

MULTIFARIOUS APPLICATIONS OF HALLOYSITE NANOTUBES: A REVIEW

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Abstract. Natural tubules Halloysite are unique and versatile material formed by surface weathering of aluminosilicate minerals and comprises of different proportion of aluminum, silicon, hydrogen, and oxygen. It has chemical formula of $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8 \cdot 4\text{H}_2\text{O}$. Nanotubular geometry of halloysites exhibit nanoscale dimensions. Basically, this tubular arrangement varies with different regions. HNTs have high mechanical strength and modulus and these features make it an ideal material for preparing different polymer based composites. Halloysites (HNT's) are being used for so many varieties of biological and non-biological applications; remediation of environmental contaminants, act as a cargo for the delivery of drugs and various macro molecules, storage of molecular hydrogen and for catalytic conversion and processing of hydrocarbons. They are usually applied in the fabrication of high quality ceramic white-ware, nanotemplates and nano scale reaction vessels. In conjunction with different epoxy (EP) composites halloysite used to improve the mechanical properties of polymer. Various features of HNT's like rigidity, higher aspect ratio, and easy dispersability in polymer matrix and more importantly its abundant availability and biocompatibility make it a subject of fascination. In this review, we tried to summarize the various facet of halloysite nano tubes for the pertinence in the various research fields.

1. INTRODUCTION

The Halloysite nanotubes (HNTs) is a kind of aluminosilicate clay ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot \text{H}_2\text{O}$ with 1:1 layer) with hollow micro and nanotubular structure, and are mined from natural deposits in countries like China, New Zealand, America, Brazil, and France. HNTs are chemically similar to kaolinite and they used in the manufacture of high quality ceramic white-ware. Many researchers have done much work on the characterization of the Halloysite clay. Recently it has reported that HNTs have typical dimensions of, 10–50 nm in outer diameter, 5–20 nm in inner diameter with 2–40 mm in length [1,2], see Fig. 1.

Halloysite's layer silicate and the crystal structure are formed by two building blocks: (i) sheets of corner sharing $[\text{SiO}_4]$ tetrahedra and (ii) sheets of

edge sharing $[\text{AlO}_6]$ octahedral. In the $[\text{SiO}_4]$ sheets the tetrahedra share three corners and the unbounded tetrahedral apices are all pointing along the same direction[3]. Within the octahedral sheet, only 2/3 of the existing octahedra sites are filled by aluminium. It is referred to be a dioctahedral layer (term normally used in mineralogy). The layers building up the final structure are composed by one of each of these sheets so that the crystal structure of halloysite is described as 1:1 dioctahedral layer silicate. The water molecules are sitting between two consecutive layers create slight differences in the relative orientation between neighbouring layers might give rise to the differences in the symmetry of the final structure. This structure of Halloysite elucidates the close similarity with structure of kaolinite and experimentally it is difficult to distinguish between them. As a matter of fact, the structure of

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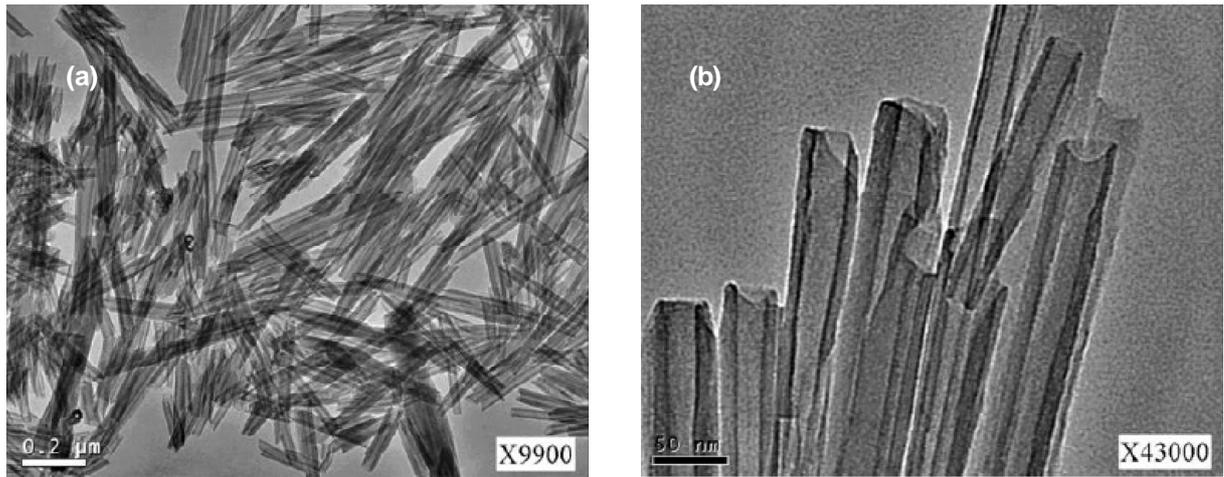


Fig. 1. TEM images of Halloysite nanotubes (Courtesy of Dr. Bing Zhang).

Halloysite-(7A °) is completely analogous to a disordered kaolinite structure. Tubular or cylindrical particles of different dimensions are normally found with halloysite even though some other morphology has also been reported (fibres, platy, etc.). Thus, the powder X-ray diffraction patterns are rather complicated with extensive overlapping of reflections accompanied by a high background. As a result, X-ray diffraction powder patterns are virtually identical for both structures. As stated in the most noticeable difference is probably the particle shape. Thus, we adopt the convention that the presence of cylindrical or tubular particles is indicative of halloysite while samples with platy particles might be named as kaolinite [4-6].

