Eco-Friendly Polymer-Layered Silicate Nanocomposite–Preparation, Chemistry, Properties, and Applications

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Abstract This chapter aims at exploring the revolutionary field of nanotechnology and some of its promising aspects in polymer nanocomposites in view of preparation, characterization, materials properties, and processing of polymer layered silicate nanocomposites. These materials are attracting considerable interest in polymer science research. Polymer layered silicate nanocomposites are an important class of hybrid, organic/inorganic materials with substantially improved mechanical, thermal, and thermomechanical properties in comparison to pristine polymers. In addition, they also show superior ultraviolet (UV) as well as chemical resistance and are widely being investigated for improving gas barrier and flame retardant properties. Hectorite and montmorillonite are among the most commonly used smectite-type layered silicates for the preparation of polymer–clay nanocomposites. Smectites are a valuable mineral class for industrial applications due to their high cation exchange capacities, surface area, surface reactivity, adsorptive properties, and, in the case of hectorite, high viscosity and transparency in solution. A wide range of polymer matrices are explored for the preparation of polymer–clay nanocomposites, however, this chapter deals with special emphasis on biodegradable polymers—cellulose and natural rubber. Also, the chapter describes the common synthetic techniques in producing polymeric layered silicate nanocomposites, its properties, and applications.

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Abbreviations

AFM	Atomic force microscope
AMPS	2-Acrylamido-2-methylpropane sulfonic acid
CA	Cellulose acetate
CAB	Cellulose acetate bioplastic
CB	Carbon black
CEC	Cation exchange capacity
CNBR	Carboxylatedacrylonitrile butadiene rubber
Cs30B	Cloisite 30B
Cs93A	Cloisite 93A
CTAB	Cetyltrimethylammoniumbromide
DNA	Deoxyribonucleic acid
DSC	Differential scanning calorimetry
e.g	Example
EA	Ethanolamine
EIC	English Indian Clay
ENR	Epoxidized natural rubber
EPDM	Ethylene-propylene thermoplastic rubber
EPDM-g-MAH	Maleatedethylene-propylene thermoplastic rubber
FHT	Sodiumfluorohectorite
HRTEM	High resolution transmission electron microscopy
IIR	Isobutylene–isoprene rubber
LDH	Layered double hydroxides clay
LS	Layered silicate
MFC	Microfibrillated cellulose
MMT	Montmorillonite
MMT-2M2HT	MMT modified with dimethyl dihydrogenated tallow
MMT-MT2EtOH	MMT modified with methyl tallow bis-2-hydroxyl quaternary ammonium
MMT-ODA	Octadecylamine
MMT-ODA	Primary amine
MMT-ODTMA	MMT modified with octadecyltrimethylamine
MMT-TMDA	Quaternary amine
Na-MMT	Sodium montmorillonite
NBR	Nitrile butadiene rubber
NMMO	N-methylmorpholine-N-oxide
NR	Natural rubber
OMLS	Organically modified layered silicate
OMMT	Organically modified clay
PANI	Polyaniline

phr	Parts per hundred rubber
PLA	Polylactic acid
PMMA	Poly(methylmethacrylate)
MMA	Methylmethacrylate
PNC's	Polymer nanocomposites
PP	Polypropylene
PUR	Polyurethane rubber
RNA	Ribonucleic acid
RTIL	Room temperature ionic liquid
SBR	Styrene butadiene-rubber
SEM	Scanning electron microscope
SNR	Synthetic natural rubber
TEM	Transmission electron microscope
TiO_2	Tin oxide
TO	Tetraoctadecylammoniumbromide
UMMT	Unmodified clay
US	United States
UV	Ultra-violet
XRD	X-ray diffraction
ZnO	Zinc oxide

Units

%	Percentage
°C	Degree celsius
A°	Angstrom
g mol^{-1}	Gram per mole
GPa	Giga pascal
H	Hour/Hours
J Kg^{-1}	Joule per kilogram
kHz	Kilohertz
kJ Kg^{-1}	Kilojoule per kilogram
MPa	Mega pascal
nD	Diffractive index
nm	Nanometer
W m^{-1} $°C^{-1}$	Watt per meter per degree Celsius
wt%	Weight percentage

1 Introduction

A polymer (the prefix *poly* referring to many and the suffix *mer* referring to units) is a macromolecule composed of many repeating subunits called monomer units. Polymers can be either naturally occurring or synthetic. The term 'polymer' derives from the ancient Greek word πολύς (*polus*) and μέρος (*meros*). The term was coined in 1833 by Jöns Jacob Berzelius, a Swedish chemist considered to be one of the founders of modern chemistry. The modern concept of polymers as covalently bonded macromolecular structures was proposed in 1920 by Hermann Staudinger, a German chemist, who spent the next decade finding experimental evidence for this hypothesis. Natural polymers are made by living organisms, representing the macromolecular components of the cell. These compounds are also known as biopolymers or polymeric biomolecules and can be enumerated according to the monomeric units used and the structure:

(i) Polynucleotides or nucleic acids as DNA and RNA, which are long chain molecules composed of 13 or more nucleotide monomers. These polymers are responsible for the storage, transmission, and expression of genetic information.
(ii) Polypeptides or proteins are short chain polymers that play a fundamental role in the functionalization of various biological activities. Many proteins such as collagen, keratin, and fibroin serve as structural building blocks, while others, such as hemoglobin, act as transport agents in living organisms. Proteins can transmit information to distant parts of a living organism (proteichormones) as well as defend against foreign pathogens (antibodies). Another very important function accomplished by proteins is through the rule of the rate of metabolism reactions (enzymes).
(iii) Polysaccharides also known as glycans, are the form in which most natural carbohydrates occur. Polysaccharides are linear bonded polymeric carbohydrate structures that may contain various degrees of branching and are composed of monosaccharide units that are bound together by glycosidic linkages. This class of polymers acts as natural constituents (cellulose, chitin) as well as energy reserves (starch). Upon hydrolysis of glyosidic bonds, polysaccharides yield its constituent monosaccharides and/or oligosaccharides. Polysaccharides are heterogeneous, or homogeneous, containing slight modifications of the repeating unit. Depending on the structure, these macromolecules can have properties distinct from their monosaccharide building blocks. Linear polysaccharide compounds such as cellulose often pack together to form a rigid structure resulting in its insolubility in water; while glycans that are composed of branched forms (e.g., gum arabic) generally are soluble in water and make pastes. Polysaccharides composed of many molecules of one sugar or sugar derivative are called as homopolysaccharides (homoglycans) while those that consist of molecules of more than one sugar or sugar derivative are called heteropolysaccharides (heteroglycans). Homopolysaccharides composed of glucose include glycogen and starch, the storage carbohydrates of animals and plants respectively. Cellulose, another homopolysaccharide, is an important structural component of most plants. Preparations of dextran, another glucose homopolysaccharide found in slimes secreted by certain bacteria, are used as substitutes for blood plasma. Other homopolysaccharides include pentosans (composed of arabinose or xylose), which are found in plant

products and fructans (levans), which are found in roots and tubers such as the Jerusalem artichoke and dahlia. The repeating unit of chitin, a component of the outer skeleton of arthropods (e.g., insects, crustaceans, crab, etc.) is *N*-acetyl-D-glucosamine, a monosaccharide derived from glucose. The cell walls of most fungi are also chitin, while the shells of arthropods such as crabs and lobsters contain about 25 % chitin. This polysaccharide is also found in certain structures of annelid worms, mollusks, and other invertebrate groups (e.g., sea jellies, bryozoans, nematodes, and acanthocephalans). Most heteropolysaccharides contain only two different repeating units and are associated with proteins (glycoproteins such as gamma globulin from blood plasma, and acid mucopolysaccharides, which are widely distributed in animal tissues) or lipids (glycolipids; e.g., gangliosides in the central nervous system).

(iv) Natural rubber (NR) also called India rubber, or *caoutchouc* is a cross-linked polymer, which is composed of isoprene monomers that are joined together to make long hydrocarbon chains. NR is mostly utilized for its elastic properties. It is obtained from the coagulation of the latex product by more than two thousand species of plants, one of them being *Havea Brasiliensis*. Currently, rubber is harvested mainly in the form of latex, a sticky, milky colloid that suspends the rubber molecules. Latex is collecting as the exudate from the deep incisions made on the bark of the rubber tree. The rubber is collecting from the latex by a coagulation process. NR is used extensively in many applications either alone or in combination with other materials.

Because of their broad range and unique properties, polymers play an essential and ubiquitous role in modern everyday life. Many polymers also have unique physical properties, which include tensile strength, modulus, toughness, viscoelasticity, and a tendency to form glasses and semicrystalline structures rather than crystals. However, due to the inferior mechanical and thermal properties in comparison to metals, many of the polymeric materials have limited use in engineering applications and they can even easily form complex shapes. The mechanical, thermal, and degradation properties of virgin polymers can be improved by preparing its composite with reinforcing materials and cheapened by incorporating fillers. Composite materials are made from two or more chemically and physically different constituent phases separated by a distinct interface with significantly different physical or chemical properties, which when combined, produce a material with characteristics different from the individual components (matrix phase and dispersed phase). Hence in the composite, the different systems are combined judiciously to achieve a system with more useful structural or functional properties non-attainable by any of it's constituents material alone. Composite materials are becoming an essential part of today's industry due to advantages such as low weight, corrosion resistance, high fatigue strength, outstanding performance, faster assembly, and favorable cost compared to traditional materials. They are extensively used as materials in manufacturing of aircraft structures, electronic packaging to medical equipment, and spacecraft. The predominant useful composite materials used in our day-to-day life include wood, concrete, and ceramics. Surprisingly, the most important polymeric composites are found in nature, thus being known as natural composites. The connective tissues in mammals belong to some of the most advanced polymer composites known to mankind. Within these composites, fibrous proteins that serve as the matrix while collagen serves as the reinforcement which functions as both as soft and hard connective tissue. Matrix phases are the primary phase having a continuous character and are usually more ductile and less hard. These matrices hold together the dispersed phase, which is another phase (reinforcing phase) that is embedded in the matrix in a discontinuous form.

In the composite, the individual components remain separate and distinct within the finished structure. In a polymer composite, when the resin systems are combined with reinforcing materials such as glass, carbon, aramid, fillers (such ceramic particles), nanoclay, carbon black (CB), carbon nanotubes, and fullerenes, the resulting polymer composite exhibit exceptional properties. Since polymer matrix composites combine a resin system and reinforcing fiber/filler particles, the properties of the resulting composite material will combine some resin properties with that of the fiber/fillers. In the composite materials, the resin matrix spreads the load applied to the composite between each of the individual fiber/filler particle and also protects the fibers from damage caused by abrasion and impact, which improve the load bearing capability of the composite. High strengths and stiffnesses, ease of fabricating complex shapes, high environmental resistance, all coupled with low densities, make the resultant composite superior to metals for many applications. The characteristic properties of polymer composites are (i) high specific strength, (ii) high specific stiffness, (iii) high fracture resistance, (iv) high abrasion resistance, (v) high impact resistance, (vi) high corrosion resistance, (vii) high fatigue resistance, and (h) low cost.

Based on the type of reinforcement used in the composite, these compounds are mainly classified as (i) particulate composites, (ii) fibrous composites, and (iii) laminate composites. The particulate composite can be either microcomposites (>100 nm) or polymer nanocomposites (≤100 nm). Within both micro- and nanocomposites, the dispersed phase is usually composed of ceramic or metal particles. Microcomposites are simply the dispersed particles on a micro scale while nanocomposites contain dispersed particles on a nanoscale. Fiber reinforced polymer (FRP) composites are comprised of a variety of short or continuous fibers bound together by an organic polymer matrix. Unlike micro- or nanocomposites, in which the reinforcement is used primarily to improve the fracture toughness, the reinforcement in a FRP composite provides high strength and stiffness. Fibrous composites can be further subdivided on the basis of biofibers or synthetic fibers. Biofiber composite can be again divided on whether its matrix is non-biodegradable or biodegradable (also known as green composites). Hybrid composites comprise of a combination of two or more types of fibers.

