCs preparation with the chemical formula $(Na, Ca)_{0.33}$ $(Al, Mg)_2$ (Si_4O_{10}) $(OH)_2 \cdot nH_2O$. MMT is widely available, and it has a high surface area and activity with high acceptance. These properties enable MMT a suitable clay for exfoliation and intercalation in the host polymer matrices. Cloisite is a modified MMT clay material that contains quaternary ammonium surfactant [78]. The structure of MMT is made up of two tetrahedral sheets linked to an octahedral sheet in the center. The modification of MMT with silicon, aluminum, iron, and cation by replacing oxide anion from the tip of the tetrahedral subunit [79]. Organophilic chemicals make up the majority of polymers. The layered silicates are miscible with nonpolar polymers, and a cationic–organic surfactant must replace the alkali counter-ions. Other "onium" salts, such as sulfonium and phosphonium, can be employed instead of alkylammonium ions. Surfactants can be utilized to enhance the clay's dispersibility. So, it is used to separate the layers (d-spacing) at different degrees according to the number of polar units in polymer, and it is termed as Organo-modified layers silicates (OMLS) or OMMT [80, 81]. MMT and OMMT have several advantages in food packaging application such as:

- MMT is compatible with hydrophilic polymers such PVOH, PLA, and biopolymers like starch, chitosan, and proteins to improve mechanical, thermomechanical, and oxygen and water vapor barrier characteristics in packaging films [82–84].
- MMT is modifiable with Ag^+ or Cu^{2+} nanoparticles due to its strong ion exchange capacity.
- OMMT can be easily combined with most hydrophobic and biopolymers to increase mechanical characteristics and water vapor and oxygen barrier capabilities.
- Antioxidants and antibacterial components are utilized to maintain the high surface area of MMT to develop nanocarriers for intelligent packaging.
- Enzymes can be embedded to the MMT surface to develop smart packaging, and metal ions can incorporate into the interlayer of MMT to create nano sensors for food packaging.

The polymer can be divided into three classes such as intercalated, flocculated, and exfoliated NCs, as depicted in Fig. 4. In the first case, polymer chains are placed with equal distances of clay sheets in a crystallo-graphical manner despite the ratio structure. Hydroxylated edge-to-edge involvement can be seen in the second interacted NCs and, finally, the third class of NCs, where clay sheets are randomly dispersed with polymer chains to make an advanced exfoliated structure. This clay and polymer chain orientation improved significant properties such as tensile and flexural strength and barrier properties [84]. A long list of polymers is utilized in developing food packaging like PE,

Table 2 Examples of synthetic polymer clay nanocomposites and their properties

Polymers	Filler types	wt%	Observation	References
Ethylene vinyl alcohol	Montmorillonite (MMT)		Improved barrier properties	[170]
polypropylene (PP)	Clay and hollow glass microspheres		Oxygen permeability performance improved	[171]
Polypropylene	Talc nanocomposite		Lightweight and strong	[172]
Low-density poly ethylene (LDPE)	Montmorillonite modified with copper ($MtCu^{2+}$)	4%	Antimicrobial effect increases up to 94%	[173]
Low-density polyethylene (LDPE)	Montmorillonite (MMT)	–	Increases compatibility and function in polymers	[174]
Low-density polyethylene (LDPE)	Montmorillonite	3%	Improved thermal stability	[175]
	Montmorillonite	10%	Tensile strength improved; O_2 and water vapor permeability decreases	
Low-density polyethylene (LDPE)	Montmorillonite	0.5–5.0%	Increases crystallinity and crystallization temperature; Tensile modulus and strength of filament increase	[176]
LDPE, maleic anhydride-grafted polyethylene (MAPE) and ethylene–vinyl acetate (EVA)	Montmorillonite	4.0%	improvement in tensile strength, tear strength, and oxygen barrier were	[177]
Low-density polyethylene	Montmorillonite	–	Tensile and barrier properties significantly	[178]
Low-density polyethylene	Silver-Montmorillonite	5%	Improved antibacterial activity against E. coli (70% reduction)	[179]
High-density polyethylene (HDPE)	Cloisite® 15A	3%	Maximum diffusion rate reduction	[180]
PE	Cloisite 20A	5%	Selectable barrier property	[181]
Polyvinyl alcohol (PVA) low-density polyethylene film (LDPE)	Vermiculite	–	Oxygen barrier properties were	[182]
Polypropylene (PP)	Montmorillonite	–	Reduced oxygen permeability	[183]
Polyamide (PA)	Cloisite 30B (C30B)	–	Increment in stiffness and oxygen barrier properties	[184]
Polyamide (PA)	Dellite 43B (D43B)	–	Lower oxygen transmission rate	
Polyethylene (PE)	Montmorillonite	0.3%	Lowering in O_2 and water vapor permeabilities about 55% and 70%	[185]
Polyethylene (PE)	Montmorillonite	2 phr	Thermal stability increases	[186]
Linear low density poly ethylene (LLDPE)	Organo-Montmorillonite	2–4%	Tensile strength improved by 45%; 48% increase in transverse stiffness; dart impact improves by 20%; the tear resistance rose 33% and the creep resistance by 20%	[187]
Polyethylene (PE)	Cloisite 20A	2%	Reduced water vapor transmission rate	[188]
Polyethylene (PE)	Organo-Montmorillonite	–	Clay dispersion and barrier property improved	[189]
Ethylene–vinyl acetate (EVA) Low-density poly ethylene, high-density poly ethylene	Organo-Montmorillonite Cloisite 20A	5% 5% 5%	Enhanced barrier by 30%; and tensile modulus by 37%	[86]
(Low-density polyethylene/maleic anhydride-grafted polyethylene (MAPE)	Organo-Montmorillonite	7%	TS improved significantly	[190]
Low-density poly ethylene/dimethyl dodecyl ammonium (DDA) Low-density poly ethylene/salt and octadecyl trimethyl-ammonium (OTA)	Organo-Montmorillonite	0.5% 2.0%	Co_2 and O_2 barrier properties increase significantly WVP permeability decrease 2.5 times	[191]