Various patents exist for the use of halloysite as nanofillers and in controlled release technology for a range of active agents. This mineral is extensively used in industry for ceramics, cements and fertilisers. Besides these it has enormous potential applications because of their peculiar tubularly shaped particles normally found in this mineral. Halloysite has also been used as a petroleum cracking catalyst in the past [6].

Such a peculiarity of Hallosite opens up the interest to use it as a template in nanotechnology, i.e. In this context, it is physically impossible to review the whole literature concerning this mineral and we just refer to a recent publication, which constitutes a compact and extensive review on this mineral.

2. HALLOYSITE NANOTUBE FOR CORROSION PREVENTION.

Corrosion of metals is a serious technological problem, and a variety of methods such as cathodic pro-

tection, insulating coatings, and corrosion inhibition has been developed to overcome it. An inhibitor-enhanced coating is one of the most effective methods. Different type of inorganic corrosion inhibitors includes chromates, phosphates, molybdates, and nitrites available. Drawbacks associated with these inorganic inhibitors is their toxicity. Therefore, an introduction of environmentally friendly corrosion inhibitors for protective coatings is important.

Recent advancement has offered an opportunity for fabrication of coatings with anticorrosion properties by integration of nanoscale containers (carriers) loaded with the inhibitor or other active compound into existing "passive" films, thus designing new coating systems based on the "passive" matrix-"active" container structure. The concept behind this is to develop nanocontainers, which can be sensitive to the external (e.g., mechanical damage) or internal (e.g., pH changes) corrosion trigger

2.1. 2-mercaptobenzothiazole for anticorrosion

Halloysite nanotubes used for active release of corrosion inhibitors. In this approach corrosion coatings composed of hybrid sol-gel films were doped within Halloysite nanotubes so they were able to release entrapped corrosion inhibitors in a controllable way. A silica-zirconia-based hybrid film can be used as an anticorrosion coating deposited on aluminium alloy. Halloysite nanotubes with inner voids loaded by corrosion inhibitors (2-mercaptobenzothiazole) and outer surfaces covered layer-by-layer with polyelectrolyte multilayers were introduced into the hybrid films. These sol-gel films with the nanocontainers provide long-term corrosion

protection in comparison with the undoped sol-gel film. In this approach corrosion trigger the release of corrosion inhibitor in controllable manner. Exertion of the inner Halloysite nanotube lumen used as a storage vacuoles for the corrosion inhibitor offers a novel way of fabricating composite.

Leakage of the loaded inhibitor from the interior of halloysite can be prevented by modification of outer surface of 2-mercaptobenzothiazole-loaded halloysite nanotubes with deposition of alternating polyelectrolyte multilayer (poly(allylamine hydrochloride)/ poly(styrene sulfonate). Function of the polyelectrolyte shell is to provide the release of the encapsulated inhibitor in controllable manner with the change in pH of surrounding environment around the Halloysite nanotube, and that's why inhibitor directly releases in the corrosion pit [7].

2.2. Benzotriazole for anticorrosion

Benzotriazole and its derivatives are the most effective inhibitors used for protection of copper and transition metals. Although benzotriazole is an efficient corrosion inhibitor for these metals, but in chloride-containing environment (e.g., seawater) environment, its corrosion-inhibitive performance is not sufficient so the combination of corrosion inhibitor with passive protection (such as paint coating) is required. A direct addition of benzotriazole into the paint is not effective, because it is water-soluble and leaves empty voids in the coating layer, which decreases the barrier properties of the coating. By introduction of benzotriazole into paint within nano or microscale encapsulating systems drastically improves anticorrosion performance.

Halloysite nanotubes with dimension of 50 nm diameter and ca. 1 μm length used as containers for the loading, storage, and sustained release of benzotriazole. Extended controlled release can be achieved by formation of the stoppers at tube openings. Benzotriazole release time in water was in range from 10 to 100 h depending on the stopper formation at the cylinder ends. Entrapment of benzotriazole into clay within nano or microscale encapsulating systems drastically improves anticorrosion performance [7,8].

3. HALLOYSITE NANOTUBES FOR THERMAL RESISTANCE

Thermal stability and fire retardancy of the nanocomposites remarkably heightened by the incorporation or addition of HNTs. Normally HNTs used in the manufacture of high quality ceramic and

white-ware. In recent time, HNTs are being attempted to utilize as nanofiller in conjunction with various polymers like natural rubber, nitrile rubber and polypropylene. Halloysite nanotubes influenced the fire performance of the composites, by developing thermal insulation barrier at their surface during burning. This created barrier either retard the burning without stop or more often double the total burning time.

3.1. Halloysite nanotubes and poly (propylene)

Incorporation of HNTs in Poly Propylene causes significantly increased thermal stability and flame retardant effect of the PP/HNTs nanocomposites. Nanocomposites based on polypropylene and HNTs are prepared by melt blending. HNTs were dispersed in PP matrix evenly at nanoscale after facile modification. Cone calorimetric data also show the decrease in flammability of the nanocomposites. Entrapment mechanism of the decomposition products in HNTs also explained the enhancement of thermal stability of the nanocomposites. This enhanced thermal stability and decrease flammability were because of barriers in heat and mass transport as well as the presence of iron in HNTs [9].