The major attractions of green composites are that they are eco-friendly, fully degradable as well as sustainable. The design and life cycle assessment of green composites have been exclusively dealt by Baillie [7]. Green composites may be used effectively in many applications such as mass-produced consumer products with short life cycles and products intended for one time or short time use before disposal. The important biodegradable matrices are cellulose, NR, polysaccharides, starch, chitin, proteins, collagens/gelatin, lignin which are natural. Matrices such as polyamides, polyvinyl alcohol, polyvinyl acetate, polyglycolic acid, and polylactic acid are synthetic. Bio-based composites with their constituents derived from renewable resources are being developed, and its applications are extended to almost all the fields. The following section of the chapter deals with eco-friendly polymer nanocomposites, specifically cellulose clay nanocomposites and NR clay nanocomposites as well as their respective applications.

2 Polymer Nanocomposites

Polymer nanocomposites (PNCs) are a relatively new class of composites for which at least one dimension of the dispersed particles is in the range between 10 and 100 nm. Since the uniform dispersion of these nanoscopically sized grains, fibers, and particles produce an ultra large interfacial area per unit volume between the nanoelement and the host polymer, the properties of these nanosized materials are altered. These nanoelements are characterized by having very *high aspect ratios,* resulting in their effective dispersion in polymer matrices, which when combined with adequate interfacial adhesion between the filler and the polymer often have properties that are superior to conventional microcomposites. Due to these unique properties, these nanoparticles can account for the same effects at lower loadings than with conventional filler content in the composite, thereby achieving considerable *weight reduction.* As compared to neat resins or microcomposites, these nanocomposites have a number of significantly improved properties including tensile strength, modulus, heat distortion temperature, gas barrier properties, flame retardant properties, etc. This aspect of nanotechnology has potential in applications such as engineering plastics, polymer products, rubbers, adhesives, and coatings [13, 90]. Because of their uniqueness, polymer nanocomposites exhibit unexpected hybrid properties synergistically derived from two components. Among a variety of promising nanomaterials for preparing polymer composites inorganic clay minerals consisting of silicate layers are promising, and are called as *polymer–clay nanocomposites* [60, 80], often referred to as polymer layered silicate nanocomposites.

2.1 Polymer Layered Silicate Nanocomposites

The revival of interest in polymer layered silicate nanocomposites was stimulated by two major findings in the early 1990s. In the late 1980s, a novel polymer composite comprised of Nylon-6 interphased with small amounts of montmorillonite (MMT) was reported. This layered silicate clay composite was prepared at Toyota Central Research Labs in Japan who teamed up with Ube Industries Ltd. The small amounts of these aformentioned layered silicate loadings resulted in pronounced improvements of thermal and mechanical properties [52]. Toyota subsequently used the material for timing belt covers and other “under the load” automotive applications, capitalizing on the material’s heat resistance and dimensional stability. The second major finding, carried out by Vaia et al. [89]. They found that it was possible to melt-mix polymers with layered silicates without the use of organic solvents. The nanoclay interphased with the polymer greatly improved the mechanical properties of the Nylon with very small filler loadings (less than 50 %wt). The work was very significant, because the clay platelets, which are just 10 Å thick, were found to be well dispersed homogenously in the polymer matrix at the nanometer level. The incorporation of small amounts of layered silicate in the polymer matrix often exhibit remarkable improvement in the material’s properties when compared with its virgin counterpart, or conventional micro- and macro composites. These improvements can include high moduli, increased strength and heat resistance, decreased gas permeability and flammability, and increased biodegradability. The prospect of dramatic weight savings and improvement in properties initiated research in the application of this technology to a wide variety of polymers, both thermoplastics and thermosets. Thus, over the past decade, polymer layered nanocomposites have been a hot topic of research among researchers from both academics as well as industry [2, 70].

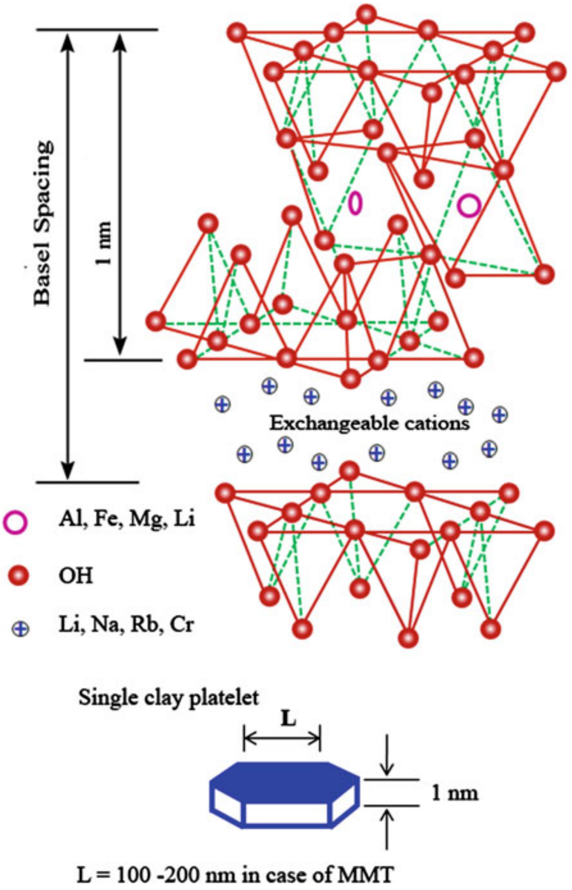
3 Nanoclays–Structure, Properties, and Modifications

3.1 Layered Silicates

The layered silicate commonly used for preparing polymer layered silicate nanocomposites belongs to the same general family of 2:1 layered phyllosilicates [22]. Layered silicates have two types of structures: tetrahedral-substituted and octahedral substituted. Details regarding the structure and chemistry of these MMT (Fig. 1) and layered double hydroxides (LDH) (Fig. 2) silicates are provided in Table 1. The basic structure of phyllosilicates consists of layers made up of two tetrahedrally coordinated silicon atoms that are fused to an edge sharing octahedral sheet of either aluminum or magnesium hydroxide. Depending on the particular layered silicate, the layer thickness is around 1 nm, and the lateral dimensions of these layers may vary from 30 nm to several microns or larger, having aspect ratios in the range of 100–1500 [27]. The interconnected six-member rings of SiO_4^{-4} (Fig. 3) tetrahedra extend outwards into infinite sheets. Three oxygens are shared by each tetrahedra leading to a basic structure unit of $Si_2O_5^{-2}$. Furthermore, the majority of phyllosilicates contain hydroxide (OH^-) ions which are placed at the center of the six member ring forming $Si_2O_5(OH)^{-3}$. An octahedral coordination is achieved when other cations are bonded to SiO_4^{-4} sheets whereby sharing of OH^- ions and apical oxygen take place. Commonly occurring cations in 2:1 layered silicates are Mg^{+2}, Fe^{+2}, and Al^{+3}.

The octahedral layers can adopt two types of structures depending on the cations. Cations such as Al^{+3} forms a Gibbsite [$Al(OH)_3$] while cations with +2 oxidation states such as Fe^{+2} and Mg^{+2} lead to a Brunite structure $Mg(OH)_3$. In both structures,

Fig. 1 Structure of montmorillonite layered silicate (MMT) [27]



all anions are OH^{-}. In brunite, the octahedral sites are all occupied while in Gibbsite, the 3rd cation site is occupied. When the phyllosilicates layers are stacked together, they lead to a formation of regular weak van der Waal gaps between the layers. These gaps are commonly referred to as gallery or interlayer [22]. Isomorphic substitution within the layers (for example, Al^{+3} replaced by Mg^{+2} / $Fe^{+2,}$ or Mg^{+2} replaced by Li^{+}) generates negative charges that are counterbalanced by alkali and alkaline earth cations situated inside the galleries. This type of layered silicate is characterized by a moderate surface charge known as the cation exchange capacity (CEC), and generally expressed as meq/100 g (milli-equivalents per 100 g). This charge is not locally constant with respect to location, but varies from layer to layer, and must be considered as an average value over the whole crystal. MMT, hectorite, and saponite are the most commonly used layered silicates. Among these, MMT is mainly used in polymer nanocomposites due to availability, high strength and stiffness, rigidity, impermeable properties [45], environmental friendliness, lower cost, and also the fact that its intercalation/exfoliation chemistry is well understood [25].

Fig. 2 Structure of layered double hydroxides silicate (LDH) [27]

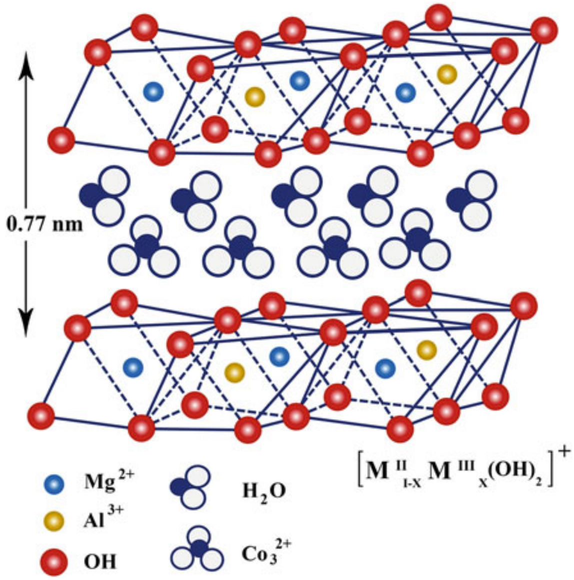


Table 1 Chemical formula and characteristic parameter of commonly used 2:1 phyllosilicates

2:1 phyllosilicates	Chemical formula	CEC (mequiv/100 g)	Particle length (nm)
Montmorillonite	$M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$	110	100–150
Hectorite	$M_x(Mg_{6-x}Li_x)Si_8O_{20}(OH)_4$	120	200–300
Saponite	$M_xMg_6(Si_{8-x}Al_x)$ $Si_8O_{20}(OH)_4$	86.6	50–60

M monovalent cation; *x* degree of isomorphous substitution (between 0.5 and 1.3)

3.2 Nanoclay Modifications

Two particular characteristics of layered silicates are generally considered for polymer layered clay nanocomposites. The first is the ability of the silicate particles to disperse into individual layers. The second characteristic is the ability to fine-tune their surface chemistry through ion exchange reactions via organic and inorganic cations. These two characteristics are, of course, interrelated since the degree of dispersion of layered silicates in a particular polymer matrix depends on the interlayer cation. The inter layer galleries of the pristine layered silicates usually contain hydrated inorganic cations such as Na^+, K^+, Ca^{+2} ions for balancing the charge of the oxide layers, which in turn leads to hydrophilicity in its pristine form [22, 25]. This respective property makes pristine layered silicates incompatible with a wide range of polymer types with the exception of polyvinyl alcohol and polyethylene oxide which are also hydrophilic in nature. Therefore, clays must often be chemically treated in order to make them organophilic. In these treatment processes,