Table 3 Examples of biodegradable polymer clay nanocomposites and the changes in their properties

Polymers	Filler types	wt%	Observation	References
Pectin	Halloysite	5–30	Improved antioxidant activity, thermal stability, high hydrophobicity	[70]
Chitosan	Montmorillonite		Better antibacterial, better oxygen barrier	[192]
Polylactic acid	Cloisite 20A	5%	Water vapor barrier properties improved	[193]
Soy protein isolate (SPI)/polyvinyl alcohol (PVA) blends	Montmorillonite (MMT)	–	The improved TS and Young's; exhibit subtle reinforcing effect	[194]
Poly (lactic acid) (PLA)	Cloisite 30B, Cloisite 15A and Dellite 43B	3–5%	Enhanced thermal stability	[162]
Polyvinyl alcohol (PVA)	Saponite	5%	Thermal properties and oxygen transmission rate (OTR)	[195]
	Bentonite	5%	Improved Thermal stability	
Hemicellulose from oil palm	Montmorillonite (MMT	–	Improved thermogravimetry analysis (TGA), mechanical properties, and decreased water vapor permeability (WVP)	[196]
Chitosan	Montmorillonite (MM)	5%	Improved barrier properties Inhibitory effect on *Staphylococcus aureus* and *Escherichia coli*	[197]
Agar-carboxymethyl cellulose (agar-CMC) bio nanocomposites film	Montmorillonite	3–10%	Antibacterial activity against Gram-positive and Gram-negative bacteria	[198]
Cassava starch	Laponite	1–6%	Textural properties of film improved	[199]
Collagen	Laponite	–	Thermal stability increased	[200]
Pectin	Laponite	1–7%	Moisture migration reduced antimicrobial effect against *E. coli* and *S. aureus*	[201]
Carrageenan	Laponite	1–7	Adhesion property improved; barrier against O_2 water vapor reduced	[202]

PP, PET, PS, and PVC [85]. This problem can be overcome with nano clay involvement in developing PCNs.

The diffusion of gases, water vapor, and volatile molecule have a critical effect on the performance of the food packaging material. So, clay-based NCs are getting profound attention in recent times. The structures of the clay nanoparticles (CNPs) have a higher aspect ratio which improves the distribution of the clay sheets in the polymer matrix that create a tortuous path with better barrier property [84].