2.2. Halloysite nanotubes and LLDPE (linear low density polyethylene)

Linear low density polyethylene (LLDPE) is an important thermoplastic for the applications such as electric wire, cable, film, pipe, and container. However, its applications are limited due to its low strength, low softening point, and flammability and so on. Simultaneously, it is necessary to modify LLDPE to get improved mechanical properties, flame retardancy as well thermal stability.

Halloysite nanotubes (HNTs) used with linear low density polyethylene (LLDPE) to prepare composites with enhance mechanical and prominent flame retardant properties. Poly Ethylene graft was used as interfacial modifier in the LLDPE/HNTs composites. HNTs have proved to be a promising reinforcing and flame retardant nano-filler for LLDPE. This mechanical properties, flame retardancy, as well as thermal stability of the composites can be further enhanced by the addition of the graft copolymer. Addition of graft copolymer in LLDPE/HNTs composites not only facilitate the dispersion of HNTs in LLDPE matrix but also enhance the interfacial bonding [10].

2.3. Halloysite nanotubes and Nylon 6

Nylon 6 (PA6) is a semi-crystalline polyamide thermoplastic with excellent properties such as chemical resistance, ease in process ability and good mechanical characteristics. So it used for wide range of fibre, film and engineering applications. Advantage associated with PA6 is its inherent degree of flame retardancy which attributed due to the presence of nitrogen beside its favours thermal degradation of Nylon 6 via hydrolysis of the amide bond, followed by homolytic cleavage of covalent bonds. However, as a fire retardant PA6 do not exhibit satisfactory behaviour since upon ignition, intensive flammable dripping causes increase chances of fire hazard. Tubular nature with crystal structure and low available hydroxyl groups at the surface HNTs makes HNTs easily dispersible in polymer matrices compare to other nanoclays.

Recently HNTs are being used to improve thermal properties of polymers, by using HNTs as an additive with polypropylene and poly (vinyl alcohol). They have also been co-cured with epoxy/cyanurate ester resins to form organic/inorganic hybrids.

HNTs in various concentrations (5–30 wt.%) are used for making of composite materials with PA6 by simple melt extrusion process. It has found that relatively high concentrations of additive (15 wt.%) are required to achieve the adequate levels of fire retardant property normally associated with nanoclay (or layered silicate) additives [11].

4. HALLOYSITE NANOTUBES AS FILLER FOR VARIOUS NANOCOMPOSITES

Nanocomposite has wide application in optical, electronic, magnetic, and thermosensitive devices. These nanocomposites are prepared by template assisted process by using various structures and diversified samples from dissimilar biological species. However, these approaches which are being employed are very costly. So more optimised approaches with cost effective modules are urgently needed for the successful and more efficient fabrication of nanocomposites.

Halloysite nanoparticles are used an additive for enhancing the mechanical performance of polymers, specifically for strengthening and toughening of epoxies. There are many benefits associated with HNTs to used as filler in polymer based composites.

i) HNTs have low surface charges so there will be no intercalation and exfoliation needed compare to

other two dimensional nano clays fillers such as Montmorillonites (MMTs). So they provide ease in processing when mixed with other polymers to give homogeneous particle dispersion.

ii) Modifications at the surfaces of HNTs provide an opportunity to expand the basal spacing of HNTs by the intercalation of inorganic and organic compounds in their inter layers, which further enhance possibility to produce a homogeneous mixture of HNTs with polymers during blending.

iii) Surface modification of HNTs enhances their wet ability and bond formation with different polymers.

iv) Expansion of base layers provides HNTs exfoliation.

v) HNTs are comprised of siloxane and hydroxyl groups, which gives HNTs potential for the formation of hydrogen bonds and hence improve dispersion.

vi) Larger luminal diameter of Halloysite nanotubes can accommodate different polymer molecules which further offer polymeric composites.

4.1. Halloysite–polymer nanocomposites

Halloysite nanotube an economically available nanosized raw material, has gained growing interest to modify by polymers to form polymer-halloysite composite nanotubes. It is important to modify the halloysite by keeping their tubular structure intact in resulting polymer-halloysite nanocomposites. Polymer chains can grow from both interior and exterior surfaces of the Halloysite nanotubes by atom transfer radial polymerization (ATRP). Atom transfer radial Polymerization (ATRP) used to give diversity to polymer brushes onto either planar substrates or individual spheres surface. Nanocomposite could be easily tuned by alteration of the monomer structure. Eventually, the composite nanotubes were evolved to a core-shell coaxial structure after the interior cavity was fully covered by the polymer. By the dissolution of the Halloysite template, polymeric nanotubes and nanowires were derived. This can be used to cast Halloysite based fabric and these resulting nonwoven composites has interesting feature of wettability [12,13].

4.2. Halloysite and ethylene propylene diene monomernanocomposites

Functionalization of clay minerals with organosilane significantly influences the properties of polymer-clay and polymer-nanotubes by raising their disper-

sion within the polymer matrix and thus enhancement of the mechanical properties of nanocomposites. Modification of clay minerals can be achieved by alkyl ammonium ions. EPDM chains were intercalated into MMT after modification with trimethyl octadecylamine and dimethylbenzyl octadecylamine, and exfoliated by using methyl bis (2-hydroxyethyl) coco alkylamine was used.

