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Structural Aspects and Applications of Natural Nanomaterials

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Abstract: Today there is a growing trend of using natural, biogenic or environment friendly materials to meet the ever increasing demand of the world population for their desire on high performance materials for construction, transportation, electronic and electrical appliances as well as in environmental remediation and health care products including lifesaving equipments and drugs. In this context, the natural materials, particularly the natural nanocomposites, have gained special attention also considering their traditional uses across civilizations for wastewater treatment, making health care products and packaging materials, and for their multitude of promising functional properties. In this paper, we are concerned with the structure, properties and applications of naturally occurring nanocomposite materials and their derivatives in wild, raw or unmodified state and the synthetic ones. We first start with an overview of the importance of the natural nanocomposite and their applications. We further discuss the structure and properties of some specific natural nanomaterials such as biomineralized systems taking examples of bones and shells of abalone followed by the discussions on naturally occurring clays, halloysites, and layered double hydroxides. Finally, we discuss the mechanical, electrical and thermal properties of nanomaterials and their derivatives while concluding the discussion with the uses of the composites in various areas such as packaging, coatings and other high-performance applications in aerospace engineering, environmental remediation and health care industry (designing drug delivery systems, tissue engineering etc).

Keywords: Clay, Environment, Health, Mechanical properties, Nanocomposite.

I. Introduction and Overview

A condensed state of material with multiple phases (one being a continuum) and at least one of it lying in the nano length regime (< 100 nm) is called a nanocomposite. Here the internal or surface structures [1] are considered and in another definition [2], the overall particle size of more than half of the population is taken. The nanocomposite is characterized by unique structural features leading to diverse physical and chemical properties [3]. Geometry with hierarchical structure is usually present in a nanocomposite material [4, 5]. Especially, the occurrence of various types of grain boundaries with interfacial interactions has been considered to be one of the salient features from which their inherent properties arise. There are numerous examples of materials available in nature possessing the above-mentioned structural morphologies and are thus known as natural nanocomposite materials [6]. Clay (a layered silicate), bones and nacre (hard mineral platelets embedded in a soft protein matrix) and wood (cellulose bonded by lignin) are some examples of naturally occurring nanocomposites [7, 8].

Nanocomposites differ from regular composite materials in that the surface-to-volume ratio (or aspect ratio) is exceptionally high (~10 times) considering the nanoparticles used as reinforcing gents or as fillers. The synergistic effect in the properties resulting from the combination of two or more domains or phases constituting the material makes it interesting in terms of application perspectives. It means that the enhancement of observables takes place by the combination of two or more relatively weak substances or domains at ambient pressure and temperature to form a highly resilient nanocomposite. The superior performance is the result of the combination of components with complementary properties. This is due to the special geometrical architecture and multiple efficient interactions between different components at the atomic scale [4]. Hence, natural nanocomposites are of utmost significance considering the science behind them and the quest of human beings in search of novel materials with unique and applicable properties.

Human civilization has been using natural nanomaterials and composites from the early times in multiple applications. One traditional use of nanoparticles has been reported to be carried out more than *ca.* 1700 years ago in the Middle East for the fabrication of high-strength steel swords with very sharp edges and non-brittle nature [9]. These properties were obtained as a result of components like cementite nanowires and carbon nanotubes in the metal [10]. Color-changing glass of the cup with the incident of light on it has been mentioned in the Roman culture more than *ca.* 1600 years ago. The alloy made up of gold and silver nanoparticles (3:7 ratio) was used in this glass in such a way that the transmitted light appeared bright red while the reflected light appeared green [9]. Similar features have also been observed in glass windows in the late medieval religious places. The difference in sizes of various nanoparticles and the shapes of crystallites are now known to impart distinct properties then unknown. In the Renaissance period, an iridescent glaze or metallic lustre was obtained from nanoparticles for the pottery work. In the Islamic culture (between 9th and 17th centuries), the metal glass nanocomposites displayed ceramic glazes with a bright lustre. It was acquired by embedding different types of metallic nanoparticles in the silica matrix [11]. In the Maya civilization, *ca.* 1200 years ago, a colored pigment called Maya blue was synthesised from natural clay (palygorskite) and an indigo dye (obtained from the leaves of *Indigofera suffruticosa*) [12]. These composites are clear examples of the use of nanotechnology by various human civilizations since historic times.

These days, there is a trend in developing new materials with tailored functionalities (including mechanical, optical and electrical properties as needed by specific applications) to meet the requirement of the growing materialistic population of the world. This goal is achieved by copying/imitating the designs that nature has adopted through the process of evolution over millions of years by adapting to the natural environment. The growing interest in synthesizing or producing state-of-the-art materials is being actively pursued in various fields of material sciences such as bionics [13], biomimetics [14], and polymer composites [15] to name a few. One of the strategies in materials design is the bottom-up approach using nanomaterials and the development utilizing the nature's approach will have a great advantage of being effective, efficient and environmentally friendly. The transition of ages from Stone, Bronze, Iron, Silicon and Plastic now foresees another type of age- the Designed Material [16]. Therefore, scientific and technological vision with intelligent design (both natural and synthetic) is the best route to be adopted for investigative and developmental purposes.

In context to the high significance of the natural nanomaterials in the present scenario as mentioned above, it is important to make a review of the structure and properties of selected nanocomposites and to explore their new potential uses. This article aims to provide a brief review of natural nanocomposites and their derivatives focusing on their structural features, relevant properties and applications.

II. Structure and Properties of Natural Nanomaterials

There are different ways by which nanocomposites are formed in nature and are classified broadly into three different categories viz. biomineralized systems, mineral systems and biological tissues. Representative examples of these different classes of natural nanocomposites are discussed next.

A. Biomineralized Systems

When a living being aids in the formation or precipitation of mineral materials then the resultant product is called a biomineralized system. The organisms from all six taxonomic kingdoms have been reported to make more than 60 biominerals (48 crystalline forms, *ca*. 30 forms containing calcium) and those compounds with at least one component in the nano-regime are called natural nanocomposites [17, 18]. They are formed either by co-operative interactions [19] between different phases or by templating [20] of a mineral in the organic matrix. Some materials are found to be formed by the combination of these two mechanisms. A few prominent examples of biomineralized nanomaterial systems are discussed in the following paragraphs.

a) Bones

Bones are natural nanocomposite materials made up of organic collagen fibril along with other proteins and inorganic mineral hydroxyapatite with a hierarchical geometry ranging up to millimetres in size. It is composed of nearly 70% by weight of inorganic crystals of calcium hydroxyapatite (hydroxy phosphate), $Ca_{10}(PO_4)_6(OH)_2$ and the remaining matrix is primarily of type I collagen [21]. The hydroxyapatite forms plate-like crystals of nearly 50 nm x 25 nm x 2 nm size and are stacked in the shortest dimension. These mineral nanoplatelets are embedded in the organic collagen framework in a specific architecture. The composite structure provides robust mechanical properties with better strength and rigidity in comparison to individual ingredients. The bone-forming cell called osteoblast with nanostructure is reported to yield tougher products than the ones with micro-sized structures. Thus the hardness of bones (macrosize) is a result of the large surface area to volume ratio of the building units (nanosize). This is an example of the bottom-up approach of design as mentioned earlier (biomineralization) in the fabrication of materials with superior properties.