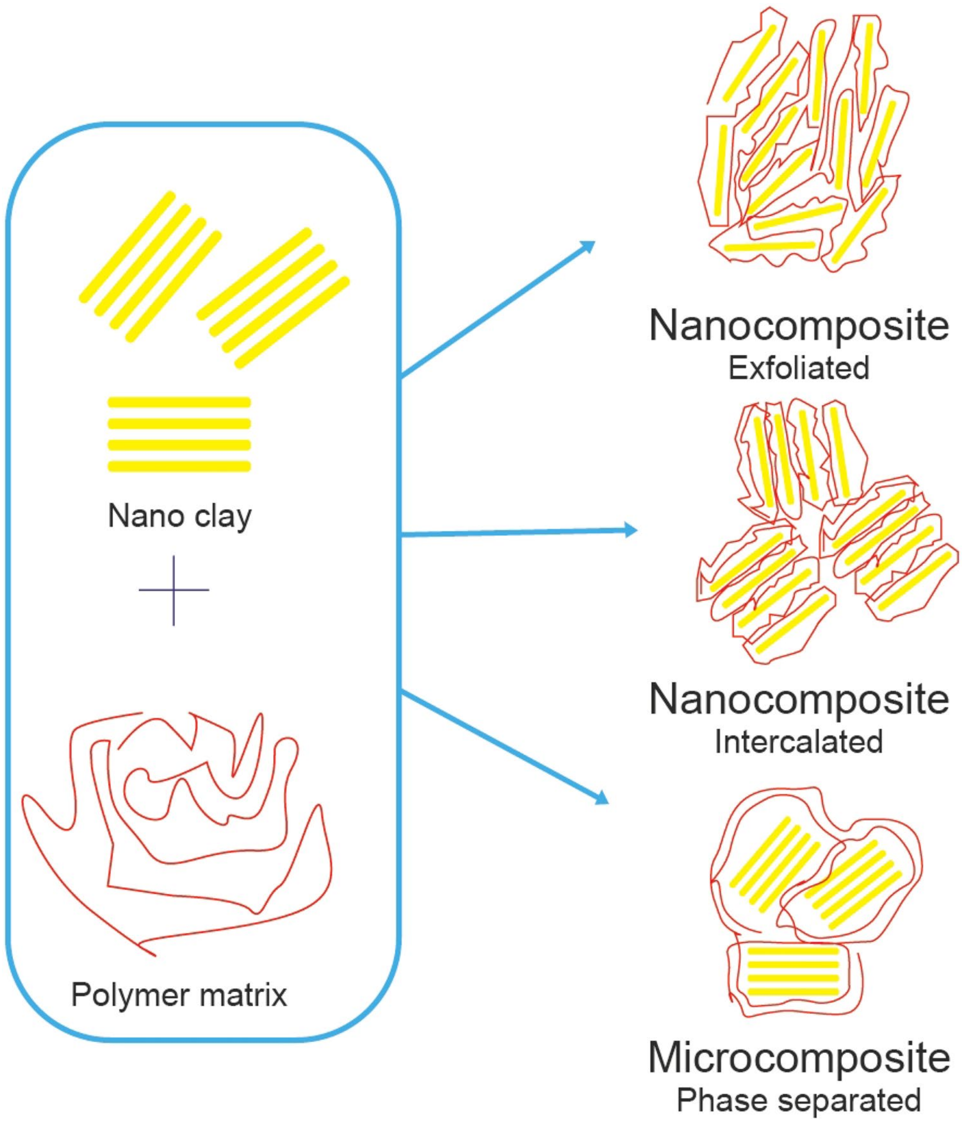
PE has been widely used in food packaging due to its mechanical and physical properties. The main types of PE are HDPE, LLDPE, very low-density polyethylene. Neat PE is branched plastic having a long molecular chain that causes low crystallinity value and possesses low tensile and compressive strength [85]. Low-density maleic anhydride-grafted (LDMAPE) reinforced with organo-modified MMT with dimethyl tallow benzyl ammonium ion to prepare PE/OMMT nanocomposite film. It has been observed that the addition of OMMT improved the clay nanoplatelet's dispersion in the polymer matrix, which led to an increasingly significant barrier property [86]. Polypropylene properties were evaluated with LDPE, PLA, and MMT incorporation. PP/LDPE at 80:20 w/w blended with PLA and MMT. PP/LDPE/PLA/MMT composite showed improved EB and tensile strength.

The morphological improved properties were found in the scanning electron microscope (SEM), transmission electron microscope (TEM), and X-ray diffraction (XRD) analysis which depicts the blend as biodegradable. The developed film exhibited holes and cracks on the surface after 60, 90, and 150 days of soil burial [87]. Polystyrene (PS)/OMMT NCs were prepared via solution blending procedure using $CHCl_3$ and CCl_4 as a solvent modified with hexadecyl trimethyl-ammonium bromide (CTAB) and improved thermal stability and water barrier properties observed [88]. Another study on the PS/MMT changed with dimethyl dehydrogenated tallow (DMDT) NCs prepared using a novel spray casting method, and they noticed a significant improvement in the barrier properties [89]. PET/clay nanocomposite prepared using OMMT cloisite 30B and cloisite Na^+, which exhibited enhanced mechanical and barrier properties [90]. Several other studies on the synthesis of biopolymers based on the MMT clay nanocomposite have shown tremendous improvement in nanocomposite properties.

Sepiolite clay-reinforced polymer nanocomposite

Sepiolite is a member of the 2:1 phyllosilicate family known as hydrated magnesium silicate, and its chemical formula is $Si_{12}O_{30}Mg_8\,(OH)_4(OH_2)_4\cdot(H_2O)_8$. It is similar to the MMT in structural base; the only difference is the insufficient

Fig. 4 Different types of clay nanocomposite structures



octahedral layer in the sepiolite structure [91–93]. This clay shows nanoscale tunnels structure in micro-fibrous morphological with particle size range 2–10 µm. This structure possesses a higher specific surface area (> 300 m^2/g) as well as porous volume (0.4 cm^3/g). The silica layer has a discontinuity in series at the tunnel's margins due to the presence of silane groups (Si–OH) [100]. It could be utilized as an adsorbent, catalyst, or catalyst carrier and thermal protector due to its unique structural orientation. A large interface area can be applied to polymer modification, which leads to solid intercalation and dispersion between the polymer matrix [93, 94]. When clay is used as an additive, it is generally known that it improves the characteristics significantly when it is nanometric in size, so it is applied as a nanofiller in NCs. These clay materials show a lower bonding tendency to the hydrophobic organic polymer, limiting its commercial application [95].