HNT gives uniform distribution in EPDM polymer with high loading capacity so it significantly improves the tensile, strength, thermal resistance and morphological properties of composite. Surface modification increased the temperature at 5% mass loss from 414 °C to 444 °C for nanocomposites filled with 10 phr HNT loading. Surface modification of HNTs can be achieved by γ -methacryloxypropyl trimethoxysilane and resultant effects of surface modification on the thermal and morphology properties of HNT reinforced PP nanocomposites. The tensile strength and tensile modulus at 100% elongation (M100) of the nanocomposites were higher than those of EPDM/unmodified HNTs (EPDM/HNT) while the elongation at break decreased a little after modification of the HNTs [14-17].

4.3. Halloysite and styrene-butadiene rubber nanocomposites

Rubber cannot be used for nanocomposites formation alone because of their lower modulus and strength so fillers must be incorporated to provide them practical applicability. The reinforcement of rubbers by particulate fillers such as carbon black and silica has been extensively studied. Basically rubber/layered clay nanocomposites exhibit outstanding mechanical properties as well as lowered permeability.

HNTs have been demonstrated to be an ideal component for fabricating high performance polymer nanocomposites. Compare to carbon nanotubes (CNTs), the naturally occurring HNTs are much cheaper and easily available. In addition, most hydroxyls of HNTs are located in the inner side and the combination of siloxane surface and tubular geometry gives HNT's a much better dispersion property compared with other layered clay. Ultimate performance of the polymer composites decide by two factors that is dispersion state of the filler and the interfacial properties.

Carboxyl methyl cellulose sodium salt, poly (acrylic acid) sodium salt or poly (2-methoxyethyl acrylate) (PMEA) or poly (vinyl acetate) can improve dispersion of clay minerals eg. montmorillonite and the unsaturated acid, such as methacrylic acid

(MAA), was used as interfacial modifier for polymer in organics composites. This affinity of unsaturated acid to the clay is due to the formation of hydrogen bonds between clay and the acid. Some carboxylic acid such as MAA is reactive to zinc oxide (ZnO) or magnesium oxide (MgO) to yield unsaturated metal methacrylates which show unusual reinforcing effects for rubber compounds [18].

MAA is corrosive in nature so it utilized minimally in nanocomposites. Sorbic acid is an unsaturated carboxylic acid which contains two functional groups, a carboxyl and a two conjugated carbon-carbon double bonds in each molecule. Sorbic acid used primarily in range of food and feed related products and lesser extent in certain cosmetics and pharmaceuticals. HNT's reinforced interfacial properties of styrene-butadiene rubber (SBR). Sorbic acid (SA) is used to improve the performance of styrene-butadiene rubber (SBR)/halloysite nanotubes (HNTs) nanocomposites. The strong interfacial bonding between HNTs and rubber matrix is resulted through Sorbic acid intermediated linkages.

It has demonstrated that by introduction of unsaturated acids such as (meth) acrylic acid, crotonic acid, and SA, into calcium carbonates (CaCO₃) filled SBR compounds improve tensile strength and the modulus compared with the vulcanizates without these acids. For obtaining high modulus and strength of filler/rubber composites incorporation of unsaturated acids like SA is necessary. SA improves interfacial interactions between of SBR/HNTs nanocomposites. Sorbic acid bonds SBR and HNTs through grafting copolymerization/hydrogen bonding mechanism. Significantly improved dispersion of HNTs in virtue of the interactions between HNTs and SA was achieved.

4.4. Halloysite-epoxy nanocomposites

Blending of epoxies in different proportion of HNTs can increase their fracture toughness, strength and modulus, without losing their thermal properties. HNTs have large surface area because of their tiny particle size, resultant HNTs tend to agglomerate under the influence of the van der Waals force, so it is difficult to get homogeneous dispersion of HNTs in epoxies. This agglomeration is very difficult to eliminate by applying only moderate shear stresses provided by the conventional mechanical blending instruments like ultrasonic vibration or using a stirrer or a magnetic bar. Thus, sometimes use of severe shear stresses, such as the use of ball mill, may break-up the agglomerates and achieve a ho-

homogeneous dispersion of HNTs in the polymer matrix [19,20].

For the preparation of Halloysite–epoxy nanocomposites with improved homogeneity of HNTs in the epoxy matrix as well as enhanced mechanical performance, either mechanical mixing or ball mill homogenisation were used and with simultaneous chemical treatment of surface. In potassium acetate based surface treatment of halloysite, after reducing the size of halloysite particle form clusters in the epoxy matrix with ball is very effective approach.

4.5. Halloysite–Carboxylated butadiene–styrene rubber nanocomposites

Nanocomposites incorporated with inorganic materials gives better performance compared with the other polymer composites. Final acceptability and performance of polymer nanocomposites incorporated with inorganic material govern by Interfacial interactions. The interfacial interactions between polymer matrix and inorganics mainly include van der Waals force, hydrogen bonds, covalent bonds, and ionic bonds. There are so many approaches have been developed to improve the interfacial interactions of the nanocomposites including the modification of inorganics or matrix. Recently, Halloysite nanotubes (HNTs), has acquire attention to reinforce polymers with unique reinforcing effects to different polymers such as epoxy resin, polypropylene, polyamide, natural rubber, etc. have been demonstrated [21].

xSBR (carboxylated butadiene–styrene rubber) is a copolymer of styrene, butadiene, and acrylic acid has the many carboxyl groups in chain which provide assistance in formation of hydrogen bonds. HNTs and xSBR by co-coagulation process are used to prepare tailor made nanocomposites with improve interfacial interactions via hydrogen bonding. ATR-FTIR (Attenuated total reflection Fourier transform infrared spectroscopy) and X-ray photoelectron spectroscopy (XPS) studies on xSBR /HNT nanocomposites indicate the formation of hydrogen bonding between xSBR and HNTs. It also showed higher content of HNT promotes higher vulcanization and consequently Lower content of HNTs tends to delay the vulcanization of xSBR/HNT compound. The mechanical properties, like the modulus and hardness, are significantly increased by the inclusion of HNTs. The significant reinforcing effects of HNTs are correlated to the co-coagulation process and strong interfacial interactions via hydrogen bonding [22].