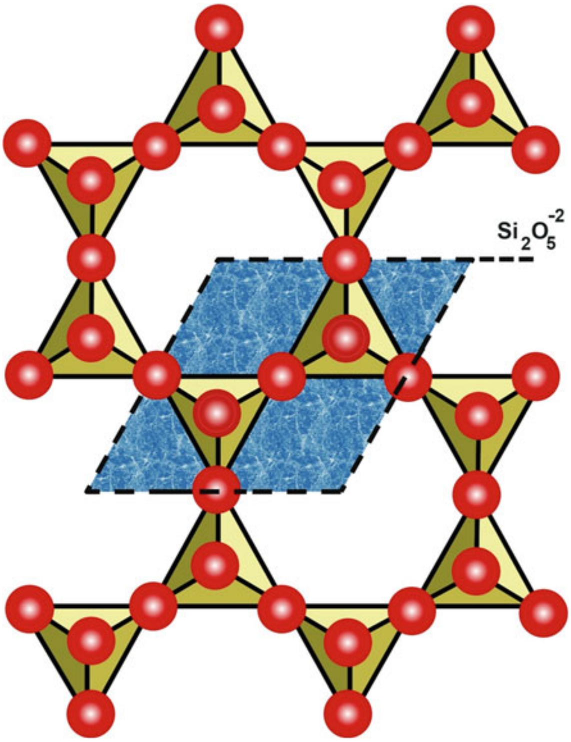


Fig. 3 Phyllosilicates basic structure consist of interconnected six member rings of SiO_4^{-4} (Image courtesy: Dr. Stephen A. Nelson)

the inter layer cations are readily ion-exchanged with a wide variety of positively charged species to make them more organophilic. This isomorphic substitution process is an integral part of these nanoclays for their use in making composites with polymers. The process involves the exchange of charges between phyllosilicate layers, e.g., Al^{+3} substituted by Mg^{+2} or Mg^{+2} by Li^{+2}. The process of ion exchange generates negative charges, which are counterbalanced by cations (mainly Na^{+} or Ca^{+2}) residing in the interlayer space making the clay organophilic, thereby compatible with hydrophobic (organophilic) polymers. In addition, the van der Waals forces between phillosilicate layers allow intercalation of polymers chains between them. When inorganic cations are exchanged by the organic cations, the yielded compound is referred to as an organically modified layered silicate (OMLS). The charges on the clay surface are generally expressed as the cation exchange capacity (CEC), which is the amount of exchangeable interlayer cations present between the surfaces. A high CEC leads to high levels of intercalation or exfoliation. For instance, MMT has a value ranging from 80 to 120 meq/100 g compared to only 3–5 meq/100 g making it difficult to disperse polymer molecules between layers of kaolinite [25].

Generally, ion exchange reactions are done by treating the clay with various cationic surfactants including primary, secondary, tertiary, and quaternary alky

$$Na^{+} + Clay + HO_2C\text{-}R\text{-}NH_3^{+}Cl^{-} \longrightarrow HO_2C\text{-}R\text{-}NH_3 + Clay + NaCl$$

Scheme 1 Rendering pristine clay organophilic [27]

ammonium [25, 27], alky phosphonium and sulfonium cations [45], or cations in various surfacants [22]. These cations in the organosilicate have a positive effect on the decreasing surface energy of the inorganic host and improve wetting characteristics of the polymer matrix. This in turn facilitates better adhesion between the clay with the polymer and in some cases can initiate the polymerization of monomers to improve the strength of the interface between the inorganic clay and polymer matrix [81]. One such example of rendering clay surfaces organophilic can be achieved by exchanging sodium ions in natural clay with unnatural amino acid derivatives such as 1, 2-aminododecanoic acid as shown in Scheme 1. Alkylammonium ions are the major cations used to modify MMT clay. Furthermore, it has been shown that surfactants with two alkyl tails result in better exfoliation and intercalation compared to those with one alkyl tail.

Recently, more surfactants have been researched extensively. For instance, Atai et al. [5] have used a proprietary surfactant called 2-acrylamido-2-methylpropane sulfonic acid (AMPS) which contains amido and sulfonic acids groups in its structure. It was postulated that exchange of Na^{+} and amido took place, thus providing reactive species that led to a better interfacial bond and improved properties of the poly(methylmethacrylate) (PMMA) composites compared to the pristine PMMA. Further comparison of Na-MMT (sodium montmorillonite) and organically modified montmorillonite (OMMT) clay using a transmission electron microscope (TEM), showed well-intercalated and exfoliated platelets in treated nanoclay compared to that of untreated clay. Functionalization of nanoclay has not been limited to organic surfactants only. An experiment was done to study the effect of water-soluble proteins as surfactants to the nanoclay [30]. It was observed that the presence of protein on MMT at all pH levels suggested electrostatic attraction and hydrogen bonding between MMT and proteins were taking place. This is a simple method to modify MMT, which can be used to manufacture bi-nanocomposite materials with improved mechanical properties. It is not only low cost method, but also utilizes biodegradable materials thereby making it environmentally friendly and mitigating the effect of pollution due to reliance on synthetic materials.

It has been observed that different surfactants have varying effects on the d-spacing of the nanoclay and many studies have been done on these phenomena. Concentration of the alky groups and chain length of the organic modifiers have been shown to increase the d-spacing of the phyllosicicate layers. In a study where three different organophilic surfactants were used (ethanolamine (EA), cetyltrimethyl ammoniumbromide (CTAB) and tetraoctadecylammoniumbromide (TO)), d-spacing was shown to increase differently according to the type of surfactant used leading to increase in the gap between the clay platelets. Better intercalation was obtained from the high concentration and long chain surfactant [105].

4 Polymer–Clay Nanocoposite Types, Chemistry, and Mechanism

4.1 Types of Nanocomposites

Low percentages of layered silicates that are properly dispersed throughout the polymer matrix create much higher surface area for polymer/filler interaction as compared to conventional composites. The complete dispersion of clay into the polymer or the strength of interfacial interactions between the polymer matrix and layered silicate (modified or not) involves reducing the micron size clay particles to nanosize and dispersing them throughout the polymeric resin. The dispersion of clay tactoids in a polymer matrix (there exists three different types of polymer layered silicate nanocomposites) are thermodynamically achievable as shown in Fig. 4. Depands on the extent of dispersion/intercalation the polymer-clay nanocomposites are categorized as:

(i) Non-intercalated nanocomposites: similar to the conventional microcomposite, where polymer is unable to intercalate between the silicate sheets/clay galleries. A phase-separated composite having a dispersed nano phase (Fig. 4a), however its properties stay in same range or slightly outperform compared to traditional mico- or macrocomposite composites.

(ii) Intercalated nanocomposites: nanocomposites in which the insertion of a polymer matrix into the layered silicate structure occurs in a crystallographically regular fashion, regardless of the clay to polymer ratio. In this structure, (Fig. 4b) a single extended polymer chain is intercalated between the silicate layers resulting in well-ordered multilayer morphology built up with alternating polymeric and inorganic layers. In other words, intercalated nanocomposites are normally interlayer by a few molecular layers of a polymer. Therefore, with respect to intercalations, the organic component is simply inserted between layers of clay such that interlayer spacing is expanded, but the layers still bear a well-defined spatial relationship to each other. Properties of the composites typically resemble those of ceramic materials. Apart from this morphology, flocculated nanocomposites structure is conceptually the same as intercalated nanocomposites may form. However, the silicate layers are sometimes flocculated due to hydroxylated edge–edge interactions of the silicate layers.

(iii) Exfoliated nanocomposites: nanocomposites in which the individual silicate layers completely separated out and are uniformly but randomly dispersed throughout the resin matrix (Fig. 4c) by an average distance, that depends on clay loading. In exfoliated nanocomposites, the clay layers do not bear a spatial relationship to each other. Usually, the clay content of an exfoliated nanocomposite is much lower than that of an intercalated nanocomposite. Most of the polymer layered silicate nanocomposites, however, are either partially intercalated, exfoliated, or a combination of these two structures.

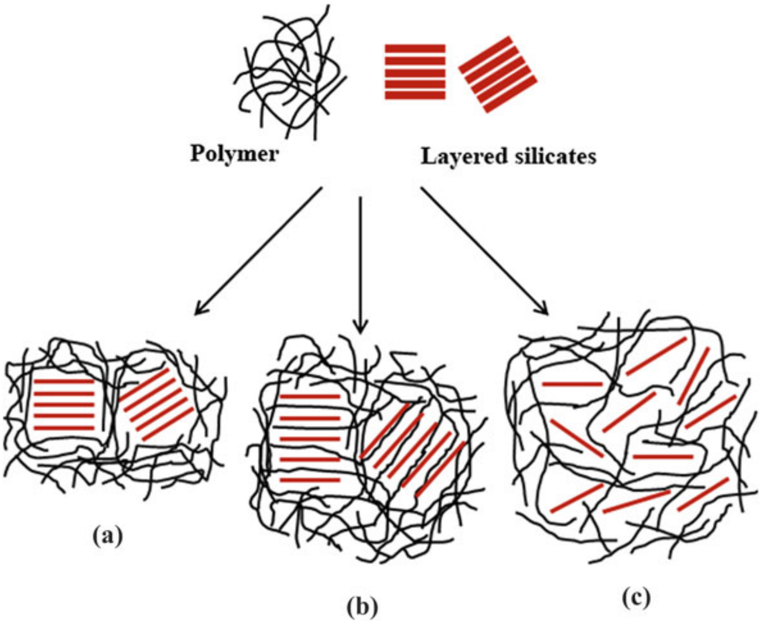


Fig. 4 Three different types of thermodynamically achievable polymer layered silicate nanocomposites; **a** phase separated microcomposite, **b** intercalated nanocomposite and **c** exfoliated nanocomposite

4.2 Chemistry and Mechanism

The need for lighter and stronger materials with high toughness has increased exponentially due to their demand in practically every industry resulting in extensive research for the fabrication of promising polymer layered silicate nanocomposites. Polymer nanocomposites are materials with ultrafine phase dimensions in the range of a few nanometers. These materials have emerged as an alternative to overcoming many engineering challenges in transportation, construction, and consumer applications [22]. Nanocomposites possess unique characteristics, which are far superior in quality compared to other composites or virgin materials. These characteristics include long-term durability, thermal and dimensional stability [98], fire retardation, and barrier properties against natural weathering [34, 98]. Furthermore, these materials offer a combination of stiffness, strength, and lightweight which make them suitable for critical engineering applications [22].

Dispersion of nanoclays into a polymer matrix are one of the most critical parameters in order to fabricate good quality end products with high mechanical, chemical, and physical properties. Fabrication method is closely related to the mixing methods employed to disperse the nanoclay into the polymer matrix, hence the selection of the mixing method will have a bearing on the final nanocomposite's properties. Various methods have been researched in order to achieve higher levels of exfoliation and intercalation, e.g., sonication, two-roll mixing, magnetic stirring, mechanical mixing, melt blending etc. The twin screw extruder method increases the mechanical properties, i.e., thermal stability, storage modulus etc. [82], and glass the transition temperature [33]. This method produces nanocomposites with superior properties compared to internal mixers due to the high exfoliation achieved [74]. However, the combination of the two methods gives excellent exfoliation [71] and intercalation which in turn leads to a high tensile modulus, tensile strength, and unnotched impact strength [66]. The same trend is observed when all the other methods are used.