The biomineralized bone in vertebrates comprises calcium hydroxy phosphate and type I collagen. It has properties incomparable to any of the nanomaterials that scientists have been able to synthesize in the laboratory. Thus the material formed under normal biological conditions has intermediate stiffness (ability to withstand changes in length) as revealed by its Young's modulus (trabecular >10.4 GPa, cortical >18.6 GPa) [22] in comparison to those of other materials like rubber (0.1 GPa) and metals/alloys (>100 GPa) [23]. The fracture resistance of bone depends on the intrinsic properties of its components, density and microarchitecture [24]. There is a variation in the strength of bones of different animals due to the difference in anatomy and physiology. This assertion is revealed by the comparison of Young's modulus (GPa) of the strongest bones (femur) in humans (14.4), deer (4.8), pigs (2.6) and sheep (2.1) [25, 26]. An increasing Young's modulus with age has been reported for a limited range [27]. Thus various variables like age group, sex, remodelling etc. seem to affect the properties of bone.

The typical example of bone microstructure is presented in Fig. 1 (a) in which the transmission electron micrographs [28] of a cross-section of the human cortical bone femur are shown. Fig. 1b represents the bottom-up approach in the build of bone starting from the nanoscaled collagen [29].

Fig. 1 (a) shows the interlinked network-like structure of hydroxyapatite as a dark continuous region. This inorganic section occurs in groups and has parallel lace-like geometry with slight curves [31]. In between these sections, the organic collagen fibrils are seen as electron transparent voids (partially eroded due to milling). The collagen fibrils possess five-fold rotational symmetry arising from the spiral assembly of five tropocollagen molecules with an offset of 67 nm observed in a long-range periodic repetition. The collagen fibril is made up of a right-handed triple helix structure of flexible tropocollagen chains (three polypeptide strands with each as a coiled-coil of 3/2 helix of amino acid sequence) [32] of dimension 300 nm x 0.75 nm x 0.75 nm, which ultimately translates hierarchically as shown above in Fig. 1 (b) to macro sized cortical bone. A gap of *ca.* 44 nm between the tropocollagens is present where crystallization of hydroxyapatite (plate-like crystals) takes place. The structural integrity of microfibril is provided by this inorganic phase and is mainly found between the tropocollagens as well. Its strength and stability are consequences of intermolecular cross-linking and are proportional to the number of cross-links until a saturation stage [15]. The size of the hydroxyapatite crystals varies from one type of bone to another, on the animal species and on the method of determination [33].

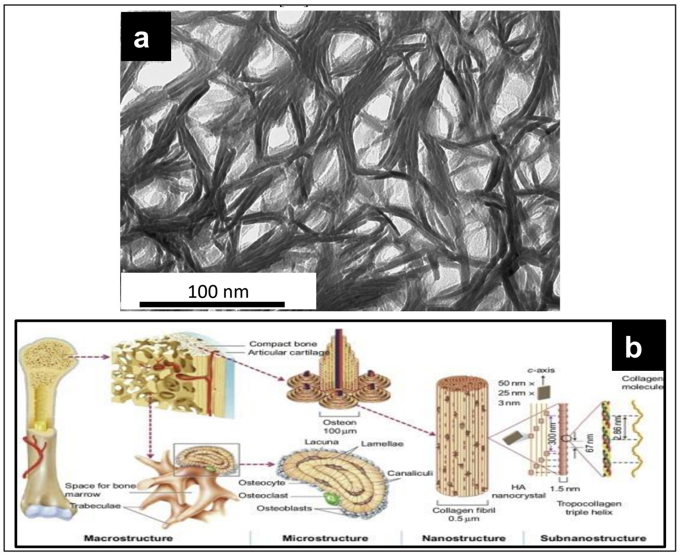

Fig. 1: (a) Tem Image Showing the Microstructures of the Human Cortical Bonefemur with Lacy Pattern Consisting of Segments of Parallel and Curved Crystals; the Nano-Sized Collagen Fibrils is the Light Region Partially Punctured during Milling [30] (b) Picture Depicting a Hierarchical Structure from Nano-Sized Collagens to Macro Sized Bones [29]

The mechanical property like stiffness is found to be a function of the mineral content in the tissue considering different types of bones [34]. Also, the characteristics of the organic component and the structural arrangement of two constituents finally determine the overall property of the composite. Up to 310 MPa of compression levels is sustained and Young's modulus is inversely related to the strain at fracture [35]. Nonetheless, the organic component helps in preventing plastic deformation and in maintaining the mechanical strength of the bone in combination with the mineral content [36]. The Young's modulus (GPa) of tropocollagen molecule has been reported by several authors to lie in the range of 0.35-12. For hydroxyapatite crystals, it has a range of 114-170 [15]. The Poisson's ratio of tropocollagen molecule and hydroxyapatite crystals have been observed to be 0.38 and 0.30 respectively [37].

The collagen fibrils provide ductility to the bone and resist fracture but degrades with time and disease. The mutations in amino acid sequencing of collagen fibrils leads to abnormalities (osteogenesis imperfecta) where bone are weak and break easily. In case of calcium deficiency, the hydroxyapatite part of the bone is not well replenished or formed and leads to decreased bone density (osteoporosis). Thus, both the organic and inorganic components have a crucial role in maintaining the overall integrity of the nanomaterial bone.

b) Abalone Shells

Abalones are marine snails and their shells (exoskeleton) are another example of natural nanocomposite material. Unlike in the snails where the mantle creates the shells from within (dorsal epithelium) in a controlled way by the secretome, in their marine counterpart, the abalone, the biomineralization of $CaCO_3$ occurs from the water to form distinct shapes, patterns and colors of the shell. The modularity and patterning mechanism of the mantle has resulted in this diversity of the shells [38]. The nanodomain of the substance is a result of strongly coordinated expression of multiple genes and regulated secretome with certain macromolecules [39].

The abalone shell consists of a tiles-like structure made up of ceramic (calcium carbonate, upto 95%) material held together by polymeric substance (biopolymer, up to 20 nm thick) and has extraordinary strength relative to its components (nearly 3000 times). Comparatively, it is two times stronger than ceramics and six times stronger than steel [40]. The average Young's modulus of nacre is 70 GPa, a value for stiff substances (rubber has <0.1 GPa and aluminum has 68 GPa for comparison) [41, 42] and is three orders of magnitude tougher than its component aragonite [43]. The strength is an outcome of thermodynamic stability gained by the product obtained over prolonged periods of time.

The formation of the shells is a natural representation of bottom-up approach. It possesses well defined geometry and robust mechanical characteristics. It has two distinct nano morphologies-inner (pearly, 400 nm thick) and outer (prismatic, 32 nm grains, dull) sections. The inner part is made up of orthorhombic aragonite (parallel to shell plane, nacre) and the outer part is made up of rhombohedral $CaCO_3$ (perpendicular to the shell plane) called calcite. Fig. 2 represents various structural aspects of the nacre.