Sepiolite was reinforced with polyamide 6 (PA6) and trimethyl hydrogenated tallow quaternary ammonium (TMTH) modification, and the catalytic modifier effects were evaluated. They observed that the elastic rigidity and heat deflection temperature in PA6/ sepiolite nanocomposite increased ~ 2.5 times compared to neat PA6 [96]. Sepiolite was used as a reinforcing element to prepare a 90/10 (w/w) nanocomposite of PLA/styrene–ethylene–butylene styrene-g-maleic anhydride copolymer/sepiolite (SEBS-g-MA/Sep). They discovered that adding 0.5 and 2.5 wt% sepiolite to the mix enhanced the tensile modulus by 36.0 and 17.0%, respectively [97]. The solution casting method developed an alginate/sepiolite nanocomposite modified with myrtle berries extract (MBE) rich in polyphenol. The physicochemical, mechanical, and antioxidant properties were evaluated and improved EB, TS, WVP, and UV barrier properties. The antioxidant property was significantly enhanced with the MBE concentration and raised the potential applicability of sepiolite incorporated NCs in the food packaging [105].

A recent study of PET/sepiolite nanocomposite and tray have been developed and evaluated the different properties. And it is found that improved permeability of 30% even with less nanomaterial loading (1.37%) in the polymer matrix. Maximum mechanical strength has been noticed at 1.88% sepiolite loading. The antimicrobial property of the nanocomposite was found significantly improved with lowering the colony-forming units of mesophilic bacteria in the tray from (log colony-forming unit (CFU)/g 6.57–5.25) as compared to neat PET tray with (log CFU/g 3.83–2.98) [98].

Laponite clay-reinforced polymer nanocomposite

Laponite is classified as 2:1 clay with a chemical formula $Si_8(Mg_{5.45}Li_{0.4})\ H_4O_{24}Na_{0.75}$, and it is hydrophilic and biocompatible. Its well-defined nano-size layered form has been employed as a model in fundamental studies of PNCs to improve their physico-mechanical properties [99]. The alteration makes of laponite clay materials with different silane coupling agents such as aminopropyl trimethoxy silane (APTS), dimethyl-octyl methoxy silane (DMOMS), and aminopropyl dimethyl ethoxy silane (APDES). It is used to reinforce laponite in polymers and bind to the clay's surface; the hydroxyl groups were replaced by silane groups [100]. Apart from the silane group, some surfactants were also used to modify laponite like CTAB [101]. Inorganic compounds carry clay materials such as silica and iron that render the clear and transparent colloidal suspension of clay in solution. Because of this reason, laponite is suitable for the manufacturing of household products, personal care, paper, and polymer film for food packaging by casting method [102]. Laponite (1, 3, 5, and 10 wt%) was reinforced into Kafirin film, and found that the addition of laponite into the film makes it more robust and less pliable, suitable for various packaging and coating applications [103]. Laponite and carboxymethylcellulose (CMC) composites exhibit improved mechanical properties, water vapor barrier function (lowered 42%), and increased degradation temperature (about 65 °C) compared to the virgin CMC [104]. Cellulose nanofiber (CNF) was reinforced with the laponite in the 3.5:1 by mass and found higher thermal stability and improved water vapor permeability (157% for CNF/Laponite 1:1 by mass) [105].

Bentonite clay-reinforced polymer nanocomposite

Bentonite clay is composed of a silicate layer with a 2:1 ratio of calcium and sodium ions. The presence of impurities, such as quartz and mica, in naturally occurring bentonite clay components reduced their thermal stability. As a result, before the modification operation, the bentonite clay components must be cleaned [106]. Purification of bentonite clay components is, thus, required before integration and modification of the nanocomposite material for various applications. "Numerous modification methods improve the physicochemical and mechanical properties of bentonite clay, including CTAB, stearyl dimethyl ammonium chloride (SDAC), ammonium polyphosphate (APP), dimethyl dioctadecyl ammonium chloride (DDAC), and tributyl hexadecyl phosphonium bromide (THPB), tetradecyl ammonium bromide (TDAB), and benzyl triphenylphosphonium bromide (BTPPB)." Clay modification results in enhanced dispersion, more robust thermal stability, tensile strength, Young's modulus, EB, increased char yield, and polymer compatibility [107–111]. Bentonite clay is a low-cost filler that can be utilized in polymer matrices to improve desired qualities. Bentonite clay-based biodegradable food packaging films development shows significant potential benefits in sustainable food application to reduce the environmental pollution load due to synthetic and conventional packaging material. Active zein biofilm with different Zataria multiflora boiss and essential oil mixed with the sodium bentonite (2 and 4%) exhibits improved physicochemical and mechanical of active films by 2% sodium bentonite clay addition.