Figure 5 exhibits an idealized processing of polymer nanocomposites fabrication. As depicted in Fig. 5, the aim is to yield polymer chains between layers of nanoclay/clay galleries. To achieve this, (the nanoclay being hydrophilic) the nanoclay needs to be functionalized by various cations to facilitate compatibility with hydrophobic (organophilic) polymers. Selection of the surfactants plays a paramount role in achieving better interfacial bonds. For instance, the use of alkyl ammonium with additional tethering groups has shown different exfoliation or intercalation degrees. In one such study, the use of styryl and methacryl functionality showed extensive intercalation, which led to a shift in the basal plane. Furthermore, surfactants with methacryl-tethering groups facilitated diffusion of the PMMA molecules into the galleries of the nanoclay, promoting better exfoliation. The methacryl tethering groups, having similar chemical composition as methylmethacrylate (MMA) were cited as a reason. In addition, the unsaturated vinyl groups reacted further with MMA leading to higher exfoliation from both tethering groups [97]. This observation clearly demonstrated that compatibility between the surfactant and polymer monomer plays a significant role in the exfoliation and intercalation of the polymers into the nanoclay. Using different types of OMMT [46] such as Cloisite 30B (Cs30B) modified by dihyroxyethyl octadecyle methyl ammonium chloride, Cloisite 93A (Cs93A) modified by methylated dehydrogenated tallow ammonium, and Na-MMT showed varying levels of exfoliation or intercalation depending on the surface modification. Cs30B exhibits better compatibility with the polymer matrix in comparison with Cs93A. Its modifying structure contains two polar groups, making it a more polar cation than a nonpolar cation like Cs93A.

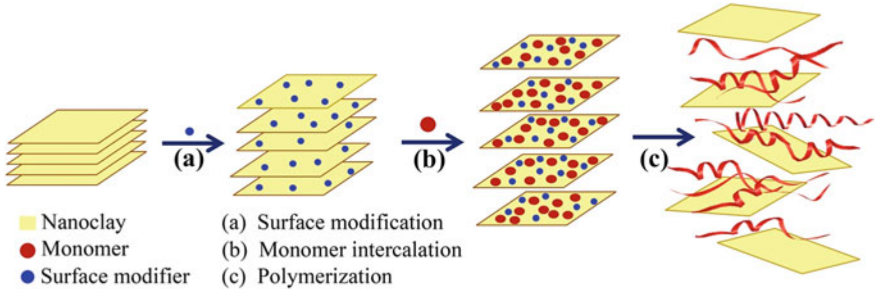


Fig. 5 Idealized process of nanocomposite fabrication using nanoclay. Images courtesy: Dr. Tie Lan

5 Nanocomposite Synthesis

Complete dispersion of clay tactoids in a monomer or polymer matrix involves three steps. The first is wetting the surface of clay tactoids by monomeric or polymeric molecules. This is followed by the subsequent intercalation of the monomer into the clay galleries. The third step is the exfoliation of clay layers. In polymer nanocomposites, these steps ensure incorporation of clay into the polymer matrix at the nano level. The different popular synthesis routes for preparing polymer-clay nanocomposites are discussed in the following sections.

5.1 Direct Intercalation

This method consists of spontaneous penetration of the polymer in the two-dimensional interlayer space by mixing the silicate and the polymer. A resulting polymer that is made by this method is polyethylene oxide. It’s a simplest and economically cheap method, however one disadvantage of this method is the fact that most of the polymers are incompatible with the silicate making this method unsuitable.

5.2 In Situ Intercalative Polymerization

This method consists of the insertion of molecules or ions acting as monomers, which could be polymerized within the tetracrystalline region of the two-dimensional solid. The presence of transition metal ions as exchangeable cations is included in the structure of the layered solids to obtain the composites. This is the most successful approach to date, although it probably limits the ultimate applicability of these systems [81]. An example is that of polyamide 6-clay nanocomposite. In a typical synthesis, modified clay is dispersed in the monomer caprolactum, which is polymerized to form the polyamide 6-clay hybrid as an exfoliated composite. Complete exfoliation may be preceded by the intercalation of the monomer in the clay.

5.3 Ultrasound Irradiation

Ultrasound irradiation, as a new technology, has been widely used in chemical synthesis. When ultrasonic waves pass through a liquid medium, a large number of micro bubbles form, grow, and collapse in a very short time. This process, which occurs in a span of a few microseconds is called ultrasonic cavitation. These ultrasonic cavitations can generate a local temperature as high as 5000 K, a local pressure as high as 500 atm, and a heating and cooling rate greater than 109 K/s. Therefore, ultrasound irradiation has been extensively applied in the dispersing, emulsifying, crushing, and activating of particles (e.g. polyaniline (PANI)/nano-SiO_2) [81].

5.4 Solution Polymerization

The layered silicate is exfoliated into single layers using a solvent in which the polymer (or a pre-polymer in the case of insoluble polymers such as polyimide) is soluble. It is well known that such layered silicates, owing to the weak forces that stack the layers together, can be easily dispersed in an adequate solvent. The polymer then adsorbs onto the delaminated sheets and when the solvent is evaporated (or the mixture precipitated), the sheets reassemble, sandwiching the polymer to form polymer-clay nanacomposite. The optimal case would involve an ordered multilayer structure [2]. Polar solvents can be used to synthesize intercalated polymer–clay nanocomposites [81]. The organoclay at first is dispersed in a nonpolar solvent such as toluene. Since alkylammonium treated clays swell considerably in nonpolar organic solvents forms gel structures. The polymer, dissolved in the solvent, is added to the solution and intercalates between the clay layers. The last step consists of removing the solvent by evaporation (e.g. polyurethane-clay nanocomposite or gelatin/MMT) [101].

5.5 Emulsion Polymerization

Emulsion polymerization is a new method to synthesize polymer nanocomposites. This synthesis is based on one step, which eliminates the environmental problems associated with the solution polymerization process and involves the addition of surfactants with unmodified silicate clay under stirring conditions. In order to begin this polymerization, a monomer is fed with an initiator and then proceeds under vigorous agitation conditions. The reaction mixture is then cooled to room temperature and the final product is obtained after filtration and washing several times with water followed by drying under reduced pressure e.g. PMMA/MMT [2].

5.6 Melt Blending (Compounding)

Intercalation with the aid of an extruder has been achieved by mixing the modified silicate with polymers in a melt [73]. An example is that of polypropylene (PP) nanocomposites, which are melted by compounding organophilic clays with maleic anhydride grafted PP [23]. This layered silicate is mixed with the polymer matrix in the molten state. Under these conditions, if the layer surfaces are sufficiently compatible with the chosen polymer, the polymer can crawl into the interlayer space and form either an intercalated or exfoliated nanocomposite under these conditions. In this technique, no solvent is required hence it is environmentally friendly and not required any post processing like solvent evaporation or drying. Melt blending (compounding) depends on shear to help delaminate the clay and can be less effective than in-situ polymerization in producing an exfoliated nanocomposite.

6 Green Nanocomposites

There is currently a collective research effort in fabricating degradable materials to replace nondegradable materials, despite their superior advantages. Much energy is required to process these synthetic polymers and the fact that they are not degradable, poses a major environmental concern for current and future generations. There is also a concerted effort among scientists to find novel materials that are not petroleum based. In this search, it has been found that cellulose- and NR-based nanocomposites are very promising. Both cellulose and NR have many available sources and the fact that they are replenished seasonally within a short time makes them perfect candidates for natural composites with potential application in many industries. These include automobile, aerospace, consumer goods, and transportation industries.

6.1 Cellulose–Clay Nanocomposite

Cellulose derived composites have received much attention by researchers recently. This is attributed to their low density, biodegradability, low cost, high specific strength etc. Much research has focused in extracting the cellulose fiber and using it with either biopolymers or synthetic polymers to make a composite. It can be seen in recent studies that cellulose–clay nanocomposites have shown better properties compared to their counterparts [47, 75, 76, 103]. In addition, cellulose nanocomposite prepared with other nanoparticles also shown improved properties. Regenerated cellulose/TiO_2/ZnO nanocomposites showed excellent photocatalytic efficiency [36], and a decrease in cure time due to addition of cellulose nanosized materials, which is [35] an important parameter to those applications that require more time before the curing of resin. It has also been reported that superior thermal stability [21] increased storage modulus and crystallinity in polyamide [54] by addition of cellulose nanofibers. An improvement in mechanical strength was observed by addition of cellulose nanofibers into porous tissue [49]. However, the addition of cellulose led to an increase in the water uptake of the nanocomposite.

Furthermore, light transmittance of nanocomposites has shown an increase when cellulose nanofibers are added [53]. Nanocomposites fabricated from cellulose acetate powder modified with nanoclay showed an improvement in optimum mechanical properties with a 5 % compatibilizer loading. The better dispersion and exfoliation of clay (evaluated by TEM, XRD and atomic force microscopy (AFM)) in cellulose shows that these composites can be used as a replacement to non-biodegradable polymers [55, 56]. Park et al. [55, 56] also studied the effect of nanoclays on cellulose acetate bioplastic (CAB) and found that eco-friendly plasticizers like triethyl citrate varied in different amounts, while organically modified nanoclays maintained a constant weight at 5 %. Their results were in agreement with the literature that showed that intercalation and exfoliation of the clay is highly dependent on the amount of plasticizer in the matrix. Improvement in tensile strength, thermal stability, and modulus were achieved using a maximum of 20 % plasticizer. It was observed that percentage amount of plasticizer above 20 % resulted in the degradation in these properties. Preparation of transparent nano-fibrillated cellulose and nanoclay biohybrid films was done using high pressure homogenization methods [6]. Favorable exfoliation of the clay was recorded as well as inorganic content as high as 20 % was achieved without compromising the mechanical properties of the nanocomposites and its transparency. Addition of vermiculite improved the oxygen barrier of the hybrid film in high humidity environments. The high barrier property is an important characteristic because it can allow for packaging of oxygen-free organic electronics. Fabrication of cellulose/layered MMT nanocomposites was carried out by its precipitation from *N*-methylmorpholine-*N*-oxide (NMMO) in water [16]. Investigation on the extent of nanoclay dispersion showed more contact time is needed to yield a partial exfoliated morphology of the nanocomposites. The hybrid nanocomposites showed better thermal oxidative properties, which is important in the production of fire resistant materials. Nanoclays hinder the transfer of oxygen, heat, and degraded volatiles leading to high degradation temperatures of the final composite. Lower stability of cellulose at low temperatures is found to be due to the clay oxidizing and dehydrating the cellulose moieties. The use of various sequential mixing methods of triethyl citrate [57] in combination with maleic compatibilizers allowed these researchers to arrive at the optimum method leading to superior nanocomposites. The addition of compatibilizers accelerated the exfoliation of the clay in the matrix. In this case, the compatibilizer which is maleated, reacts with free OH^- groups in the clay structure and intercalates into the clay galleries, leading to a tensile strength and modulus improvement of 20 and 68 % respectively.

Glycerol triacetate, another glycerol plasticizer, has also been used with cellulose acetate and nanoclays to prepare nanocomposites [24]. Bio-based nanocomposites have been manufactured by melt intercalation of nanoclays with cellulose acetate (CA) in both presence and absence of a plasticizer. In the case where plasticizers were indeed present, they were varied up to 30 % together with OMMT and unmodified MMT clay (UMMT). UMMT clays can lead to poor exfoliation and intercalation compared to OMMT. The TEM studies found that less than 5 % unmodified clay led to an improvement in tensile strength and Young's modulus.

The interaction of cellulose acetate hydroxyl groups and free cations present in the clay galleries are cited as a possible cause for this observation. Elongation at the failure point remained constant. This was expected to drop as the addition of nanoclays normally lead to brittleness of the matrix.