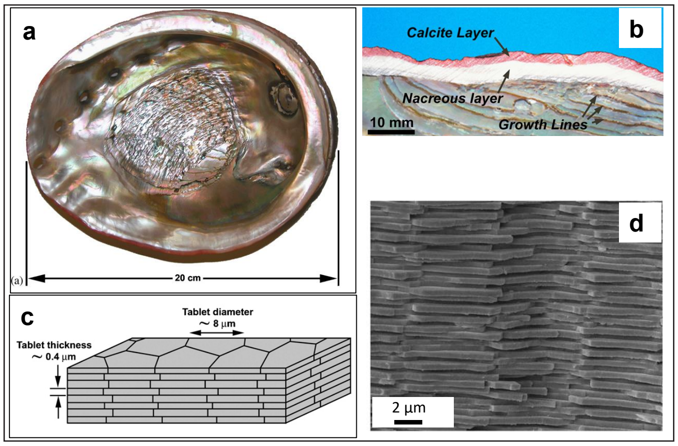

Fig. 2: (a) Picture of the Inner Nacreous Layer of a Red Abalone Shell with Size (b) Unique Arrangement of Shells (c) Cartoon Representation of Tablets' (or Aragonite Platelets') Geometry (Nacreous Layers) with Size (d) SEM Image of Fracture Surface [44]

An iridescent shell shown in Fig. 2 (a) is the inner layer and Fig. 2 (b) shows two distinct layers of calcite and aragonite (nacreous) polymorphs. The growth direction is shown towards the outer layer and distinct markings are present as growth lines. Normally, the aragonite platelets or tablets are *ca.* 8 μm across and they are co-oriented as shown in Fig. 2 (c) with each having a thickness of *ca.* 0.4 μm. Fig. 2 (d) shows the SEM image of fracture surface with the stacking of tablets one upon another with the apparent periodicity.

The tiles of $CaCO_3$ are held together by stretchy protein and when subjected to stress it slides over one another keeping the material intact [45]. The energy is greatly absorbed along with crack travel by lengthening the crack propagation towards an unsuitable stress state. This is possible because of the geometry of the crystals in the nanocomposite [46]. Large sized analogy to this structure is the wall made up of brick and mortar. The thin sheets of the organic matrix of protein/polysaccharide trap the aragonite polygonal tablets in some shells and the dimension of the inorganic phase is controlled by it [47]. This architecture decreases the empty regions and the damping of crack energy occurs efficiently without propagation in inorganic layers [48] minimizing the extent of the destruction.

Mimicry of abalone shells by synthetic means has not been able to generate material of equivalent strength and toughness [49]. In a raw form, nacre has been applied in jewellery and ornamental works. Also, it has been used as inlays of musical instruments and as buttons. The outer prismatic layer is removed and the inner pearly layer which appears colorful and mirror-like is exposed in most of the applications. This iridescent property (orient) is due to the reflection of light from the regular orientation of layered bands of ridges and grooves in the shell (overlapping aragonite layers) that result in constructive interference and augmentation of colors.

In addition, the individual crystals of aragonite act as miniature prisms producing rainbow-like effects due to refraction. Here the specific wavelength of light at a certain viewing angle is reinforced and also due to internal reflection the surface looks more brilliant. The nanostructure of the material has rendered this phenomenon of light possible because the wavelength of light and the spacing of the layers both are similar in dimension for better interaction and display of property. Thus, two different phenomena makes nacre a special natural nanocomposite material in terms of optical properties.

B. Earthen Minerals

There are multiple examples of materials present in nature which are minerals by definition and their morphology reveals that their size in at least one dimension lies in the nano-regime. Thus they are also a kind of natural nanocomposites. In these systems, the individual components are all inorganic compounds or a combination of inorganic and organic compounds. Some representative examples of natural mineral nanocomposites are discussed below:

a) Clay

Clays are earthy materials composed of fine particles of silicates or alumino-silicates with lamellar morphology possessing enormous surface area. It has plastic-like properties (moldable) in a hydrated state and is hard after high-temperature treatment. It is capable of absorption/desorption of water, reversible intercalation (up to a DNA molecule) [50] and exchange with other chemical species in between its layered-like geometry [51]. Because of these features of clay, it has been hypothesised as being an origin point of life on earth [52]. In a broader sense the term clay also refers to any earthy material with a particle size less than 2 μm.

Physical and chemical weathering of rocks and minerals in nature results in the formation of clay. Also, the spontaneous physical, chemical and/or biological alteration to a more stable phase through diagenesis produces the material. They are thus formed naturally by the action of water, steam and air and are the products of long geological time scales. The difference in temperature, pressure, free water and air at the earth's crust compared to that underneath where the rocks and minerals are initially formed results in the formation of clay. Some examples of the mode of formation from rocks are weathering by warm water, constant flow of wind, crystallization at pores or fractures, leaching or hydrolysis by acidic water, numerous freeze-thaw cycles, change in depositional environments etc [53]. The clay minerals are also one of the examples of natural nanocomposites and have been categorized into many classes based on their structure and chemical compositions. Some major types as shown in Fig. 3 are briefly outlined in the following paragraphs-

i) Kandites [54] - It is made up of a layer of silicate tetrahedron and a layer of aluminate octahedron bonded to form a slab-like structure with each separated by a void region called inter layergallery where intercalation chemistry can take place. It is considered a 1:1 compound because of the composition (one Si atom and one Al atom) of the slab (shown as a repetition of two slabs with blue and grey blue colors in Fig. 3).

ii) Smectites [55] - It is made up of two layers of silicate tetrahedra and a layer of sandwiched aluminate octahedra bonded to form a slab-like structure with each separated by an empty space where intercalation chemistry can take place like that of kandites. The gallery can be occupied by cations like K^+ as in clay called montmorillonite. The layers can expand in (001) direction upon absorption of water or organic molecules. It is considered a 2:1 compound because of the composition (two Si and one Al) of the slab (shown as a repetition of three slabs with blue, grey blue and blue colors with a large interlayer gallery in Fig. 4).

iii) Illites [56] - It is similar to smectites and the difference is that the layers are not that swellable (shown as repetition of three slabs with blue, grey blue and blue colors with tiny spacing for cations in Fig. 4).

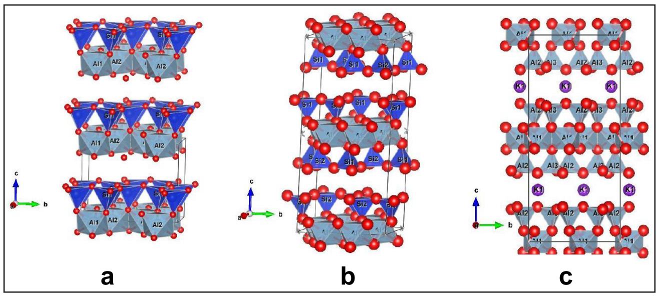

Fig. 3: Schematic Crystallographic Structures of (a) Kandites (b) Smectites and (c) Illites Clay Minerals; the Solid Rectangular Box Represents the Crystallographic Unit Cell

Clay is made up of alternating silicate sheet (tetrahedrally coordinated silicon atom, Fig. 5 (a) and aluminate and/or magnesium oxide sheet (octahedrally coordinated aluminum atom, Fig. 5 (b) with an interlayer gallery of interchangeable ions and mobile water molecules. It is thus a two dimensional material with the elementary building unit being a layer and is capable of undergoing reversible intercelation and reintercalation reactions [57]. It belongs to a broader class of silicates called phyllosilicates. The tetrahedral silicates are corner shared whereas the octahedral aluminates (or magnesium oxide) are edge shared. Various other compositions of clay materials where substitution by other metal cations like iron, potassium, sodium, calcium etc. have also been observed. The chemical formula of some clay minerals are $Al_2O_3.2SiO_2.2H_2O$ (kaolinite), $Al_2O_3.4SiO_2.H_2O$ (montmorillonite), $Mg_{0.33}Al_2(Si_{3.67}Al_{0.33})O_{10}(OH)_2$ (smectites), $K_{0.65}Al_{2.0}[Al_{0.65}Si_{3.35}O_{10}](OH)_2)$ (illites) and $Al_2O_3.3SiO_2.5FeO.4H_2O$ (chamosite). The ratio of SiO_2 in the composition determines the clay mineral types.