Additionally, antibacterial activity improved against *Listeria monocytogenes*, *Escherichia coli* [112]. "Cassava starch/ sodium bentonite/cinnamon oil (0.75% sodium bentonite, 2% glycerol, and 2.5% cinnamon oil w/w basis)-based film showed significant antimicrobial potential against *Escherichia coli*, *Salmonella typhimurium*, and *Staphylococcus aureus*". The meatball microbiological quality was evaluated at ambient temperature with the developed clay-based film. It has significantly reduced the bacterial proliferation to 96 h below the standard limit compared to the control film with 48 h [113]. Starch/glycerol/bentonite coating showed a higher barrier to water vapor as the water vapor transmission rate (WVTR) of the layer reduced significant level with 780 to 340 ± 20 g m^2/day with starch alone, this was further reduced 48–66 g m^2/day with bentonite added to the coating formulation [114]. A recent study of bentonite effects on the cellulose nanofiber for food packaging application was evaluated. Bentonite at different loads (15, 30, and 45 wt%) was incorporated into the CNF matrix, and observed physicochemical and barrier properties of the matrix were lowering the CNF degradation temperature was monitored and reduced the WVTR of the nanocomposite. The prepared nanocomposite with bentonite and CNF shows the potential solution as an eco-friendly alternative packaging material [115].

Hectorite clay-reinforced polymer nanocomposite

The 2:1 phyllosilicate is the most widely utilized layered clay material for PNCs, particularly smectite. Hectorite is plane and whitish in color smectite with the chemical formula $Na_{0.3}(Mg, Li)_3Si_4O_{10}(OH)_2$ [116]. It has a soft greasy texture and expensive clay with unique thixotropic nature. Natural hectorite has varied crystallinity, numerous impurities, and different geological and environmental conditions, limiting its application. Hectorite is a clay material easily produced in the laboratory and the industry using a hydrothermal method. These active edges react with one another; hence, modification is necessary. Acid treatment, ion exchange, grafting, and pillaring are significant improvement methods [117]. PA 66/hectorite nanocomposite has been observed under bending strain using a custom-built bending fatigue test setup in the controlled condition of the laboratory. Dynamic mechanical analysis (DMA) data showed a considerable rise in loss of modulus rigidity in frequency from 1 to 0.1 Hz and lowering the value of cyclic softening in the 2–0.5 Hz range of fatigue test frequency [118].

A biopolymer based on potato polysaccharide reinforced with hectorite starch-clay nanocomposite (SC-NC) exhibited higher mechanical characteristics and reduced crystallinity with an increasing percentage of hectorite clay in the composite. This improved the biodegradability of the nanocomposite SC-NC, while the swelling behavior decreased, an essential property of food packaging films [36]. "Fluorohectorite is a mixture of silicate, oxides, fluorides of lithium, and magnesium. It has a high aspect ratio, surface area, and good ion exchange capacity". EVA nanocomposite reinforced with nanofiller demonstrated high reinforcing capacity in the produced film [119]. Hectorite offers a heat stability advantage over montmorillonite despite being smectite because it lacks acidic sites that could promote polymer breakdown during melt-mixing procedures. Nanocomposite PVA has been used in packaging to strengthen the barrier (water, volatile chemical, gaseous) with hectorite [120].

Rectorite clay-reinforced polymer nanocomposite

Rectorite clay possesses an alternative arrangement, a dioctahedral mica-like layer of (non-expandable) and a dioctahedral montmorillonite-like layer (expandable) in 1:1 ratio has a structure of both MMT and mica. Rectorite layer thickness is about 2 nm and can extend up to several microns. Rectorite has utilization in nanocomposite filler to develop the food packaging films and coating; however, the reported work is limited. In general, the rectorite has hydrophobic, which is incompatible to reinforced with hydrophilic matrices [120]. Modified asphalt's physical and aging properties with waste polypropylene packaging (WPP) and rectorite were evaluated. The result showed that the developed composite had excellent flexibility and plasticity when four WPP and 1.5 wt% of rectorite content were added. The composite improves softening, deformation, and high-temperature stability than base asphalt without rectorite content [121].

In another study, lysozyme (LY)/rectorite incorporated into chitosan film exhibited enhanced antibacterial properties with higher mechanical strength. The composite of the film reveals that the dispersion of the LY and rectorite homogeneously in the chitosan film. The addition of LY and rectorite enhanced the hydrophobic characteristics of the chitosan films, as measured by the water contact angle. After adding LY-rectorite, the mechanical parameters of the composite films were reduced by 27.58% compared to chitosan films, yet they still had high tensile strength [121]. Epoxy acrylate (EA) coating was incorporated with modified rectorite through ultraviolet curing technique. Rectorite was modified using octadecyl trimethyl-ammonium chloride (OTAC) and [2-(methacryloyloxy)ethyl] trimethyl-ammonium chloride (MAOTMA) rectorite. The nanocomposite morphology was investigated with the SEM and TEM, and it exhibited better dispersion in the composite. The nanocomposite with three percent rectorite showed better thermal stability; flexibility decreased with clay percentage [122].