Many studies have been done to improve the properties of nanocomposites from NR and cellulose. In one such study, in order to compare the thermal degradation of cellulose/clay nanocomposites and polyvinyl alcohol-starch-carboxymethyl [83] was carried out and, the results was shown that the addition of clay to the blend matrix led to high improvement in thermal stability in the films with the 5 % nanoclay giving the best results. Nanoclay was theorized to form a barrier which prevented mass and heat transfer. The high degradation of the matrix at high temperature was curtailed by clay layers allowing further reaction and thereby holding the degradation products for a longer time. One of the biggest hurdles faced by cellulose-based nanocomposites with respect to its application in fire retardants is the poor thermal stability of cellulose when exposed to high temperatures. There is a need to develop nanocomposites based in cellulose to exhibit better thermal stability at higher temperatures. The majority of current flame retardants in use are synthetic materials, some of them exhibiting toxicity and required high energy to produce. The use of layered silicate nanoclay has shown more promise to be used as better flame retardant. In addition, this composite is environmentally friendly and readily degradable. In his dissertation, Delhom [20] used various methods to achieve better exfoliation and intercalation of nanoclay in the cellulosic matrix. He used different solvents and pretreated clay using various techniques. Using NMMO as a solvent for cellulose and functionalized nanoclay, he optimized the degradation temperature by 45 °C. However, this resulted in a lower crystalline melt temperature of 15 °C.

An innovative method to prepare cellulose reinforced MMT nanocomposite films was developed by Mahmoudian et al. [44] and his colleagues using room temperature molten salts collectively known as room temperature ionic liquid (RTILS). This is an environmental friendly method where 1-butyl-3-methylimidazolium chloride is used as ionic medium. Cellulose and MMT are mixed separately with the ionic media. Cellulose can be magnetically stirred at approximately 85 °C for 4 h, while MMT is dispersed into the ionic media using a sonicator. The two solutions are later mixed together and stirred for a day at 85 °C to form a homogeneous MMT/cellulose composite in ionic media. The mixture was then vacuum degassed and casted on glass plates. There was an improvement in thermal stability and tensile strength until a clay loading of 8 % by weight of cellulose. The composite properties were decreased due to the aggregation of clays at higher content. Thus, this nanocomposite can be applied in packaging and membrane technology.

Extrusion is an important method in fabricating polymer composites commercially, and therefore has been well established and used widely in industry. This method was used by Bondeson [12] to study its effectiveness in producing nanocomposites reinforced by cellulose nanowhiskers. Two methodologies were adopted for the preparation of cellulose nanowhiskers; these include the hydrolysis of either sulfuric or hydrochloric acid. Furthermore, the nanowhiskers were either dry mixed or freeze-dried prior to extrusion, and then compounded and extruded. To improve dispersion of the whiskers in cellulose acetate butyrate and polylactic acid (PLA), water and a surfactant were used. The results showed no improvement in thermal and mechanical properties in polylactic acid due to degradation and possibly poor dispersion of whiskers. However, on the other hand, there was an improvement in both thermal and mechanical properties in cellulose acetate butyrate. The possibility to make nanocomposites by pumping the cellulose nanowhiskers in an extruder with polymers was demonstrated. Contrary to the reduction of thermal and mechanical properties by using cellulose nanowhiskers, the use of cellulose nanofibers in polylactic acid was shown to lead to an improvement in tensile strength and modulus from 58 to 71 MPa and 2.9 to 3.6 GPa, respectively, and a great increase in the storage modulus and glass transition temperatures were observed by an addition of 5 wt% cellulose nanofibers [32]. Taking into consideration these extrusion methods that were used, it can be seen that different structures of the cellulose can lead to varied results.

6.2 Natural Rubber–Clay Nanocomposites

6.2.1 Natural Rubber

Natural Rubber (NR) is one of the most important elastomeric materials consumed in the industry, half of its total consumption being used for rubber products. It is harvested as latex from a class of plants growing in the tropics. Latex is the colloidal dispersion of rubber particles in an aqueous medium, which is collected by making an inclined cut on the bark of the rubber tree. This process is known as tapping. Nowadays, more than 95 % of NR is harvesting from Heveabrasiliensis which originates from South America, growing primarily in the rubber plantations of Indonesia, Malay Peninsula, Sri Lanka, and India. The field latex is concentrated by centrifugation, creaming, or electro-decantation for cost-effective transportation or making latex products such as condoms, balloons, gloves, or elastic threads, collectively called dipped rubber goods. For dry rubber products such as molded goods and tire manufacturing, the collected filed latex is strained and diluted with water and coagulated mostly by adding diluted acids (mostly diluted sulfuric acid or acetic acid) to cause destabilization of the colloid, which leads the agglomeration of the suspended rubber particles by sticking together within the latex called coagulation. The clumps or agglomerated rubber particles are separated and pressed between a series of plain rollers and grooved rollers to form thin sheets and then subsequently dried in air, smoke or sunlight before shipping to the processing plants. The average size of the rubber particles are 3 μm in size. The purified form of NR is chemically 100 % cis-polyisoprene. The molecular weight of the NR is normally in the range of 10^4–10^7 g mol^{-1} depending on the age of the rubber tree, weather, nature of the soil, rain fall, method of rubber isolation, etc. The molecular

Table 2 Properties of unvulcanized natural rubber

Properties	
Density (g cm^{-3})	0.91
Glass transition temperature (°C)	−70
Thermal conductivity (W m^{-1} °C^{-1})	0.134
Heat of combustion (J Kg^{-1})	4.5×10^6
Equilibrium melting temperature (°C)	28
Heat of fusion of crystal (kJ kg^{-1})	64
Refracyive index (nD)	1.52
Dissipation factor(1 kHz)	2.4
Dielectric constant (1 kHz)	0.001–0.003
Dirt content (% by mass)	0.03
Volatile mass (% by mass)	0.50
Nitrogen (% by mass)	0.30
Ash (% by mass)	0.40
Initial plasticity number (P_0)	38
Plasticity retention index	78

weight distribution of rubber is relatively broad, which offers excellent processing behavior. Although it has high initial viscosity, it breaks down easily to a processable viscosity. The glass transition temperature (T_g) of this polymer is −70 °C and is subjected to a unique property known as stress-induced crystallization, the crystallization of the rubber molecules under strain. Table 2 shows the properties of the unvulcanized NR. The advantages of the use of NR include outstanding flexibility at use temperature, excellent mechanical strength, exceptional tear strength, good abrasion resistance, and low hysteresis (heat buildup under flexing). However, the aging properties of this material are poor. In addition, since it is of biological origin, NR is renewable, inexpensive, and creates no health hazard problems. The properties of the NR are improved by compounding or making composites with filler particles or reinforcements. By addition of reinforcing elements such as silica, clay, or CB and occlusion of rubber tremendously increase the tensile strength, wear and tear resistance, and modulus, but adversely affect the heat buildup.

6.2.2 Types of Clays for Rubber Nanocompoiste

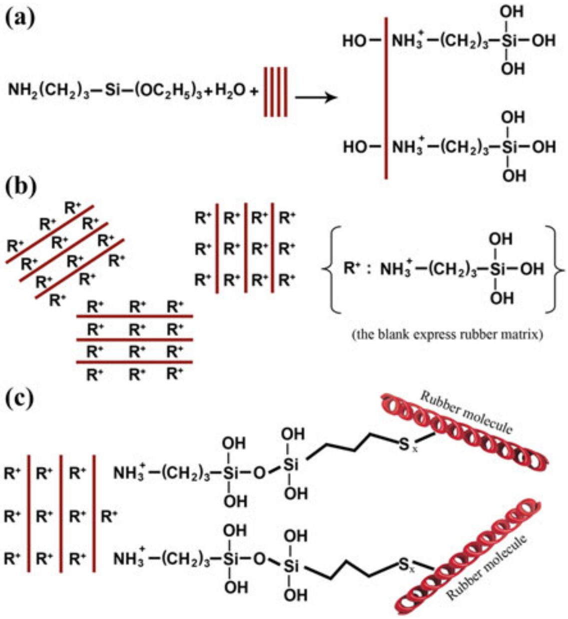
Reinforcing of NR has been exclusively done by CB, but more environmental friendly nanoparticles are now being explored. Apart from silica or other ceramic fillers, different types of nanoclays are being used to reinforce the NR. Studies show that properties of the composite are greatly influenced by the type of nanoclay. For instance, the effect of two types of nanoclay such as MMT and LDH showed differing results due to the makeup of the nanoclays. As mentioned earlier, MMT is a cationinc clay while LDH is an anionic clay with the possible formula [M^{II} x $M^{III}_{1\text{-}x}(OH)_2](A^{n-1})_{x/n}*yH_2O$ where M^{II} represent divalent metal ions, the M^{III}

representing trivalent metal ions. The x values range between 0.2 and 0.33 and in this case y is equal to 0.4.

It was shown that unmodified LDH leads to reduction in the cure rate of certain rubbers [19]. The interaction between MMT or LDH with rubber molecules is via hydrogen bonding of the nitrogen atom attached with thiourea, the cross-linking agent of the rubber molecules and electronegative oxygen in the clay layers. The anionic properties of LDH make it have high affinity for electron rich species leading to higher interaction with rubber. The cationic effect of the nanoclay improved the physical properties of the rubber, i.e., tensile, dynamical mechanical properties, etc. From this study, thermal stability can be improved by noting that LDH and CB always have a tendency to restrict crystallization of polychloroprene rubber, but not the case with OMMT.

6.2.3 Method of Preparation of Rubber–Clay Nanocomposite

Presently, there are four principal methods used for preparing rubber–clay nanocomposites: (i) melt mixing or compounding, (ii) in-situ polymerization, (iii) latex blending, and (iv) solution intercalation. Among these methods, melt intercalation and in-situ polymerization are considered as simple and commercially attractive approaches for preparing “rubber–clay nanocomposites.” However, in-situ polymerization is not a possible method for preparing NR–clay nanocomposites as it is extracted as latex from the rubber tree. Latex blending is a promising method for the rubbers available in aqueous dispersions (e.g., NR or styrene butadiene rubber abbreviated as SBR) because in this case pristine layered silicates can be used [10, 11,72, 91, 93, 99]. The latex blending method is not possible for many synthetic rubbers due to non-availability of its latex form. Solution intercalation methods can be used for preparing rubber–clay nanocomposite of most of the elastomers, which is soluble in hydrocarbon solvents [31, 96]. However, melt intercalation has received much attention since it offers significant processing advantages that would greatly expand the easiness of commercial production of rubber–clay nanocomposites with conventional or slightly modified rubber processing machineries such as extruders, banbury mixer, or two-roll mills [94]. Also, melt compounding would be significantly more economical and simpler than in-situ polymerization minimizing capital costs because of its compatibility with existing industrial rubber processing equipment. Since there is no solvent or liquid medium required, melt processing is environmentally friendly, more economical, and avoids postprocessing such as solvent stripping or coagulation. In addition, it enhances the specificity for the intercalation of polymer, by eliminating the competing host-solvent and polymer-solvent interactions. Indeed most of the rubber–clay nanocomposites were prepared by melt blending technique. The melt processing method used for the preparation of rubber–clay nanocomposites is similar to that used for conventional polymer–clay nanocomposites. Therefore, nanocomposite production is swung downstream, giving end-use manufacturers many possibilities



Scheme 2 Proposed schematic of modification mechanism with silane coupling agent: **a** cation exchange in clay suspension with 3-aminopropyltriethoxysilane (KH-550), **b** after co-coagulating, the sturucture of RCK flocculate, **c** after adding bis[3-(triethoxysilyl)propyl]tetrasulfide) (Si-69) and sulfur curing ingredients on a two-roll mill, and curing the compounds at 150 °C, the interaction among KH-550, Si-69 and rubber molecules in rubber-clay nanocomposite. (Adapted from Ref. 29)

with respect to final product specifications (e.g., selection of polymer grade, choice of organoclay, level of reinforcement, etc.).