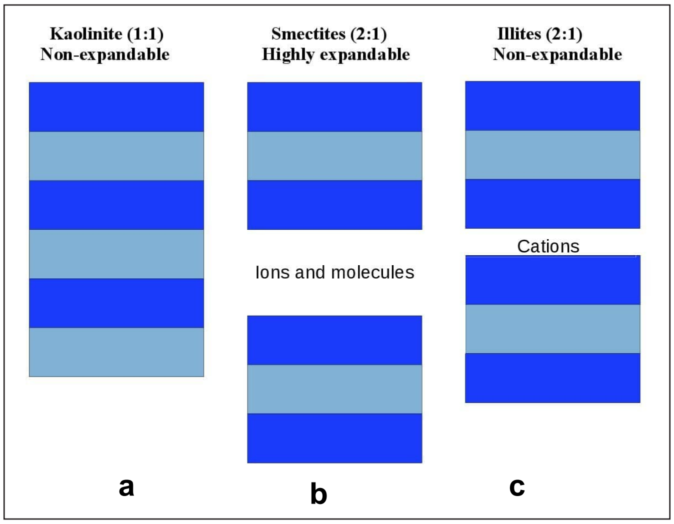

Fig. 4: Illustration of the Structure of Different Types of Clays as Layers (a) Kaolinite, TO ($Al_2O_3.2SiO_2.2H_2O$) (b) Smectites, TOT, $Mg_{0.33}Al_2(Si_{3.67}Al_{0.33})O_{10}(OH)_2$) and (c) Illites, TOT ($K_{0.65}Al_{2.0}[Al_{0.65}Si_{3.35}O_{10}](OH)_2$)

Multiple types of clay minerals considering the ratio between layers have been reported. The tetrahedral bonding environment is present with silicon atoms whereas aluminum has octahedral bonding environment with oxygen atoms as shown in Fig. 5. The periodic repetition of these building blocks separately in two dimensions creates a distinct morphology of the material. Thus each layer contains either tetrahedral arrangement or octahedral arrangement of oxygen atoms around the metal center. The number of these layers and their arrangement differ in different types of clays as shown in Fig. 4. The 1:1 type (TO) has one tetrahedral (T) and one octahedral (O) layer (*ca.* 0.7 nm thickness) whereas the 2:1 type (TOT) has two tetrahedra and one octahedral layer (*ca.* 1 nm thickness) in between. Another 2:1:1 type (TOTO) possesses alternating tetrahedral and octahedral layers (*ca.* 1.4 nm thickness) and in another way of comprehension, the 2:1 layer is thought to be separated by an extra octahedral layer for balancing the charges [58]. The nanosheet layer is negatively charged in many clay minerals because of the partial substitution of silicon, aluminum and other cations at their respective sites in the crystal lattice by different cations of similar sizes but with lower charges. The electroneutrality is achieved by the presence of cations at the surface or interlayer gallery. These cations are exchangeable and are present along with the water leading to the expansion of the lattice. The layers can be exfoliated into discrete form in a dilute aqueous medium. Smectites and vermiculite clays can swell upon water uptake whereas mica does not. Hence, rich chemistry is possible in clay materials and is the subject of active research in the quest for the design of superior materials [58b].

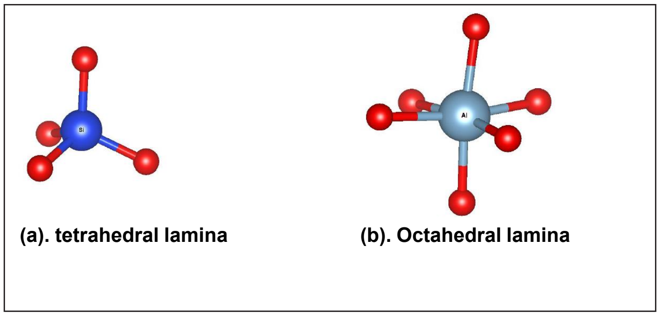

Fig. 5: Bonding Environments of Metals in Clay (a) Tetrahedral Coordination of Silicon Atom (Dark Blue Sphere) (b) Octahedral Coordination of Aluminum Atom (Grey Blue Sphere); Blocks Represent the Coordination in the Layers and the Arrows Show the Repetition of the Distinct Chemical Structure in a Distinct Bonding Environment in the Laminae (2 Dimensional Layers)

The clays can also be broadly classified into the following three types based on the ratio of silicon and aluminum in the structure and are described briefly below:

i) Phyllitic Clay - The metamorphic rocks being the origin, these clays are already discussed as 1:1 (kaolinite), 2:1 (smectite) and 2:1:1 (chlorite) types. They are the most common ones and can be dioctahedral or trioctahedral based on the extent of the filling of the octahedral positions [31].

ii) Fibrous Clay - It possesses a fibrous habit with sepiolite and palygorskite being two types of it. They are aluminosilicates with a 2:1 ratio of layers with truncation of sheets to few tetrahedra and octahedra resulting in the formation of rectangular-shaped structures [59].

iii) Interlayered Clay - The stacking of two or more layers occurs along the axis normal to the sheets in multiple ways and three of it present in most of the compounds are alternating, segregated and irregular types.

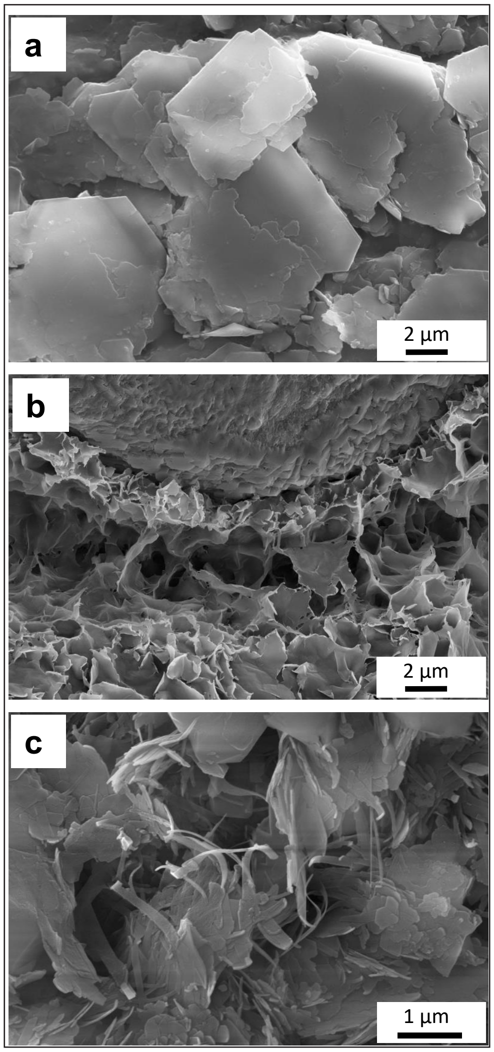

Fig. 6: Electron Micrographs [60] of Three Different Types of Clay Minerals (a) Kaolinites (b) Smectites and (c) Illites