Other nano clay materials-based nanocomposites

Kaolinite is a simple clay found on the earth's surface that is widely applied as a raw material in various household and industrial utilities. Kaolinite is a 1:1 phyllosilicate with an octahedral aluminum hydroxide with a tetrahedral silicon oxide sheet. This asymmetric structure allows strong hydrogen bonds between layers, resulting in high cohesive energy. The introduction of polymer chains between the kaolinite platelets is considerably hampered due to the high layer-to-layer contacts [123]. Surface modification of kaolinite employing a silane coupling agent improved the mechanical characteristics of a virgin polymer mix significantly [124]. Cassava starch/kaolinite composite film is prepared with dimethyl sulfoxide (DMSO) modification. The developed film exhibited improved transparency, water uptake in the matrix, and UV light transmission reduced [125].

A similar study was conducted with nanocomposite of EVOH/kaolinite by melting process. The nanocomposite exhibited higher mechanical and thermal performance, the water diffusion coefficient in the developed matrix decreased by 50%, and the oxygen barrier increased by 50% [126, 127]. Sago starch/kaolinite/polyolefin and PCL/Ag-kaolinite with iron modified developed for active food packaging [68, 128, 129]. The application of vermiculite in food packaging has been reported; however, its application is not as extended as other clay materials. Butyl rubber/vermiculite composite and polylactic/vermiculite blended by in situ intercalation polymerization. Polyethylene/organo-modified vermiculite nanocomposite showed blend has high mechanical, physical, barrier properties, and antibacterial properties [74, 130, 131]. Some phyllosilicates, such as asbestos (chrysotile), halloysite, and sepiolite/palygorskite, are fibrillar rather than laminar. Both halloysite and palygorskite have a lot of applications in food packaging.

Challenges of using clay in food packaging applications

Nano clays have attracted much attention due to their excellent physical and mechanical strength, antibacterial property, and high barrier. Hence, it allows them to be included in nanocomposite production with various synthesis. Despite all the advantageous features, the application of nano clay is still a matter of concern for the safety and well-being of customers. The major problem is nanoparticle migration from food packaging to food or beverages. According to some studies, the smaller the nanoparticles are and the lower their density, the more likely they are to be transferred to food and cause health concerns for the consumer [132, 133]. The migration of nanomaterial from nanocomposite to food depends on the exposure level. The development of nano clay-enabled NCs for commercial food packaging applications prioritizes consumer safety. Nanoparticles may have varying toxicity due to differences in physical, chemical, optical, and magnetic properties, but their impact on human health cannot be underestimated. There is no evidence of nanoparticles causing acute toxicity, but the long-term effect of accumulation in the food chain remains unanswered [134]. The liver, kidneys, spleen, heart, lungs, and brain receive bio-distribution through systemic circulation.

It is well understood that the liver, kidneys, and colons are principally responsible for nanoparticle and potential metabolite excretion [135]. There is no standard regulation in Europe or elsewhere to monitor the application of nano clay in food packaging formulation. As a result, "nanotechnologies in food packaging covered by existing legislation comply with the provisions of the European framework regulation EC 1935/2004 (European Commission, 2004) that sets the general standard to ensure that migration of the substance from the packaging into the food can be prevented" [136]. Food and Drug Administration (FDA) has also not established any regulatory definitions for "nanomaterial," "nanotechnology," "nanoscale" [137, 138]. The European Food Safety Authority's (EFSA) strategic line is based on a proper risk assessment technique and the potential risk associated with PNC utilized as food contact material. In particular, on nanomaterials, especially new technologies that create substances in particle sizes that exhibit physicochemical properties considerably diverging from those at a larger scale. Nanoparticle risk assessment is conducted on individual events until further understanding about the innovative technology is obtained [139].

As a result, the risk assessment associated with nano clay in food packaging applications is far broader than the nanoscale paradigm, which entails two unique challenges:

- Migration of nanoparticles and their constituents form nanocomposite into the food;
- The impact of nanoparticle incorporation on other components (monomers, food additives, or processing aids) with potential toxicity.

The inclusive evaluation of any polymer NCs for direct contact must necessarily include these above two investigations [139].

Migration and exposure of nano clay materials to human body

Nano clay is natural; however, nano clay-based PNCs for food packaging necessitates careful consideration of the harmful effects on consumer and environmental health [140]. Nanoparticles can enter into food after interacting with components during processing, storage, and distribution. Clay-based nanocomposite materials must demonstrate the safety of the nanoparticles during regular use, disposal and recycling. Nanoparticles can enter the biological system via various routes or migrate to food from contact material and eventually interact with body cells, as shown in Fig. 5. As a result of recycling and disposal, they may contact plants, animals, and humans [141]. Migration is generally defined as the mass transfer of low molecular particles into the host product. Since packaging material cannot be chemically inert, direct contact can substantially migrate into the product. It becomes vital for the non-intended transfer that has been occurred of undesirable packaging constituents that may affect the consumer's safety [142]. Nanomaterials can migrate into food from composite, which can change the quality of food products such as TiO_2 cause rancidity in high-fat foods [143]. Several researchers have been interested in gaining attention to the potential and possible conditions for the migration of nanoparticles from the PNCs in recent years. Evidence is available associated with nanoparticle release during machining, weathering, washing, contact, and incineration. The available publications show the migration of nanomaterials from the food packaging materials like Ag-nanoparticle, TiO_2, TiO_2, ZnO [144, 145].