6.2.4 Natural Rubber–Clay Nanocomposite (Dry Rubber Process)

Nanoclays are being researched as an alternative to CB, the principal reinforcing filler in rubber compounds. The biggest problem with nanoclays thus far has been dispersion into the NR to achieve the desired improvement. It is difficult to achieve exfoliation or intercalation of nanoclays into NR, because nanoclays have a tendency to agglomerate with increasing amount into rubber or polymer matrix. Various methods have been used to solve this problem. One promising method was reported by Mohan et al. [48] and his co-workers mentioned previously as the Banburry method. This is a two-stage method where in the first stage uncured rubbers with all additives are mixed in the mixer at 60 rpm at 145.8 °C. Once maturation is achieved at roughly 26 h, the nanoclay is then added at different amounts, until the desired amount is achieved. At this stage, mixing speed is reduced to 40 rpm and the temperature is around 100–110 °C. The mixture is then allowed to reach maturity after 24 h. This is followed by sheeting the compounds using a two roll mill. The molds are steam heated at 148 °C at a pressure of 10 MPa. A two roll–roll mixer is then employed for the 3 % nanoclay in rubber. Results from XRD showed increase in d-spacing between the nanoclay, allowing rubber to enter into the clay galleries. Nanoclays also reduced curing time due to the reaction of the cationic ions of clay with rubber. Although nanoclay has been known to lead to brittleness of the matrix, the brittleness was only confirmed by transmission electron microscopcopy at 3 % nanoclay by weight of matrix. Increase in cross-linking of the nanoclay in rubber leads to increase in hardness and gas barrier properties. The thermal tests showed nanoclay/rubber having higher stabilities at high temperatures compared to pristine rubber.

Another dispersion method which shows promising results by providing highly dispersed nanocomposites with excellent interfacial bond strength was devised by Jia et al. [29]. This method, called the two-step method, employs the use of two silane coupling agents; 3-aminopropyl triethoxysilane (KH-550), and bis(triethoxysilylpropyl)tetrasulfide (Si-69). To generate hydroxyl groups, 3-aminopropyl triethoxysilane (KH550) is added to a mixture of water and clay in an in-situ organic modification. It was found that hydrolysis of Si-$(OR)_3$ leads to the production of hydroxyl groups. Bis(triethoxysilylpropyl)tetrasulfide is later added into the mixture of rubber and clay and mechanically blended by two-roll milling. In the vulcanization process, ethoxysilylpropyl groups from bis(triethoxysilylpropyl)tetrasulfide react with S-OH of the dispersed clay in rubber leading to a chemical bond between rubber and clay phases. This results in a strong interfacial bond which leads to high tensile strength, thermal stability, and high stresses at certain strains. Possible mechanisms for the reactions are shown in Scheme 2.

6.2.5 Hybrid Natural Rubber-Clay Nanocmoposite

In multi-component compounding, two or more different types of fillers are used, called hybrid compounds or hybrid structures. A hybrid structure combines the effect of different materials [17, 28, 50, 51, 87]. Recent investigations on composites having multi-component filler systems focus mainly on thermoplastic and thermoset polymers and are not so familiar with rubbery materials. In most of the applications, CB and the silica have been used together as a hybrid filler system to optimize the advantages and disadvantages of the individual filler system [69]. Among all the fillers, CB plays an important role in the rubber industry as reinforcing filler. By incorporation of CB into the rubber matrix, many of the desirable properties like dynamic mechanical properties, fracture behavior, tensile strength, tear strength, modulus, hardness, and abrasion resistance are increased, which make CB an ideal candidate as a reinforcing filler in NR compounds and has been extensively exploited in numerous rubber engineering products, hence it is known as universal reinforcing filler in rubber industry. Despite these advantages, CB is a product of petroleum processing and much energy is required in its production. In addition, it must be mentioned that it is a hazardous material. Compared to silica, the widely used reinforcing filler for non-black rubber products, CB reinforced rubber has a higher modulus. In tire treads, silica provides lower rolling resistance at equal wear resistance and wet grip than CB. Like silica, nowadays the emergence of natural fillers, like nanoclays which is cheaper and friendly to the environment, have been utilized in rubber compounding along with CB to overcome certain negative aspects of CB include tire tread wear and tear. However, it is virtually impossible to completely eliminate CB from the NR composite for certain applications. For example, nanoclays do indeed improve the properties of NR, but not to the extent required for many end-use products such as tires, consumer goods, and/or automobiles.

6.2.6 Natural Rubber–Clay-Carbon Black Nanocomposite

An innovative approach to improving nanocomposite properties is to use a hybrid of two reinforcing fillers such as nanoclay and CB; one such study was conducted by Praveen et al. [62]. The study established that high improvement on vulcanizate properties of NR nanocomposite can be achieved by using the two fillers due to synergic effect of the different fillers. The study showed that even CB increases the gap between clay nanoplatelets, thereby contributing an appreciable increase in the strength of the resulting nanocomposites. Furthermore, there was a substantial increase in modulus attributed to the network structure of CB, which tends to restrict slippage of macromolecular chains. Improvement of glass transition temperature of the composites was due to decrease in interfacial slide and relaxation, which resulted in better intercalation of clay/CB with the rubber. The effect of hybrid nanoclay/CB, and the effect on its ratios on the curing kinetics, cross-linking behavior, and activation energy of NR [78, 77], mechanical and dynamic mechanical properties of the vulcanizate for application in truck tires [3], cut growth behavior and gas permeability were studied. The results showed that the hybrid filler has a pronounced effect on certain properties of the nanocomposites.

The influence of organically modified nanoclay-CB hybrid filler on the curing behavior of NR was studied by Janak Sapkota et al. [79]. Two types of modifications (dimethyl-dihydrogenated tallow alkyl ammonium salt and octadecylamine) of the clay was employed. The partial replacement of CB with nanoclays influences the curing behavior substantially, and the addition of the clay significantly decreases the activation energy of the networking system. Also, results show that quaternary ammonium modified clay compounds increased the curing rate and lowered the torque. The activation energy for initiating the cross-linking reaction is decreased with addition of clay and thus cross-linking tends to take place in an easier manner in the presence of the modified nanoclays. Dynamic mechanical tests performed under a strain sweep showed the Payne effect due to better dispersion of CB. In addition, Mooney viscosity results showed that the replacement of CB with modified nanoclay can help in the dispersion of fillers. Strong interactions between CB, nanoclay, and NR matrix were also found. In another study carried out by Anwendungen [3], the nanoclay was modified with stearic acid before adding it with CB and used unmodified organoclay as the baseline. The hybrid prepared with modified clay had better reinforcing capability compared to the unmodified clay. It was further observed that hybrid nanoclay/CB had an effect of reducing fossil fuel resource use by almost 40 % for truck tires manufacturing, in addition to better performance in rolling resistance. In addition, when premixing with the organoclay, the stearic acid serves to swell the clay layers, allowing the rubber molecules to be intercalated into the gallery of the layered silicate. This process enhances the mechanical properties of the composites with low loading of CB without sacrificing other physical properties like tensile strength, modulus, hardness, and rebound resilience. In another study, [67] two types of nanoclays, calcined clay and devolite, were used and it was shown that 2 phr (parts per hundred rubber) of both types of clay can be replaced with 1 phr CB to maintain the same hardness value. There was also a decrease in curing and resilience of the composites when the clay/CB was lowered while torque, strength, and thermal aging resistance were improved. Calcined clay/CB also showed lower gas barrier properties and cure time but higher modulus, tear strength, cut tensile strength, and higher cross-link density. The addition of nanoclay/CB changes the crack growth from a simple lateral to a more oblique one resulting in its higher tensile strength.

6.2.7 Natural Rubber–Carbon Black-Silica-Clay Nanocomposite

Hybrid nanoparticles of CB, silica, and nanoclay have been utilized to study various properties of NR. The influence of nanoparticles on mechanical properties of the final composites was conducted by research groups such as Rattanasom et al. [68], while other researchers such as Lo and Chu [40] used the same kind of nanoparticles to study their effect on the environmental resistance of hard rubber. In the study by Rattanasom et al. [68] the nanoparticles were mechanically mixed at 50 rpm, followed by the use of a two-roll mixer and 10 end-roll before sheeting, and then finally carrying out a compression molding at 150 °C. It was observed that MMT filled NR vulcanizate shows higher values of hardness at lower content compared with the other filler particles; silica and/or CB which require a higher loading to achieve the same hardness. The comparison of the composite with equal loading of clay into NR exhibited higher values in tensile strength, compression, and modulus, but poor crack growth and heat buildup resistance. Scanning electron microscopy (SEM) showed better dispersion of CB in NR and higher cross-link density, which resulted in overall better mechanical properties. In the Lo and Chu [40] study, NR and additives were mixed in a mixing chamber at 20 rpm and compounded at 150 °C for 2 h. The optimum CB content in clay/CB-filled hard rubber samples was 45 phr when total filler content is either 105 or 120 phr. Environmental tests were carried out using laboratory electrolytic cleaning tank immersion setup. The CB showed better resistivity but unlike the previous study [68], it had improved hardness after immersion. The CB/silicate NR composite did not pass the electrolytic cleaning test due to dissolving of the silica in the testing process.

6.2.8 Natural Rubber–Clay Nanocomposites: Solution or Latex Route

Solution Route

NR clay nanocomposites using rubber solutions or latex have been successfully prepared and reported by many groups. Magaraphan et al. [43] studied the effect of different amine intercalants on the mechanical properties of NR clay nanocomposites prepared using the solution process. The composite was prepared by dissolving NR in toluene along with MMT modified with primary or quaternary intercalants bearing different hydrocarbon alkyl tails. The curing agents were then subsequently mixed with the composite. After drying, the mixture was homogenized on an open mill. It was found that the composite prepared with primary amine intercalants had better mechanical performance over its counterpart that was prepared with quaternary amine intercalants. Liang et al. [39] compared the effectiveness of melt and solution intercalation methods on the dispersing of organically modified clays. In another study, the structure and properties of rubber/organophilic MMT nanocomposites carried out by Lo′pez-Manchado et al. [41], MMT was modified (although it was intercalated initially) with octadecylamine (MMT-ODA). It was found that both methods delivered similar nanocomposite structures with intercalated and exfoliated nanoscale clay layers. The basal spacing of the clay was almost doubled for those dispersed into the composites due to the intercalation of rubber molecules into the clay galleries. However, the solution technique (toluene served as solvent) yielded a higher amount of bound rubber, improved the dynamic mechanical properties and enhanced the compression set hardness [41], and exhibited a higher aspect ratio (compared to the melt method). In addition, this technique also resulted in outstanding mechanical and gas barrier properties [39].

Because NR is highly nonpolar, a better method for uniform dispersion of the clay in the matrix needs to be developed. It has been reported that the use of an epoxidized natural rubber (ENR) as a compatibilizer can lead to better dispersion of clay into the rubber matrix. Rajasekar et al. [65] performed this experiment by preparing an ENR by solution mixing. The nanocomposites were mixed into SBR and sulfur was used as a curing agent. High resolution transmission electron microscopy (HRTEM) showed highly intercalated clay layers. Dynamic mechanical tests showed a highly improved storage modulus and lower damping characteristic as well as an improvement in the mechanical properties of the resulting composites.