Three different types of clay minerals as discussed above are shown as electron micrograph images [60] in Fig. 6. The thin idiomorphic and discrete tablets of kaolinite with a diameter of *ca.* 5 μm are shown in Fig. 6 (a). The dioctahedral pore-lining smectites with an average nanosheet size of 3 μm are shown in Fig. 6 (b). Fig. 6 (c) displays a mixture of fibrous (0.2 μm width) and platy (1 μm diameter) illites. General differences in the structure of clays cannot be fully justified based on these micrographs and require identical settings for proper comparative analysis.

b) Halloysite

It is a refractory aluminosilicate clay mineral and occurs naturally as tiny hollow cylinders lying in nano-regime. Its chemical formula is $Al_2Si_2O_5(OH)_4.xH_2O$ and is found in multiple colors due to the presence of various types of impurities. It was first mentioned in 1826 as a kaolin group clay mineral and a 1:1 dioctahedral compound [61]. It has pearly, waxy or dull lustre and crystallizes in monoclinic space group settings [62]. The most abundant form is the halloysite nanotube with a length extending up to 1000 nm.

Halloysite is formed from hydrothermal modification of aluminosilicate minerals (mainly the glassy basaltic rocks and pre-glacially weathered minerals) and is found in the vicinity of volcanic and tropical soils, especially the carbonate rocks. It occurs as a mixture with other different types of minerals and the current global estimate is absent in the literature. Its spiral structure contains siloxane network at exterior walls whereas the interior region is made up of aluminol network as shown in Fig. 7 (a). The sheets of halloysite are curled multiple times leading to the formation of tubular structure without termination, that is the edge of the curved sheet is open as shown in the micrograph image Fig. 7 (b). The interior and exterior parts of the tube differ in the chemical constitution. The outer layer is terminated with siloxane (Si-O-Si) whereas the inner layer is terminated with aluminol (Al-OH). Between two types of cations oxygen bonding, water is trapped at the interlayer gallery. The atomic composition of the tube starting from the interior surface upto the outer layer is shown below in Table I.

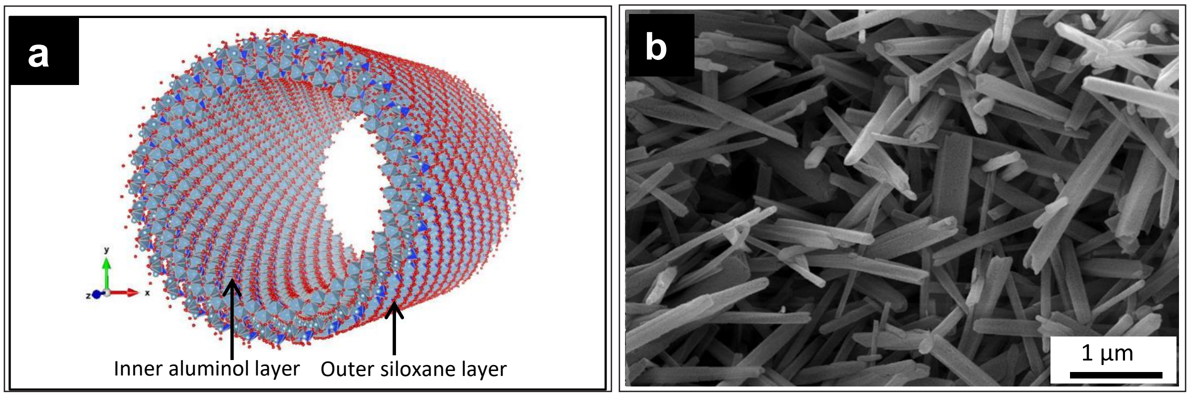

Fig. 7: (a) Schematic Structure of a Natural Nanocomposite, Halloysite Nanotube [63] (b) Electron Micrograph Image of Halloysite Nanotubes (The Nanotube is *ca.* 1000 nm Long) [64]

TABLE I: THE SEQUENTIAL COMPOSITION OF THE INTERIOR AND EXTERIOR PARTS OF THE HALLOYSITE NANOTUBE IN THE SPATIAL STRUCTURAL ORDER

Inner Aluminol Surface	*Outer Siloxane Surface*
Innermost - OH	Interlayer space - H_2O
Al	OH
O	Al
Si	O
O	Si
Interlayer space- H_2O	Outermost- O

Halloysite nanotubes have been applied in diverse fields owing to their multitude of properties. The characteristic surface area is 50-137 m^2/g and the aperture volume is 1.25 mL/g. Its specific gravity is 2.14-2.59 g/cc and its refractive index is 1.54. The inner/outer diameter of the tube is 10-40/40-70 nm and 200-40,000 nm long. The elastic modulus has been reported upto 600 GPa. Halloysite crystallizes in monoclinic crystal system with the lattice parameter a = 5.14 Å, b = 8.9 Å, c = 14.7 Å, β = 104° [65]. They possess a unique tubular structure with different internal (positively charged) and external surface (negatively charged) terminations with the open edge having both. This leads to selective reaction centres for the specific types of chemical reactions and tailored modifications are possible for desired applications. The presence of thermal stability, high porosity and re-entrant curvature makes it a rich featured material. Due to all the above-mentioned peculiar characteristics, halloysite has been exploited in a diverse set of applications. Some of it are the controlled release of chemically and biologically active molecules [66], adsorbent for dye removal [67], water treatment as nanocomposites [68], fabrication of super-amphiphobic coatings [69], synthesis of liquid marbles for miniaturized devices [70] etc.

c) Layered Double Hydroxides (LDH)

Layered double hydroxides are biocompatible lamellar ionic compounds comprising of hydroxides of *di*-valent (Mg^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) or *tri*-valent (Al^{3+}, Ga^{3+}, Mn^{3+}, Fe^{3+}) metals with one of the dimensions lying in the nano-regime. They occur naturally with the general chemical formula $[(OH)\ (M^a)_{1-x}(M^b)_x(OH)]^{n+}(A^{n-}{}_{x/n})\cdot yH_2O]$ where M represents metal cations and A the anionic species with *n* charges. They are also called layered hydroxide salts and can be simplified as $[PmQ\ Y\ PmQ]_r$ where P and Q are hydroxides, m is the metal cation, Y are other species and r is the number of repeating units. The formation of covalently bonded atoms into a two dimensional sheet-like structure with water and ions between adjacent sheets is shown in Fig. 8. Since these guest species in the interlayer gallery can be intercalated, the basal spacing can be tailored to the desired extent.