The researchers classified the migration of nanoparticles based on the particles' quantity, type, and size. However, the informed incidents of nano clay migration from the nano clay NCs are scarce. In a study, a theoretical approach to MMT diffusion is considered negligible from the packaging material due to its slow transfer rate because of larger size and morphological differences between platelet-like nano clay and spherical silver, iron, zinc, or titanium nanoparticles

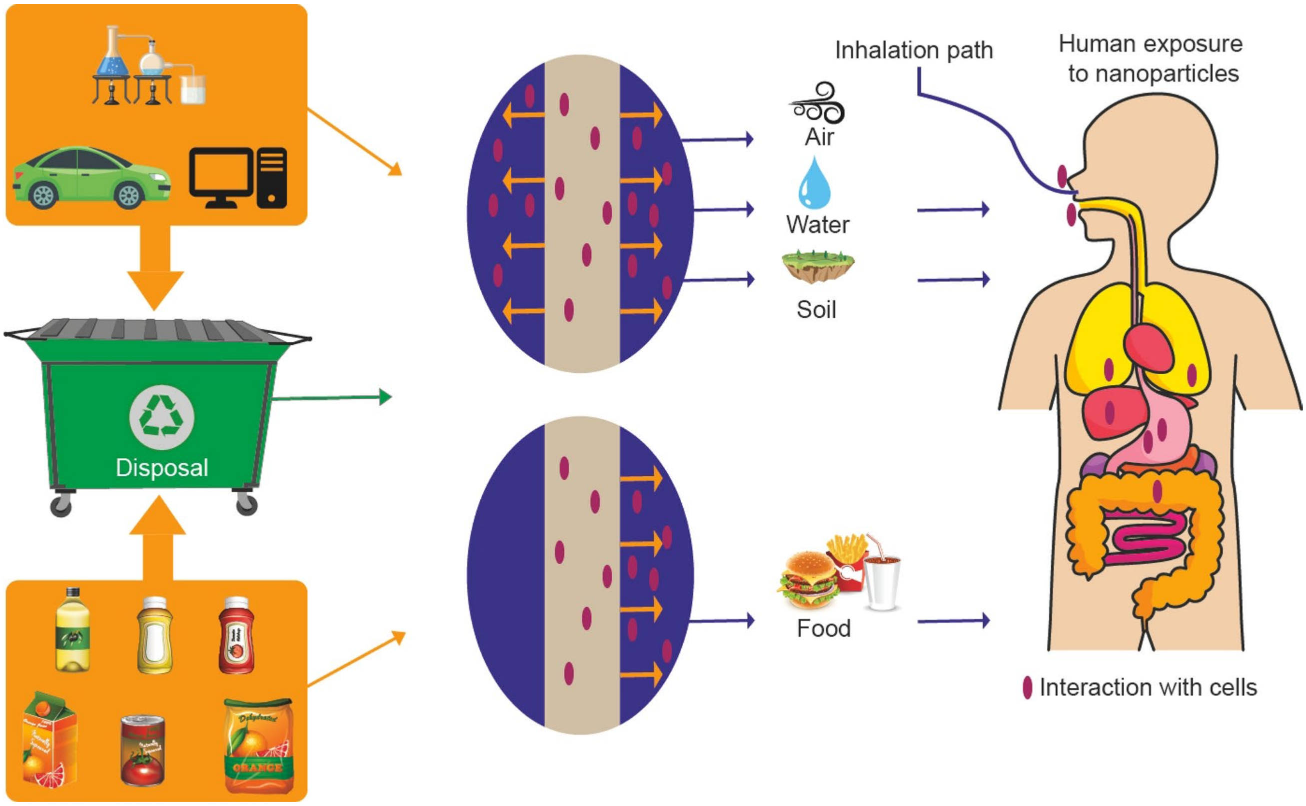


Fig. 5 Potential routes for the migration of nanomaterials to humans and the environment

[146]. There are some investigations available that demonstrate the MMT release by measuring the essential component (mainly Si) from 3 to 5% (w/w) of nano clay loading into the PNCs [147–149]. The migration value of MMT measured from the PNCs in various food simulants is very low, which did not exceed the considered level frequently seen in food materials. In this regard, consumer exposure and safety risks PCNs were minimal, even though recent research indicated migration of the nano clay MMT from commercial packaging during shredding [150]. A study observed that PP/MMT composite has lower migration of airborne particles than the neat PP during shredding.