Latex Route

In contrast with solution processing, the latex compounding method employs the use of water instead of organic solvents as a host medium. The latex is the colloidal suspension of submicron sized rubber particles in water. To prepare the nanocomposite, pristine clay or its suspension/dispersion in aqueous medium (slurry) can be added directly into the rubber latex. As discussed earlier, clays are strongly hydrophilic and thus easily adsorb water molecules, which is associated with an expansion in its intergallery spacing. In other words, hydration decreases the attractive forces between the phyllosilicate layers, resulting in more exfoliation during stirring. After mixing the clay uniformly in the lattices, the compounded composite rubber latex was casted into a mold and left to dry. In this case, the rubber clay nanocomposite collected remains unvulcanized. The curatives can then be incorporated into the composite and molded into different products. In contrast, suitable rubber curatives, which can be dispersed in water, can also be mixed with the clay-containing rubber latex before casting and drying. This latter mentioned process is most suitable for dipped goods such as condoms or gloves where the former are dipped into the compounded rubber composite latex mixture. The mixture can then be dried in either air, or temperature controlled air ovens followed by curing at high temperature (above room temperature in air or in boiled water).

Varghese et al. [93] investigated the properties of NR layered silicate vulcanized nanocomposites with different clay types. These types included sodium bentonite (natural) and sodium fluorohectorite (FHT, a synthetic layered silicate) that were studied in conjunction with a non-layered inert filler (English India clay or commercial clay) as a reference material. The study found that FHT gave the highest mechanical performance and the lowest toluene swelling compared to inert non-layered clay or layered bentonite clay. This can be attributed to the high platelet aspect ratio, intercalation/exfoliation of the silicates due to its prominent water swelling ability of FHT, and the formation of a skeleton (house of cards) silicate network in the NR matrix. In another study by the same group, [92] polyurethane rubber (PUR) and prevulcanized NR latex were blended with a pristine synthetic layered clay, known as sodium fluorohectorite. They prepared films of nanocomposite structure with enhanced stiffness characteristics to study the morphology-dependent mechanical properties of layered silicates. Compared to NR, it was found that a higher degree of intercalation due to better compatibility of the layered silicate with PUR (thus being nano-reinforced) and has a pronounced reinforcing effect. The ultimate tensile strength as well as tear strength was strongly increased (more than three times) and a dramatic improvement was found in the moduli at different elongations. The property improvement was traced to a layered silicate (LS) skeleton-type ('house of cards') structuring in the corresponding nanocomposite. Fourier transform infrared spectroscopy (FTIR) and broadband dielectric analysis were adopted to examine the NR/LS, PUR/LS and NR/PUR/LS nanocomposites formed via the latex route [64, 63, 92]. It was found that the PUR chains, due to their polar character, facilitate the intercalation/exfoliation of the layered silicate. Further, LS was preferably located in the PUR phase in the blends, which exhibited excellent mechanical properties despite the incompatibility between NR and PUR.

Different structures of rubber clay nanocomposites were prepared by co-coagulation of latex with aqueous clay suspension to form NR–clay, SBR–clay, carboxylated acrylonitrile butadiene rubber (CNBR)-clay and nitrile butadiene rubber (NBR)–clay. The TEM and XRD were performed on the resulting nanocomposites [99]. In this method, an aqueous suspension of clay and rubber latex were mixed and stirred vigorously for a required time. The mixture is then co-coagulated in an electrolyte solution of dilute triethylenetetrammonium chloride solution for NR and SBR, while a calcium chloride aqueous solution is used for NBR and CNBR. The mixture is later washed with water and oven dried at approximately 80 °C for 18 h. Vulcanization additives are then incorporated into the nanocomposite using a two-roll mill. The structural characterization performed on nanocomposites showed that the rubber molecules led to the separation of the clay into individual layers and/or silicate aggregates with thickness in the nanometer range with no intercalation of rubber into the clay galleries. This was mainly due to the competition between reaggregation of clay layers and latex particle separation during co-coagulation. Further results showed a higher aspect ratio and a higher glass T_g due to the increased network of rubber/clay nanocomposites in comparison with pristine rubber. In addition, it was also found that tensile strength was increased (by a factor of 6), and there was an observed decrease of almost 50 % of gas permeability when 20 phr clay was added to the rubber.

In an effort to understand the effects of different types of organically modified clay on NR, [42], a comparison study of methyltallow bis-2-hydroxyethyl ammonium-modified montmorillonite (MMT-TMDA) and MMT-ODA was carried out. For further comparison purposes, layered silicate sodium bentonite was also used in addition to un-layered clay. Results from XRD and TEM showed better dispersion of MMT-ODA clay and poor dispersion of un-layered clay. In addition, organically modified clays exhibited better mechanical properties such as tensile strength, compression set, resilience, hardness, and tear strength. The high interlayer distance between the layers of modified clay was cited as the reason for these improved properties. In another study, a conventional compounding method was used to prepare latex–clay nanocomposites [26]. This method is limited by the fact that, as the loading of the clay increases, there is a buildup of high viscosity, generating difficulty in nanoclay processing. The XRD results agreed with the literature where it was shown that the layered phyllosilicate was ordered or delaminated, which led to better intercalation but partial exfoliated structure. A study on the effect of clay on the transportation properties of the nanocomposite was conducted by measuring the sorption, permeation, and diffusion coefficient using toluene at 303 K. A tortuous path provided by nanoclay [33] resulted in a decrease in the coefficient of diffusion. Better gas barrier properties were recorded for oxygen molecules. This was observed even for lower loading of the clay into the rubber latex. There was also better compatibility of the clay and the rubber leading to the formation of elastomeric networks. Improvement of the nanocomposite properties by adding nanoclay in rubber highly depends on the exfoliation of phyllosilicate layers or intercalation of the rubber molecules into the clay galleries.

6.2.9 Effect of Clay on Microstructure

The effect of clay on the microstructure and morphology of NR network is a complex process. Much research has been conducted to study this effect in order to predict the final microstructure of rubber matrices after intercalation or exfoliation of the clay. For instance, Carretero-Gonza et al. [15] used dielectric spectroscopy and wide angle XRD to study the effect of organically modified clay on NR microstructures. The introduction of nanoparticles into the NR led to a homogeneous and well-distributed structure. The homogeneous structure resulted in an early occurrence and increased crystallization under uniaxial deformation. The enhancement of the crystallization was brought about by the alignment of the nanoclay during stretching. Mobility of the clay into the natural matrix during crystallization led to a highly networked structure having cross-linked chemical chains. A shift in the tanδ curve showed that there was limited mobility of the NR matrix into the clay nanoparticles.

Changes in mechanical properties of non-vulcanized dialyzed NR by addition of nanoclay have been studied by performing uniaxial deformations. It was shown that non-rubber molecules contributed to the auto-reinforcement of the nanocomposites [72]. Nanocomposites prepared by aqueous dispersion of clay and latex mixing contained exfoliated clay with the presence of tactoids. It was expected that presence of tactoids in the matrix would lead to poor mechanical properties, but this hypothesis was not observed, possibly due to the alignment of clay.

Cellulose nanoparticles in the form of either whiskers or nanofibers have been used as reinforcement into natural fiber matrices in order to achieve high performance nanocomposites [1, 9, 95]. The following conclusions can be stated; addition of cellulose whiskers from waste bamboo led to increase in thermal stability, storage modulus, and decrease in elongation at failure [95]. A comparison between cellulose whiskers and micro-fibrillated cellulose, the latter performing better when used as reinforcement in NR. Presence of residual lignin and fatty acids on the micro-fibrillated cellulose promoted better adhesion resulting in high stiffness and tensile strength of the nanocomposites [9]. A reduction in solvent absorption and a decrease in the diffusion coefficient of nanocellulose NR composites were attributed to the presence of a double network of cellulose–cellulose and rubber–rubber [1]. Lastly, there was a decrease in viscosity as the nanocellulose content was increased.

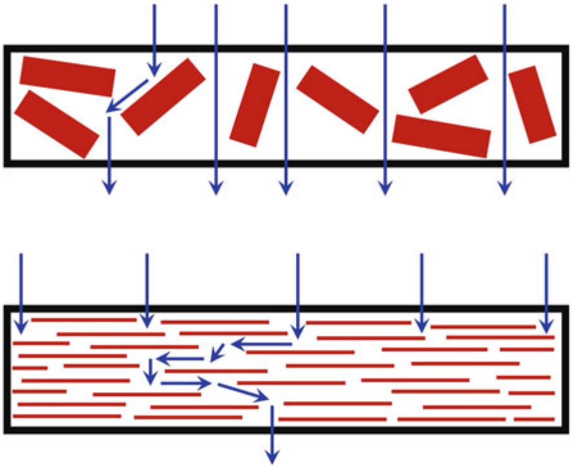
7 Physical Properties of Natural Rubber-Clay Nanocomposite

7.1 Without Compatibilizer

Vu et al. [96] took the first effective effort in the preparation of rubber-nanoclay composites. In this initial study, different rubber–clay nanocomposites based on synthetic natural rubber (SNR) and ENR were prepared by both melt mixing and solution intercalation techniques. Either an OMMT or Na-MMT clay modified with alkyl ammonium cations by an ion exchange reaction to make the galleries more hydrophobic and thus more compatible with the nonpolar rubbers. XRD studies verified the intercalation of NR and ENR into the silicate interlayers and/or exfoliation of the silicate layers into the elastomer matrices. However, the surface morphology of the composite was not studied to visualize the clay dispersion and exfoliation by SEM or TEM. The vulcanizates with organically modified clay exhibited better tensile properties due to the better polymer-filler interactions and weaker filler–filler interactions. Compared with silica fillers, the effect of the dynamic strain amplitude on the storage modulus with Na-MMT was higher, possibly due to a greater hydrodynamic reinforcement as a result of melt intercalation of the rubber in to the Na-MMT galleries. The storage modulus increased with epoxidation of NR and clay loading. This increase was attributed to the stronger rubber–filler interactions due to the higher degree of epoxidtion. The increase of the interfacial adhesion between the clay tactoids and the polymer matrix is remarkably improved due to the formation of partially intercalated structures with clay loading, hence the storage modulus was higher with clay loading [37]. Varghese et al. [92] and Modhusoodanan et al. [42] studied the properties of NR-clay nanocomposites prepared by melt mixing. In the Varghese et al. [92] study, NR–clay nanocomposites containing 10 phr of organoclay, found that the interlayer spacing of the rubber nanocpomposite was higher for clay modified with primary amine (MMT-ODA) than for one modified with quaternary amine (MMT-TMDA). In the study, the property improvements caused by the fillers were ranked as follows: organophilic clays > pristine synthetic layered silicate (sodium fluorohectorite) > pristine natural clay (purified sodium bentonite) > precipitated non-layered silica (used as a reference) (actually state the actual property improvement when listing these superlatives).

In a study carried out by Modhusoodanan et al. [42], the highest interlayer distance of 3 nm was observed for organoclay filled NR nanocomposites studied by XRD and TEM. The addition of organoclay into the NR decreased the cure time as well as the scorch time of the rubber compounds. However, the effect is not pronounced compared to NR gum compounds with bentonite and English Indian Clay (EIC). The organoclay filled compounds showed high Mooney viscosity revealing that intercalation occurred during mixing of the silicate into the rubber. The physical–mechanical properties such as tensile strength, modulus, hardness, abrasion resistance, and tear strength of NR improved in the presence of organoclays, even at low loading due to the exfoliation of the silicates, which caused an increase in surface area several fold, resulting in better interaction between the filler and rubber molecules. Carretero-Gonzalez et al. [15] reported that the presence of nanoclays introduce a dual crystallization mechanism due to the alignment of nanoparticles during stretching. The improved properties in NR–clay nanocomposites was also attributed to both the microstructural and morphological changes induced by nanoclay as well as to the nanoclay mobility in the NR matrix during crystallization. Usuki et al. [88] also reported that strong ionic interaction between polymer and silicate layers, which generate some crystallinity at the interface, is responsible for the effect of reinforcement. Carli et al. [14] revealed that silica can be replaced with a considerably low amount of organoclay with a reduction of filler content by 12.5 times without adversely affecting the mechanical properties of the final composite, even after aging. Yahaya et al. [102] found that NR–clay nanocomposites achieved a maximum value of tensile and tear strength with 6 phr of clay loading after which a fall was observed. The reduction in tensile strength of the modified, filled

Fig. 6 Tortuous path formed by the interaction of clay



vulcanizates was above 6 and 8 phr for the unmodified vulcanizates. This can be attributed to the excess amount of filler particle or the result of physical contact between agglomerates [102]. The higher amount of agglomerates in high filler dosage composites played a role in obstructing molecular chain movement of the NR, thereby initiating failure under stress. The tensile and tear properties for the organomodified vulcanizates showed higher values than the unmodified filled nanocomposites, these properties increased linearly as a function of the organoclay loading. The enhancement on tensile and tear strength of the clay nanocomposite is mainly due to clay tethering and uniform dispersion of clay particles, which improved the interfacial properties between the filler and rubber molecules, inhibiting the stress concentration and leading to delayed crack propagation [58, 67].