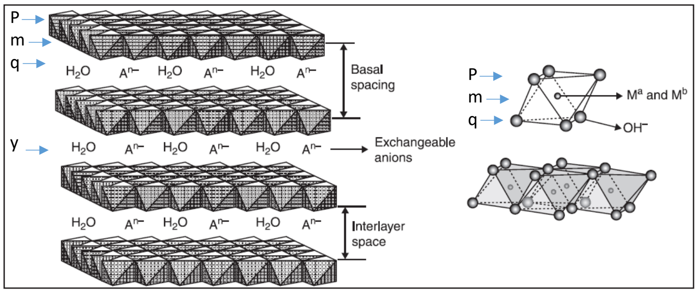

Fig. 8: A Schematic General Depiction of LDH with Atomic Level Bonding (Edge Sharing Octahedra) and Features [71]

The thickness of the two-dimensional infinite hydroxide layer is *ca.* 0.49 nm and is stacked one upon another to yield the three-dimensional geometry [72]. The hydroxide layers are positively charged with the counter anions present in the interlayer gallery along with water molecules. The term double hydroxides stem from the presence of two types of metal cations (M^a and M^b) as hydroxides in the cadmium-iodide type layered geometry of the material [73]. Structures with more than two types of metal cations have also been reported [74]. In case of individual layers in the crystalline structure, the geometry is brucite-like with magnesium octahederally bonded to six different hydroxide groups considering the local bonding environment for $x = 0$. The octahedra (MO_6) are edge sharing and form a 2-dimensional continuous network of covalently bonded building blocks. The apical -OH are not bonded to any other metal cation thereby terminating the network of covalent bonding in the stacking direction. This feature creates a surface termination-like effect inside the LDH crystal and tremendously increases the surface area or the aspect ratio of the material. Between the layers of covalent network, water or other ions are present and the interlayer spacing or gallery readily undergoes interesting chemistry.

Since the layer is positively charged (as shown in Fig. 8), anions are located in the gallery to attain charge neutrality. The components of this interlayer spacing are mobile in nature and can be exchanged with other species. The distance between two layers can be altered to different extents by the intercalation [75] of chemical species of various sizes. The maximum being the ultimate separation of the layers by soft exfoliation (delamination) techniques leading to the formation of discrete particles in the nanodomain and especially the functional nanosheets have been reported [76]. Many parameters of the exfoliation process can be controlled to obtain the nanomaterial of desired dimension (single layer of multiple layers) or the composition [77]. Interestingly, the sheets can be even restacked and thus tailored for a particular application [78]. Low dimensional solids are easily tunable for their chemical, magnetic, mechanical, electronic, photonic etc properties. This phenomenon makes the material attractive for a wide array of chemical modifications and for the development of advanced materials possessing multiple applications perspective.

Electron micrograph images of a (Zn-Al) LDH at two different resolutions are shown in Fig. 9. The layered morphology of the material with a tablet-like geometry can be discerned at high resolution in Fig. 9 (a) and the discreteness of the compound with very low aggregation with curvature can be seen at low resolution in Fig. 9 (b).

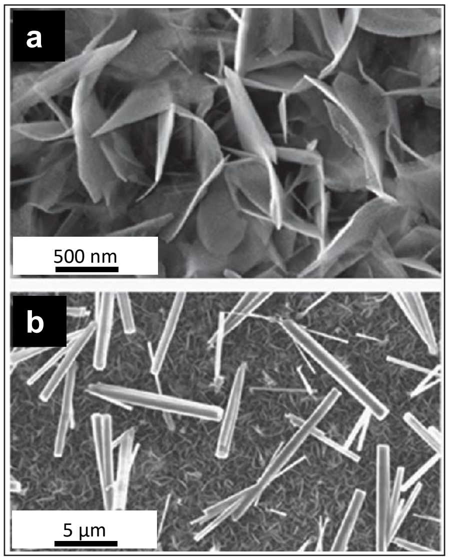

Fig. 9: Representative SEM Images [79] of LDH (Zn-Al) Grown on Al Layer (a) High Resolution (b) Low Resolution

Because of their high surface-to-volume ratio, non-toxicity, good capacity to intercalate and deintercalate various types of materials from small molecules to DNA, acceptable thermal stability and capability of versatile structural modification and resilience, they have been applied in multiple areas like catalysis [80], drug deliver [81], sensing [82], photochemistry, electrochemistry, energy production and storage, antimicrobial biomaterials [83] and others [84]. Since LDH nanocomposites with polymer sum up both the properties of inorganic phase and organic compound, they can be used to develop various types of functional materials. Here different scientific fields can be merged that can contribute to the modern age of designed materials.

C. Natural Rubber

Natural rubber (NR), as the name suggests is another example of a natural composite material though not strictly containing an organic-inorganic framework. It is an elastomer and a thermoplastic. It contains polymers of isoprene *(~95%),* proteins, fatty acids, resins, inorganic salts and water. It is obtained from the milky white running liquid called latex from plants. The latex has a molecular weight from 10^5 to 10^6 daltons and is a polymer cis-1,4-polyisoprene [85]. Around 200 plants produce this compound but 99% of it is extracted from *Hevea brasiliensis* or rubber tree, native to the Amazon jungle [86]. One variation in NR is the occurrence of trans-1,4-polyisoprene obtained from a plant called *Palaquium gutta* or gutta-percha. The two varieties differ in that the former forms an amorphous structure while the latter forms crystalline geometry.

The unique properties like high stretch ratio and resilience along with waterproofing applications make them attractive for commercialization and scientific studies [87]. Most of the use of NR is carried out with its modified version due to the attainment of enhanced properties, ease of processing and strength [88]. The high strength in the rubber is due to the strain-induced crystallization whereby the crystals thus formed act as reinforcing filler. It makes rubber a sort of nanocomposite at tightly stretched state.

III. SPECIAL PROPERTIES AND APPLICATIONS

A. Properties of Nanomaterials

a) Mechanical Properties

Natural nanocomposites are substances with superior mechanical properties in comparison to its constituents. This makes them attractive for various applications and also in scientific studies encompassing different areas. In bio-nanocomposites, the large aspect ratio of minerals tends to augment the stiffness of the soft protein. Quantitatively it has been estimated that the aspect ratio of 30-40 would bring 3 orders of magnitude higher stiffness of protein [89]. The nanometer-sized critical length scales act as shock or stress dampeners as crack-like flaws do not affect the structural integrity. The hierarchical ordering results in the best optimization and adaptation at all levels to form a structure with intricate order and great strength, yet to be mimicked by synthetic materials [90]. Among many natural nanocomposites, spider silk is considered to possess higher strength (*ca.* five times) and toughness than steel considering the weight of the material. It is very elastic and one of its kind is stretchable up to four times its original length. Other natural nanocomposites like bone, shell, wood, cuticle and tooth all have similar classes of ingredients and notable mechanical properties are due to similar mechanisms of action.