The nano clay particles remain attached to the PNCs, preventing the nano clay from migrating into the atmosphere. According to the findings, recycling nanocomposite should not cause any health concerns to workers or the general public than recycling neat polymer [151]. Similar results were obtained during mechanical drilling with PA 6/silica and PA 6/MMT NCs, implying that the presence of nano clay can lower the concentration of generated particles during drilling and particle deposition [152, 153]. Mechanically driven processes such as desorption, dissolution, and degradation of the matrix with clay also influence nano clay release. Weak hydrogen bond led to the desorption of the nano clay into the migrants, and concentration gradient also induces migration of the nanoparticles from the interior of the NCs. Another critical factor is high temperature or UV exposure of nanoparticles, leading to polymer matrix degradation during processing [154]. Time is also a significant factor because nano clays have a large surface contact area with the polymer; it may take longer for food simulants to erode the polymer and dislodge a nanoplatelet than a spherical NP. Although nano clay is embedded into the polymer matrix with different organo-modifications to enhance the overall nanocomposite performance's compatibility and properties, these particles are still released during wear and tear. According to EU regulations, the total limit for migrating plastic-based food packaging material or particles is 10 mg/dm^2 of packaging material surface area. However, for bigger containers, such as 500-mL–10-L food containers or filled products. The measurement surface area of the stopper, caps, gaskets, or closing area is problematic; the restriction mentioned above is increased to 60 mg of particle emitted per kilogram of foodstuffs [155, 156]. The existing migration studies suggest that the migration from clay composites is modest and acceptable to be used for food packaging. There is a need for more extensive research that focuses on each food simulant individually; on the other hand; it could help with more effective evaluation and regulation.

Toxicity of nano clay in food packaging materials

The wide application of nanoparticles has gained in recent time with the advancement in the material performance it has brought attention towards safety-related issues. The environmental emission via air, groundwater, and soil has reached the internal part of organs which might be sensitive to this nanoparticle to some extent. The migration of nanoparticles into the environment harms resources like water, soil, plant, and living organisms. Moreover, for food packaging, these nanoparticles can bind nutrients or interact in an undesired way, which could be the source of harmful reactions of nanoparticles to the consumers [27]. Nanoparticles can enter the environment through different mechanisms, but their stability duration in the atmosphere is still an unanswered question. Boxall et al. estimated nanoparticle concentration in the air, soil, and water in the range of ng/L–µg/L. They observed the level of nanoparticles in the environment is lower than lethal and sublethal effects with low indication level of risk [157].

There are three possible ways of nanoparticles entering the body: inhalation, penetration through the skin, and ingestion through an oral path. Still, there is doubt in the customer's mind that indirect exposure due to migration can ultimately affect the health and safety of individuals. The workers in the nanomaterial-producing factories are prone to inhalation, and penetration of nanoparticles through the skin is entirely a safety issue. It is recommended them to protect using gloves, eyeglasses, and mask with highly efficient filters. It is vital first to investigate the migration extent of nanoparticles from the packaging material to food for food packages related to migration. If there is any migration, the duration of ingestion and penetration of nanoparticles in the human body from mouth to the gastrointestinal tract is essential to investigate its effect on the body. It is imperative to understand the accumulation and excretion mechanism of nanoparticles in human organs [27]. The penetration of nanomaterials depends upon the skin type and the properties of the nanomaterial. Available data suggested that nanoparticles with a size of more than 10 nm are not penetrating through the skin. If any event is observed, toxicity depends on the penetration site's barrier function and clearance mechanism.

Additionally, the translocation of these nanoparticles from the penetration site depends upon the nanoparticles and organism interaction [158–160]. There are proofs available on the toxicity of nano clay on a living organism. Bentonite, MMT, cloisite 30B, and organ modified nano clay did show some cytotoxicity [161–166]. Researchers found that platelets structured nano clay are more toxic than tubular ones, so the toxicity depends upon the nano clay materials [166]. According to EU regulation, the implementation of food packaging is considered to be a safe practice. The size of the host polymer and nano clay sheets in the NCs is a crucial characteristic from the EU standpoint. The surfactant employed for organic modification of nano clay must also be approved for food contact by EU law or the FDA [136, 167–169].

Conclusion

Understanding the physicochemical properties of food and the packaging material plays a vital role in food packaging development practices. There is no absolute inert material that has zero migration at all from packaging to food. Nano clay has shown the potential for emerging filler materials for the host composite matrix. Synthetic polymers hamper environmental health. Hence biopolymers are getting priority over synthetic polymers due to their biodegradability and compatibility. Nano clay provides a remarkable improvement in the resulting material's physicochemical, mechanical, barrier properties, and degradation capacity. Compatibility and excellent dispersion qualities are essential in the preparation of PCNs. The application of nano clay has broadened its paradigm with different promising functions such as antimicrobial activity, active processes, colorimetric indicator, and additive partitioning. Environmental protection has become a priority, and food packaging has a considerable contribution in terms of conventional synthetic polymer-based material which, is non-biodegradable.

It is an urgent requirement to protect the environment from replacing synthetic material with biobased or degradable material for food packaging applications in the future. Again, understanding and knowledge of the available biodegradable resources for commercial application implementation remain an obvious challenge. The lack of consumer and environmental safety legislation for nanoparticles appears restrictive in applying nano clay in food packaging development. The advantage and limitations of the nano clay have become evident now. But there is still a long way to go to attain and tune this attribute. Research and development in these areas will not only benefit current uses but also lead to new markets in developing new materials for commercial applications in the future. The construction of PNCs with clay materials expanded for extended desired properties of packaged food is a recent concept with recognized future potential.

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Declarations

Conflict of interest The authors declare that there are no conflicts of interest.

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