4.6. Halloysite– based ‘green’ nanocomposites

Halloysite nanotubes (HNTs) with natural rubber (NR) are used to prepare ‘green’ composite. To enhance the mechanical and thermal properties of the composites, HNTs are being used as a filler for polymers. High aspect ratio of HNT is the responsible factor which makes it possible to use this clay in place of silica filler. Clays containing silica surfaces can be chemically modify by organosilanes like bis (triethoxysilylpropyl)-tetrasulphide (TESPT), and this modification of HNT was carried out by amino silane (3-aminopropyl) triethoxysilane (APTES). Sometimes, A silane coupling agent, bis (triethoxysilylpropyl)-tetrasulphide (TESPT), used to enhance the dispersion and physical properties of these composites in natural rubber. Reinforcing activity of HNTs was superior to commercial silica coupled with the same amount of silane coupling agent. This has further been confirmed by Transmission electron microscopic imaging studies of dispersion of the HNTs in the rubber matrix, whereas X-ray diffraction studies showed a little change in interlayer spacing between the two silicate layers of HNTs [23].

5. HALLOYSITE NANOTUBES FOR CELLULAR RESPONSE

Recently nanotubes are being used for tissue engineering as well as macro molecular delivery systems. But as far as tissue engineering is concern compatibility of nanotubes with biological matrices is a limiting factor. HNTs has similar geometry like CNTs but have a much lower price and most importantly they are available abundantly, besides all they are biocompatible with cellular organelles and provide high mechanical strength. Alumina and silica groups are located on the surfaces of HNTs especially on their crystal edges ease the formation of hydrogen bonding interactions between HNTs and biological components so it may make HNTs as an ideal candidate for bionanomaterial and formation of bionanocomposite film.

5.1. Halloysite as a cargo for biomaterials

Biocompatibility of Halloysite is essential for its potential application in biopolymer composites, bone implants, controlled delivery of bio molecules, and for in vivo protective coatings.

Quantitatively trypan blue and MTT (Methyl tetrazolium salt) measurements performed with

different origins cell line (cervical adenocarcinoma, HeLa, or breast cancer cells, MCF-7 cell line) suggest a model systems to measure the functions with respect to nanotubes concentration and incubation time. These studies also indicate that halloysite exhibits a high level of biocompatibility and very low cytotoxicity, which renders it to be to a good candidate for household materials and medicine. HNTs interaction with cells and their intracellular cell uptake by different originating cell lines has been observed. These functionalized halloysite by amino propyl triethosilane (APTES) or fluorescently labeled polyelectrolyte layers, allow halloysite uptake by the cells and were observed with confocal laser scanning microscopy (CLSM) [24].

5.2. Halloysite for osteoblasts and fibroblasts response

Poly vinyl alcohol (PVA) is a biodegradable and biocompatible synthetic polymer. Due to presence of hydroxyl groups in polymer side chain of PVA, it has high water solubility as well as high cross linking ability (film or hydrogel forming). Thou PVA poses so many desirable properties for biomedical applications such as dialysis membrane, macro molecular delivery systems, wound dressing, artificial cartilage, and tissue engineering scaffold as well as mechanical properties in the dry state but its high hydrophilicity limits its applications to use in living systems. To improve the biological application as well as for enhancement of mechanical properties of PVA, PVA based bionanocomposites has designed. Studies on PVA and PVA/HNTs based bionanocomposite films has shown its potential applications in bone tissue engineering and drug delivery systems. There are so many nanoclays such as mont morillonite, kaolinite, attapulgite, and other nanoparticles such as carbon nanotubes (CNTs) and nano-scaled metal powder are shown to have a significant effect on the performances of PVA based bionanocomposites which are attributed to the strong interactions between the nanoparticle phase and polymer matrix. HNTs comprises of alumina and silica group located at the crystal edges, which ease the formation of hydrogen bond between HNTs and PVA so it may make HNTs as an perfect candidate for PVA bionanocomposite film. Hence internalization of HNTs in the PVA is necessary for their high performance in biomedical applications.

Cross linked PVA/HNTs bionanocomposite films prepared via solution mixing method by using glutaraldehyde as the crosslinking agent. The morphol-

ogy and physical properties of bionanocomposite film were investigated thoroughly. The surface topography and chemistry of the films was characterized by atomic force microscopy (AFM) and attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, respectively. Blending with HNTs induced changes in nano topography and surface chemistry of PVA films this will further enhance the mechanical properties of PVA by the incorporation of HNTs.

PVA and HNTs based bionanocomposites characterized by cell cultured studies. Osteoblasts (MC3T3-E1) and fibroblasts (NIH 3T3) cultured on neat PVA and PVA/HNTs bionanocomposite films and characterized by cell viability assay. Cell morphological studies shown that modified film increase the cell adhesion and in vitro growth. These studies also indicated that MC3T3-E1 cell behaviour strongly responded to surface nanotopography. On nanotube dominant surface, cells exhibited a significantly higher level of adhesion than on neat PVA film, whereas neat PVA showed higher degree of osteoblast proliferation compared with PVA/HNTs. In compendious, these results provided insights into understanding of PVA and PVA/HNTs bionanocomposite films for their potential applications in bone tissue engineering as well as macro molecular delivery systems [25].