Elastic properties of the material are a subset of mechanical properties and will be dealt in brief. Natural rubber, a good example of a natural nanocomposite as discussed above, exhibits better resilience and stress-strain behaviour than all-natural nanocomposites available [91]. In an unstretched or relaxed form, the rubber possesses a randomly intertwined molecular structure of multiple polymeric chains and when stretched the cross-linked structure become nearly linear. This process is reversible up to a limit and thus the material is said to possess elastic property. The straightened chains are lowered in the entropy and this give rise to the elastic stress or force opposing the strain in the material [92]. The mechanical and dynamic mechanical properties of natural rubber have been augmented with the addition of filler material like nanocarbon [93]. The role of strain energy density function in terms of thermodynamics (continuum ideas) and mechanics in rubber has also been described [94]. Overall the modification of natural rubber by curing, vulcanizing and other post processing techniques have resulted in betterment of selected properties [95].

b) Electrical Properties

Some natural nanocomposites and their modified forms with fibres/fillers have good conducting properties and as a result have found applications in wide areas as drug transporters, neural probes, sensors, fuel-cells, antennas, chemical probes etc [96]. There are broadly two types of conducting polymeric nanomaterials- intrinsically conducting polymers (property built-in) and conducting polymer composites (property induced). The first is used in smart materials while the latter is in organic electronic devices [97]. Apart from this, several metal based-nanocomposites fabricated from biosources have been reported in a large number of applications and in scientific investigations [98, 99, 100, 101]. The DC conductivity of natural rubber with filler (polypyrrole) was found to be 6.25 x 10^{-2} S/cm and possessed a dielectric constant of 55.5 at 100 parts per hundred rubber at 3.98 GHz [102]. In the case of silk fibroin with polypyrrole, the conductivity was reported to be 4.2 x 10^{-1} S/cm [103]. The presence of cellulose nanowhiskers increased the conductivity by 11 orders in magnitude in polyaniline and natural rubber composites than that without it [104]. Another nanocomposite material with conducting properties is made up of clay and polymer. It is engineered only after pre-modification of the clay and has been discussed in detail by Valapa *et al.* [105]. With the pre-modification, the electrical conductivity was augmented by six orders of magnitude [106]. Similarly, the organophilic clays tend to have higher values in their nanocomposite relative to hydrophilic or pristine ones which have been attributed to better intercalation, exfoliation and wetting [107]. Nearly 6 S/cm of DC conductivity was measured in montmorillonite clay evenly intercalated with polypyrrole at room temperature [108]. By using a self-assembled nacre-like polymer clay nanocomposite, the value as high as 560 S/cm has been reported [109]. Here instead of natural clay, a synthetic variety was used to obtain high performance. The incorporation of various types of conducting polymers with high surface area to volume ratio into the layers of clay has been discussed in detail by K. Jlassi *et al*. [105].

c) Thermal Properties

The natural nanocomposite in their intrinsic forms have low thermal conductivity (κ) and better insulation properties [110]. The κ values of cellulose, wood wool, rubber, clay and bone are respectively 0.037, 0.065, 0.13, 0.25 and 0.55 W/mK (air 0.025 W/mK) [111, 112]. The transfer of heat occurs through phonons, electrons or photons [113] and due to several defects in the structure of the material, κ tends to be low [114]. Addition of fillers especially graphene (10%) has shown an increase up to 23 times the conduction in nanocomposite polymeric systems due to its high κ value and some ordering of the chains [115]. Also an increase in κ has been reported in natural rubber with the addition of graphene [116]. A highly anisotropic κ has been observed for a system of nano-fibrillated cellulose containing graphene oxide with in-plane values greater than 12 W/mK [117]. In the case of transparent cellulose nanofiber and epoxy resin nanocomposites there was also a very high increment [118]. A homogeneously dispersed reduced graphene oxide over natural rubber yielded betterment in thermal as well as mechanical and electrical properties of the nanocomposite. The web-like platelet network of the filler contributed to the increase in thermal and electrical conductivity [119]. More than seven times increment in κ was seen in nanofabricated cellulose films on nanodiamond with a hierarchical structure containing intermolecular hydrogen bonds [120]. Nearly twelve times increase (*ca.* 14 W/mK, highest value) was reported when additional graphene sheets were used [121]. This was the mimicry of nacre where zero-dimensional (nanodiamond), one-dimensional (nano-fibrillated cellulose) and two-dimensional (graphene sheets) were used to form a hierarchical geometry. Up to 9 W/mK was measured for a nanocomposite plastic consisting of cellulose and functionalized graphene (6%) [122]. A review article containing multiple properties of graphene polymer nanocomposite is referred to for more information on thermal conductivity on this specific class of material [123]. In most of the cases as discussed above, there are multiple factors (brief notes in parenthesis) that augment the thermal conduction in a nanocomposite material as:

i. Filler or reinforcing material with high κ (graphene and its family has the highest values up to 5,000 W/mK).
ii. Hierarchical morphology (nacre mimetics for added strength and thermal stability).
iii. Homogeneous dispersion of filler with continuous linking (web-like connection for unhindered thermal transport).
iv. Presence of hydrogen bonding for strong interfacial interactions (good bonding of filler with matrix for mechanical stability).
v. Proper orientation of the components (unidirectional flow of heat without dissipation).

B. Applications of Nanocomposites

a) Packaging, Coating and High-Performance Materials

i) Packaging

Nanocomposites made up of natural biopolymer and layered silicates have high modulus and strength, water resistance and diminished gas diffusion. This makes the material a good candidate for packaging. Moreover, the desired functionality and bio-degradability can be achieved in the material by incorporating bioactive ingredients. This helps in the current need of environment-friendly materials and in reducing the ever-growing plastic waste. Thorough information on packaging materials can be obtained from the published review article [124].

ii) Anti-Corrosion Coating

In order to prevent materials from corrosion, many types of coatings containing nanocomposites have been reported [125]. One of the nanocomposites with polystyrene and modified graphene oxide has shown to possess excellent anti-corrosion properties [126]. It was attributed due to the better dispersion of graphene in the polymer matrix. The use of clay along with bitumen as a natural nanocomposite material was found to inhibit the corrosion of steel surface [127] and the mechanistic aspects in similar systems has also been elucidated [128]. The use of surface coatings and solution phase inhibition by different polymer nanocomposites has also been reported [129]. A novel 2D nanomaterial called MXene, has been applied as reinforcement in polymeric materials to produce a nanocomposite with many interesting properties [130]. A good review of synthetic nanocomposite materials exhibiting anti-corrosion and anti-biofilm has also been published [131].

iii) Fire Retardant

Layered material like clay when incorporated into the polymer matrix enhances the thermal stability of the nanocomposite. It reduces the heat conduction and the mobility of various products is decreased during the fire. The formation of char also assists in retardancy [132]. Specifically, the nanocomposite formed by organically modified montmorillonite clay with different types of polymers have been reported to have good thermal properties (lower peak heat release) but with the limitation of excessive smoke formation [133]. Graphite based nanocomposites (eg. styrene-butyl acrylate copolymer/ graphite oxide) have better performance with lower smoke production and are free of halogens. They are considered eco-friendly green materials and are non-toxic in nature [134]. The presence of well dispersed paramagnetic iron in clays helps in radical quenching and preventing degradation [135]. Other nanocomposites with layered double hydroxides acquire the same level of performance only with higher loading and the dispersion is reduced in the matrix [136]. Nanocomposites with silica, metal oxides and hydroxides have also been reported to reduce heat release rate and possess a higher capacity in flame retardancy [137, 138, 139, 140, 141]. The homogeneous dispersion in the matrix is the key factor in the betterment of the property. More research is required in this area with other elements not limited to sulphur and phosphorous and matrix to produce efficient alternate materials.

iv) Aerospace Engineering

Also in the aerospace engineering sector natural nanomaterials are used in combination with other substances in the form of nanocomposites. Since virgin polymers alone or the composite material in the micro or macro domain do not possess better properties, its combination and that also in nano domain leads to the formation of materials with desired and advanced characteristics suitable for applications in aerospace engineering. Since the requirements for space materials are harsher due to excessive heat and cold, lower pressure, high velocity, solar and cosmic radiations etc, highest possible parameters are mandatory in terms of thermal stability, toughness, mechanical stability, shielding, density etc. These criteria can be fulfilled by producing nanomaterial-polymer composite using appropriate synthetic strategy, modifiers and curing chemicals [142].