It was reported that gas barrier properties [3, 4, 33, 39, 48, 67], swelling behavior, and flame retardant properties [3, 48] of the rubber composite are marginally enhanced by the incorporation of nanoclays. Yahaya et al. [102] observed that, sorption behavior of nanocomposites filled with 8 phr modified organoclay is better compared to unmodified clay in toluene at room temperature. The organomodified vulcanizates evidently possess silicates that are uniformly dispersed in the NR. This is in contrast to the unmodified filled NR which has poor dispersion of the clay layers, hence increased solvent uptake. Other studies also found that rate of solvent uptake decreased with the incorporation of the organoclays [3, 48, 59]. The trend can be attributed to the presence of the nanodispersed impermeable clay layers, which decreased the rate of transportation by increasing the average diffusion path length in the rubber matrix [59]. The gas barrier properties were also enhanced due to the improved tortuous path as shown in Fig. 6. The US patent, Barbee [8] claims an invention that relates to a polymer-clay nanocomposite having an improved gas permeability comprising a melt-processible matrix polymer, thereby incorporating a layered clay material intercalated with a mixture of at least two organic cations. The clays are believed to increase the barrier properties by creating a tortuous path that retards the progress of gas molecules (i.e., gas diffusion) through the matrix resin as reported by Cheol et al. [18]. The organoclay platelets have an aspect ratio of 10,000:1 and significantly increase the path/travel distance for the gas molecules.

The thermal, flame retardant, and chemical stability properties of the nanocompoaiste were also improved by the incorporation of organosilicate layered clay into the rubber matrix [3, 48]. The flame retardant mechanism in clay nanocomposites involve a higher performance of carbonaceous silicate char, which builds up on surface during burning. This insulates the underlying material and slows the mass loss rate of decomposition products [100], which leads to higher thermal stability.

7.2 With Compatibilizer

The properties of NR-clay nanocmposites [4, 86] and a blend of NR/SBR-clay nanocompsoites [85] with compatibilizers were studied. Teh et al. [86] and Arroyo et al. [4] prepared NR-organoclay nanocomposites by melt compounding methods. In these studies, ENR25 and ENR50 (NR epoxidized with 25 and 50 mol% epoxy groups, respectively) were used as compatibilizers. Pristine MMT was modified with octadecyltrimethylamine and abbreviated as MMT-ODTMA. In the Teh et al. [86] study, the pristine MMT was modified with octadecyltrimethylamine and the amount of organoclay was fixed to only 2 phr while the amount of ENR was varied. NR/MMT-ODTMA showed mostly an intercalated structure of the organoclay and the best dispersion of organoclay in NR nanocomposites was achieved in the presence of ENR50. This observation was attributed to the incorporation of ENR50 in NR which facilitated the penetration of both molecules into the interlayer space of MMT. The rheological studies showed that organoclay filled NR vulcanizates have the lowest torque values, while the improvement of tensile strength, as well as the elongation at break and tear properties were considerably higher compared to CB and silica filled compounds.

Arroyo et al. [4] prepared the NR-clay nanocomposites by mixing the clay modified with two different modifiers, namely dimethyl dihydrogenated tallow (MMT-2M2HT) and methyl tallow bis-2-hydroxyl quaternary ammonium (MMT-MT2EtOH) and blended with ENR25 and ENR50. The exfoliated structure of the organoclay was observed in the presence of ENR due to its higher polarity, which favors the intercalation of long rubber chains in the interlayer space of clay. Because of the poor compatibility between the unmodified clay and hydrophobic rubber molecules, unmodified clay slightly changed the cure characteristics of NR and nevertheless, the optimum cure time was reduced steeply in the presence of the organoclay. Similar behavior was also observed in the case of CB, but the extent of decrement was smaller compared to the organoclay. NR filled with 10 phr of organoclay exhibited higher torque compared to the NR with 40 phr CB. This observation can be attributed to the higher cross-link density which was further confirmed by swelling and differential scanning calorimetry (DSC) experiments.

The mechanical properties of the composite with 10 phr organoclay are observed to be comparable with the compound with 40 phr CB.

Tavakoli et al. [85] prepared nanocomposites based on 70/30 blends of NR/SBR, and organoclays by melt-mixing processes. In the study, maleated-ethylene-propylene thermoplastic rubber (EPDM-*g*-MAH) and ENR50 were employed as compatibilizers. The morphological studies showed that the use of EPDM-*g*-MAH as a compatibilizer enhanced the clay nanolayer dispersion and their interaction with rubber phases more readily than ENR in the rubber matrix. Both XRD and TEM examinations verified that two rubber phases of the rubber blend compatibilized by both EPDM-g-MAH and ENR50 could be intercalated into the galleries of organoclay. These analytical techniques also showed that a high extent of clay intercalation/exfoliation could be obtained in these nanocomposites. Tavakoli et al. [85] also studied the effectiveness EPDM-g-MAH as an interfacial compatibilizer in enhancing the extent of interaction between NR matrix and organoclay nanolayers [84]. As in the earlier morphological studies carried out by Tavakoli et al. [85], the microstructural characterizations revealed that EPDM-*g*-MAH have more potential for separating and dispersing the clay nanoplatelets in the rubber matrix with better interface enhancement compared to ENR50. The pronounced compatibilizing effect of EPDM-g-MAH is attributed to the lower polarity, which leads to more affinity for the NR matrix to be diffused onto the galleries of organoclay. The uniform dispersion of orgnoclay nanolayers and better interfacial properties of the nanocomposite resulted in higher elasticity and physico–mechanical properties, which is verified with the unvulcanized NR/organoclay/EPDM-g-MAH nanocomposites in melt rheological measurements. The studies concluded that, compared to ENR as a compatibilizer, EPDM-*g*-MAH has greater potential for separating and dispersing the clay nanoplatelets in the polymer matix with better interface enhancement in the nanocomposite.

8 Applications of Green Polymer-Clay Nanocomposite

Nanocomposites based on polymeric matrices are showing promising success in various industries due to their excellent properties that include lightweight, low cost, and improved thermal, mechanical, electrical, optical, and gas barrier properties [67, 104]. The nanophase in the composite is superior compared to other conventional materials. With emphasis on biodegradability, much work is now focused to find fillers which are environmental friendly. Studies carried out by Abraham et al. [1] showed that they can be used in the critical industry of solvent membrane transportation where they have shown better flow properties and are also resistant to thermal degradation. The materials are able to provide a tortuous path to solvent flow and hence they can be tailored to only allow certain solvents though. This is an important parameter in rubber manufacturing where transportation of solvents should be minimized to enhance the durability of rubber tires. Nanoclays have been used to reinforce elastomers with an aim of lowering its flow properties as it can reduce the viscosity of the result composite better than conventional fillers. This allows for ease in processability of the reinforced composites [19]. Cellulose whiskers and microfibrillated cellulose (MFC) have also been used to reinforce NR to improve the stiffness and reduce the solvent uptake of toluene and water. The whiskers and MFC increase the T_g of rubber which can allow the final nanocomposites to be used in slightly higher operating temperatures compared to their pristine composite counterparts [9, 95]. Currently, in order to increase mechanical properties of rubber tires, chemical cross-links as well as the addition of fine particles of CB or silica with minimum weight of 20–30 % are needed. This not only leads to an expensive rubber composite but also enviromental hazards, because the fillers are not environmentally friendly [15]. Functionalized nanoclays, e.g., MMT have shown that they can be used to replace expensive CB as reinforcement filler in vulcanized rubber in very low loading weights. The clay improves the aging of the rubber by prolonging its durability and it can increase the stiffness of the rubber tires greatly [104]. To improve the properties of thin films and fibers, nanoclay has been added with tremendous improvement. The most preferred method used was melt intercalation and electrospinning where fibers with improved mechanical properties were realized [25]. Superior properties, biocompatibility, and ease of fabrication, layered silicate clay reinforced nanocomposites have been used as dental adhesive reinforcing fillers compared to the established nondegradable fillers. Its durability to be used as a dental filler adhesive was shown through the fact that the shear bond was much superior for the nanoclay reinforced adhesive [5]. Nanoclay is also increasingly being used to modify bitumen in order to improve its properties. Jahromi et al. [27] and his colleagues showed that it can lead to high stability, high indirect tensile strength, resilient modulus, and superior performance compared to the unmodified bitumen under dynamic creep loading and low fatigue properties in low temperatures. The larger surface area and aspect ratios of the particles are responsible for these improvements. NR filled with nanoclays have also shown better improvement in fire resistance, hence the materials can be used as fire retardants, which are cheaper and less toxic than other conventional fire retardants such as fluorinated polymers [29]. Gas barrier properties are an important performance characteristic of rubber products due to their operation in highly compressed air in air springs, cure bladders, and tire inner-tubes. Nanoclays have shown better performance in the food and beverage industry as an enhancement in barrier properties of the composite. Isobutylene–isoprene rubber (IIR) reinforced with nanoclays can meet the high gas barrier requirements of industries like high-vacuum systems, aerospace, and aircraft where there are reduced gas permeability required standards [38]. The demands for better food packaging materials with improved gas barrier properties that satisfy the safety requirement have led researchers to turn to natural materials. Biopolymers are touted as the best materials for this revolution, however, their biggest hindrance is in their inherent permeability to vapor and gases, poor barrier to gases, and poor mechanical properties. Nano-reinforced materials are seen as the solution to this problem. Nanoclay-reinforced biopolymers have shown great promise in the food and packaging industry with enhanced barrier properties [45]. Nanoclay reinforced nanocomposites have also been used to improve the scratch resistant and adhesion properties of the composites as shown by Mohamadpour et al. [46] where there was a substantial improvement in these properties depending on the loading weight of the nanoclay.

9 Conclusion

In this chapter, various reinforcing routes for NR and cellulose-based nanocomposites have been explored. It is a well-researched area and much more work is still ongoing. A general observation showed that there is a vast improvement in mechanical, chemical, and physical properties of resulted nanocomposites due to addition of all the mentioned polymer reinforcing nanofillers. The improvement was noticed to highly depend on the weight of the nanoparticles in the NR polymer matrix. It was also observed that different types of nanoclays lead to varying improvement depending on the types of functionalization or surface modification. However, in general, functionalized nanoclays do indeed perform better. A major problem that still presents a challenge in the use of nanocellulose is through its hydrophilic nature, though there are some promising results from surface modification. It was also shown that small amounts of nanoclays can be used to provide the same or better quality compared to the considerable amount needed of CB to reinforce NR. Furthermore, hybrid cellulose/nanoclays also lead to high improvement of the final nanocomposites.

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