6. HALLOYSITE NANOTUBE FOR POLYMERIZATION REACTIONS

Clay minerals and other inorganic materials used as a host for the polymerization of several conductive polymers. Various nanomaterial based approaches are available for polymerization but halloysite as support matrix for polymerization either by intercalation or by immobilization is more reproducible.

Halloysite nanotubes used as catalytic support in different polymerization as well as various biological processes because of following reasons:

- i) Halloysite nanotube improves the catalytic activity of different molecular species.
- ii) Halloysite not only enhances the separation of catalyst but also it improves the recovery of catalyst from reaction media.
- iii) Halloysite due to their ionic interaction, facilitate the recycling as well as improve the disposal of catalyst.
- iv) Halloysite has pre-defined tubular diameter which allows the entrance of molecules with specific sizes. This caters the shape and size selectivity to the catalyst.

v) Compare to other clay minerals, Halloysite show higher reactivity and higher cationic exchange capacity.

These characteristics of Halloysite which make them an attractive candidate to be used for support matrix for immobilization of catalyst in polymerization reactions.

6.1. Halloysite nanotubes in in-situ chemical polymerization

Polyaniline coated halloysite nanotubes (PANI/HNTs) prepared by the in-situ soap less emulsion polymerization of the anilinium chloride adsorbed halloysite nanotubes. Polyaniline (PANI) has been known as one of the most technologically important conducting polymers because of its high electrical conductivity, easy producibility and environmental stability.

Polyaniline usually combined with different inorganic components to form nanocomposites with improve physical, mechanical, and electrical properties like enhanced solubility, conductivity, magnetic and optoelectronic properties, etc.

There are number of methods has been designed for generating the polyaniline coated inorganic nanomaterials such as nanoparticles, nanotubes, nanobelts, and silicate clays by in situ oxidative polymerization, gamma radiation-induced chemical polymerization or electro polymerization. Among these nanocomposites methods synthesis by encapsulation of inorganic nanomaterials inside the shell of polyaniline are more popular.

First report of the intercalation and polymerization of aniline within Halloysite nanotube was by exposure of the Cu (II)-doped Halloysite film to aniline vapor. In this method polyaniline was coated on the surfaces of the Halloysite nanotubes via the in-situ soap less emulsion polymerization after the anilinium chloride was adsorbed onto the halloysite nanotubes. HNT was dispersed in aqueous acidic solution of aniline with continuous stirring and by ultrasonic irradiation with using ammonium persulfate (APS) as oxidant. Morphological studies on PANI/HNTs hybrids, it influenced by acidity of polymerizing media and adsorption of anilinium chloride on halloysite nanotubes [26].

6.2. Halloysite for biomimetic polymerization of aniline

Nanostructured material is being used for support material since long time. In recent years interest has been shifted to use of these nanostructured

material as a support for hematin in the aniline polymerization. Polyaniline (PANI) is a conductive polymer has some advantages, like easy synthesis, environmental stability as well as wide electronic and optical properties. Various chemical as well as enzymatic polymerization methods are available for polyaniline synthesis but among available methods for polymerization enzyme based polymerization has become very attractive because of its environmental friendly approach in which hydrogen peroxide used as oxidizer and it generates water as by-product. The only drawback associated with this method is its high cost of the enzyme.

Biomimetic catalysts such as porphyrins (iron (III) tetrasulfonated tetraphenyl porphyrin), metallophthalocyanine and of tris (pyrazolyl) boratocopper are very effective for the polymerization of aniline. But these all are synthetic in origin. Hydroxyl ferriprotoporphyrin IX, commonly known as hematin is a biomimetic catalyst from a natural origin. Hematin is insoluble in acidic media so it cannot be used directly in the synthesis of PANI, however, it can be used for PANI synthesis after its functionalization with a water soluble polymer like polyethylene glycol. Chemical functionalization of hematin broadens its pH range of catalytic activity. An environmental friendly approach based on chemical functionalization, hematin was immobilized on to halloysite nanotubes, which was evaluated as biomimetic catalyst for polymerization of aniline in aqueous acidic media. This method not only enhances catalytic activity in acidic environment but also involves minimum purification steps [27,28].

6.3. Halloysite for the atom transfer radical polymerization

Atom Transfer Radical Polymerization (ATRP) is a transition metal based catalysis. One of the limitation associated with this method is, it require high concentration of catalyst to obtain acceptable rates for the polymerization and because of this high concentration of catalyst present in polymerization reaction causes the polymeric solution become coloured, thus process requires addition of one more additional separation step and that may further raise the duration as well as cost of the process. This can be minimize or overcome by Immobilization of the catalysts on inert support materials so that catalyst can be easily recovered and potentially recycled after the termination of reaction.

There are several methods used for the immobilization of ATRP catalysts on different supports but use of Halloysite clays as inert matrix for immobili-

zation purpose is a subject of more interest. First catalyst supported ATRP was reported by Haddleton. In this supported catalyst matrix CuBr complexes with Pyridyl methanimine ligand and that was absorbed on support either physically or covalently. In the beginning of polymerization, supported ligand chelate with CuBr and form supported catalyst. The physically adsorbed catalysts produced polymers with narrower poly dispersities than those produced by the covalently bonded catalyst. Main limitation of this method is loss of catalytic activity and that may be because of loss of supported catalyst during transfer, change in Cu(I) to Cu(II) and may be degradation of catalyst during polymerization.