A good class of material suitable in aerospace engineering is polymer/clay nanocomposites. Mainly, montmorillonite, a naturally occurring clay mineral has been employed along with epoxy [143] and acrylonitrile butadiene styrene systems [144] to produce nanocomposite materials with better properties. Because of superior intercalation chemistry, aspect ratio, low cost and availability, clays are considered ideal nano reinforcement chemical compounds for polymers. Due to the strengthening of interface interactions and intricate bonding in an epoxy matrix by the well-dispersed nanomaterial, the composite tends to possess augmented properties especially enhanced tensile modulus, storage modulus and tensile strength. With exfoliated clay, these properties were increased even further [145]. The high aspect ratio of the nanomaterial tends to increase the stiffness and the composite modulus was augmented by the larger interlayer spacing of the clay mineral. High thermal stability was observed in epoxy-montmorillonite nanocomposite due to better insulation properties of the clay mineral [146]. Flame retardancy and optical transparency were found to be augmented in case of organically treated montmorillonite particles with epoxy resin. Clay layers induce tortuous path in the matrix and diffusion or penetraion is hindered. This results in prevention of leakage due to retarded permeation of gas, moisture or other small molecules [147]. Also anti-corrosive properties have been shown to increase along with the clay content [148]. Similar properties have been reported for another nanocomposite system consisting of acrylonitrile butadiene styrene and montmorillonite clay [148]. Because of all the above-mentioned features, the epoxy-clay nanocomposites can be considered as a representative material suitable for aerospace engineering where lighter structural integrity and superior quality materials are required.

b) Health and Environment

i) Bone Tissue Engineering

Synthetic nanocomposite substitutes (biomimetic) resemble the human bone in terms of both ingredients and geometry and has been reported to undergo osteointegration and bone reconstruction. One of the successful kinds is made up of *ca.* 67% ultra-long hydroxyapatite nanowires and collagen to give a porous structure and the rehydrated form shows good elastic property as well [149]. Also, chitosan-based nanocomposites have been proposed with similar outcomes [150]. There are numerous studies in this aspect with different scaffold materials like alginate, silk fibroin, hyaluronic acid hydrogels, chitin, keratin, peptide hydrogels, fibril nanocomposites etc and some cumulative articles have been published [151, 152, 153, 154].

ii) Drug Delivery Systems

A wide variety of natural nanocomposites and their modified forms have been used as drug delivery systems. As a therapeutic measure for diabetics, the nanocomposites made up of chitosan along with a zeolite have been proposed as a carrier for the *in vivo* distribution of metformin [155]. For the oral delivery, a composite with clay (montmorillonite intercalated with insulin and TiO_2) has been reported [156]. The nanocomposite of bacterial cellulose with graphene oxide has been employed for the drug, Ibuprofin [157]. One of the anti-cancer chemotherapy drugs named Doxorubicin has been used with pH and heat-sensitive magnetic nanocomposite for location and time-controlled release [158]. For the treatment of colon or rectum cancer, a drug named Camptosar has been incorporated into a composite made up of clay and a polysaccharide [159]. The clay and polyamide nanocomposite containing diazoles showed significance *in vivo* microbiocidal activity [160]. Thorough information on the role of clay nanoparticles in drug delivery and their therapeutic efficacy can be obtained from the recently published articles [161, 162, 163, 164, 165].

Apart from clays, other natural nanocomposites made up of layered double hydroxides and anti-cancer drug methotrexate and genes has also been found to be effective [166].

iii) Wastewater Treatment

Natural nanocomposite and its derivatives have been used as a means of renewable resources for water and wastewater treatment that involves sorption, flocculation, pollutant degradation, disinfection and membrane filtration [167]. Especially the cellulose nanomaterials (crystals and fibrils) in different forms act as abundant low carbon footprint resources and have been the subject of global sustainable research. The cellulose nanocomposites are synthesized either by hydrolysis or by the disintegration of plant-based materials [168]. There are also other methods using bacterium as sources producing bacterial cellulose [169]. The key reasons for the efficient use of cellulose nanomaterials are their large surface area (more active sites for adsorption) [170], high aspect ratio (better flocculation due to percolation or entanglement) [171], high density of changeable functional groups (easily tailored for specific purposes) [172], better mechanical strength (rigidity and chemical inertness with decreased bio-fouling) [173], surplus abundance (naturally occurring in large quantities and as by-products) and better colloidal dispersion (no aggregation or lumping) [174]. They have been used in the adsorption of different dyes [110, 175, 176] and various metal ions [177, 178, 179] in multiple oxidation states including radioactive species [180] present in water. Also, the removal of drugs [181], proteins [177, 182] and hazardous pollutants [183] have been reported. Modified cellulose nanocomposites have been successful in the treatment of oils [184] and other organic liquids [185] from water. The membrane form of the material with various functionalization has eliminated up to nano-sized components [186], industrial wastes [187] and some microbes [188]. One interesting nanocomposite is made up of silk fibroin and cellulose nanofibril that can filter nanoparticles, and remove dyes and some heavy metal cations [189]. Polymeric matrices with different loading of cellulose nanostructures have resulted in the variation of tensile strength and have better membrane features than those with carbon nanotubes [190]. The coagulation and flocculation have been carried out by cellulose nanocomposite with different compositions and functional groups to remove dirt [191], microbes [192] and dyes [193] from water. Even though it has shown some disinfecting properties [194, 195], its use in potable water plants is yet to be started. This has left open a challengeable field of research work to be pursued in a quest for sustainable low carbon footprint natural nanocomposite resources. One of the works for wastewater treatment with an abundant natural biopolymer, chitosan has shown promising results in sorption and chelation for the elimination of heavy metals, dyes and different types of organic pollutants [196]. Due to the limited scope of this chapter other similar works with natural nanocomposites will not be mentioned here.

IV. Concluding Remarks

The structural and functional aspects of some important classes of natural nanocomposite materials have been reviewed. The geometrical variation of various types of natural nanocomposites was studied focusing on the atomic level details, salient morphologies and on the secondary structures like tetrahedra and octahedral subunits that compose the material. Nature-based nanocomposites materials were being investigated excessively owing to their excellent functional properties and also with the hope of obtaining novel functional materials for various applications. The natural nanomaterials have gained tremendous research interest considering their traditional uses across civilizations owing to their promising functional property. In this article, the structure and properties of natural nanomaterials (such as clays, halloysites, and layered double hydroxides) and their properties have been explored. Natural nanocomposites have great potential for their uses for environmental remediation and public health such as designing drug delivery systems, tissue engineering etc. and bio-inspired materials development. They find ever-accelerating uses in developing new materials for construction, transportation, and electronic and electrical appliances.

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