Immobilization of homogeneous catalysts on the surface of a solid support, usually results in a significant loss of the catalytic activity of catalyst, halloysite because of their nanometer size and regular shape may reduce these drawbacks of immobilization.

Surface chemistry of Halloysite nanotubes allows efficiently heterogeneous catalyst for the polymerization of methylmethacrylate (MMA) via an atom transfer polymerization process. Silane is used as ligand for this ATRP catalyst, as silane may enhance the physical adsorption of the catalyst on the support [29,30].

7. HALLOYSITE NANOTUBES AS A POTENTIAL DRUG DELIVERY VEHICLE

Efficient delivery of drug requires delivering the drug at intended site with predefined rate. These days, Halloysite has recognized as potential carrier for loading of cationic agents either by chemisorption on its polyanionic faces or by entrapment into its hollow lumen or core. Many alternatives like Lipid microtubules or carbon nanotubules have similar morphology as well as similar drug loading capacity to Halloysite nanotubes but Halloysite because of their abundance and various surface properties are a good candidate for the drug loading.

- i) Bi layered alignment gives Halloysite's nanotubes a cylindrical shape.
- ii) The inner and outer faces of tubular walls of halloysite nanotubes carries a net negative charge so it function as polyvalent anion.
- iii) Halloysite nanotubes with amphoteric edges give negative charge at high pH and positive charge at low pH.
- iv) Unusual shape and charge distribution of Halloysite's favours face-to-edge attachment in

aqueous suspension at slightly alkaline pH and facilitates binding particularly of cations to unreacted faces.

All these properties of Halloysite nanotubes make the Halloysite a possible candidate for drug loading either with entrapping agents within the lumen of tubules using retardant polymers or by cationic coating and other approaches for moderate release rate, or by swapping intercalated water if present for low molecular weight agents.

Recently, Halloysite is also being tried for sustained delivery of drugs and one of these studies done by using diltiazem HCl as a model drug because of cationic nature of diltiazem HCl, it facilitate binding with Halloysite faces and high solubility help in loading of drug into lumen of halloysite. But higher diffusion rate of diltiazem make it difficult to achieve adequate sustain release action.

A range of cationic polymers like polyvinyl pyrrolidone, chitosan cross linked with glutaraldehyde also bind to Halloysite and used to achieve significant delayed drug release.

Beside these a range of non aqueous solvent like alkyl-2-cyanoacrylate and poly-iso-butyl cyanoacrylate are also effective to reduce burst effect reported with aqueous coating systems [30,31].

Different nanomaterials used for entrapping of drugs but clay minerals provide dispersions at submicron level in aqueous media. Entrapping of drug molecules in micro- and nanoparticulate systems is a helpful strategy for protecting drugs against the chemical as well as enzymatic degradation, enhancement of aqueous solubility, to reduce dissolution rate and target drug release.

Among various clays minerals, Halloysite with hollow microtubule has been recently proposed as a natural vehicle for microencapsulation and controlled release of both hydrophilic and lipophilic drugs. 5-Aminosalicylic acid [5-ASA] is an anti-inflammatory drug. In the treatment of ulcerative colitis, it is require delivering 5-ASA at large intestine.

But problem associated with 5-ASA is, it rapidly absorbed at small intestine, and there is little localization of the drug in the colon. So to get the require effect of 5-ASA and to deliver the drug content at colon, 5-amino salicylic acid [5-ASA] adsorbed on Halloysite. Kinetic and equilibrium studies of halloysite absorbed 5-ASA are comparable at different temperatures and drug concentrations [32,33].

8. HALLOYSITE NANO TUBES AS AN IMMOBILIZATION MATRIX

Halloysite nanotubes used to mitigate the degradation of enzymes and metal ions through their immobilization or encapsulation on to supports like as silica, zeolites, cationic exchanger montmorillonite clay, silanized kaolinite, intercalated/delaminated kaolinite, chrysotile, and other matrices. These tubular nanotubes can easily intercalate water monolayers as well as other organic and inorganic compounds such as formamide. In among other available clay minerals, Halloysites has their own benefits to use for immobilization.

- i) Metal complexes can be immobilized on Halloysite nanotubes both interior as well as exterior surface of tubular structure.
- ii) Halloysite associated immobilization are barred from undesirable effects like molecular aggregation and bimolecular self-destruction.
- iii) Halloysite nanotubes based immobilization facilitates the recovery of catalyst so cost of material preparation get reduced.
- iv) Halloysite nanotubes based immobilization is stable chemically as well as thermally beside they are having good mechanical properties. They are based on non-toxic elements (Al and Si), so they also non toxic.
- v) Halloysite because of its pre-defined diameter, allowing the entrance of molecules with specific sizes that causes it gives shape and selectivity to the catalyst.
- vi) Halloysite's give regioselectivity to catalyst when only part of molecule allow penetrating the tube and coming in contact with active site which are not selective in homogeneous media.

Halloysite offers higher reactivity and higher cationic exchange capacity as compared to other clays so it makes the Halloysite a potentially useful support for the immobilization of catalytically active molecules.

8.1. Halloysite for immobilization of silver nanoparticle

Silver (Ag) nanoparticles extensively used because of their catalytic potential. However, limitation associated with silver nanoparticles guided catalysis is their recovery from the reacting mixtures after completion of reaction. In order to reuse the catalysts or enhance their catalytic activities, silver nanoparticles can be immobilized onto the various supports such as a clay minerals, carbon nanotubes and polymeric materials. Halloysite nanotubes used

as support to immobilized silver nanoparticles based catalyst. The silver nanoparticles of about 10 nm diameter were immobilized onto the halloysite nanotubes (HNTs) via the in situ reduction of AgNO_3 by the polyol process. This immobilized matrix of silver nanoparticles used for the reduction of aromatic nitro compound, 4-nitrophenol (4-NP) in presence of NaBH_4 in alkaline aqueous solutions [33].

8.2. Halloysite for immobilization of metalloporphyrins

Metalloporphyrins are macrocyclic complexes with ability to perform hydrocarbon oxidation under modest conditions. Iron (III) and manganese (III) based porphyrins have been the most flourishing metalloporphyrins used for this purpose. The problem associated with these metalloporphyrin systems used for hydrocarbon hydroxylation and epoxidation are degradation of oxidative catalyst in the presence of inert substrates. There are many approaches used to mitigate the degradation of metalloporphyrin either through their immobilization or encapsulation on to supports like silica, zeolites, montmorillonite clay, silanized kaolinite, intercalated/delaminated kaolinite, chrysotile, and other matrices.

There are many benefits associated with Immobilization of metalloporphyrin.

- a) Site specific isolation of the metal complex reduce the self-destruction of catalyst and dimerization of resultant metalloporphyrin complex.
- b) Facilitated and efficient isolation of the heterogeneous catalyst from the reaction media.
- c) Catalyst can work as flow reactor cells.
- d) Catalyst can be recycle, which minimizes environmental impact.

Selectivity of oxidation reactions depend on the manner of metalloporphyrin attached to support matrix and this selectivity difference govern by different binding modes. This metalloporphyrin control the formation structure of pore as well as three dimensional network of matrix. Many types of layered material, fibres and nanotubes or nanoscrolls are potential material for immobilization and encapsulation of metallocomplexes. By immobilization, the homogeneous active species is transformed into a heterogeneous catalyst, but their selectivity and activity retained.

Halloysite, because of its crystal shape and geometry offers vast opportunities for immobilization of metalloporphyrin. It takes place not only at the surface but also inside the tubes thus leading

to highly active and selective oxidation catalysts. Immobilization of metalloporphyrin on Halloysite can be performed by either under pressure or under stirring /reflux [34].

9. HALLOYSITE NANOTUBES FOR REMEDIATION

Clays are being considered as promising adsorbents due to their accessibility, least cost constraint, large surface area and high adsorption capacity. Numerous clays, such as perlite, dolomite, nontronite, montmorillonite, bentonite, zeolite, and sepiolite have been tested for their adsorption ability for dyes. However, their local availability and nano-size in contrast with other materials HNTs show greater promise.

9.1. Halloysite and dyes

Dyes are widely used in industries such as textiles, pulp mills, leather, synthesis of dyes, printing, food, and plastics, etc. Since many organic dyestuffs are harmful to human being and their discharge into water causes environmental problems, toxicity to aquatic as well as non aquatic microorganisms, and carcinogenicity. So the removal of dyestuffs from wastewater has required with great urgency. The dyes has broad spectrum of activity due to their chemical structures which are primarily based on the substituted aromatic groups. This complex chemical structure of dyes are responsible factor because of which they are resistant to breakdown by chemical, physical and biological means. Furthermore, any degradation by physical, chemical or biological methods may produce small amount of toxic and carcinogenic products. Adsorption is known to be a promising technique, which has great importance due to ease of operation and comparable low cost of involve in the discoloration process.

Adsorption has been developed to remove colour from dye-containing effluents and it is relatively low-cost technique for the treatment of dye contaminated waste water. Halloysite nanotubes (HNTs), a low-cost available clay mineral, were tested for the ability to remove cationic dyes such as Neutral Red (NR), Methylene blue, Malachite green and methyl violet from aqueous solution. Natural HNTs used as adsorbent and their adsorption potential increased with increase in dose of adsorbent, initial pH, temperature and initial concentration [35-37].

9.2. Halloysite for intercalation

The capability of minerals of the kaolin group to intercalate organic and inorganic compounds has been evidenced long ago. Among the various members of the kaolin group, halloysite differs by the presence of interlayer water and the morphology of the crystal, which are curved or rolled structure. Halloysite has been intercalated by a variety of guest molecules such as amides, dimethyl sulfoxide, potassium acetate, aniline, hydrazine and formamide.

Numerous studies performed to differentiate Halloysite from kaolinite as well as give understanding of intermolecular interactions arising in the interlayer space between the intercalated molecule and the host matrix. Clay minerals have a great potential to adsorb pollutants, such as heavy metal ions and organic compounds. The Algerian Halloysite, which is also a type of Halloysite were also characterized for study the intercalation of Na⁺, NH₄⁺, and Pb²⁺ acetate and apply these solids for removing copper (II) ions from aqueous solutions.

Algerian Halloysite can be modified with Na⁺, NH₄⁺, and Pb²⁺ acetate and by XRD and FTIR studies also confirmed that intercalation exceed with time. The adsorption of copper ions was explained by electrostatic interaction between the copper (II) ions and negatively charged binding sites on halloysite surface and ion-exchange of the cations associated with acetate within the interlayer space [38].

9.3. Halloysite nanotubes based hydrogel as an adsorbent

Halloysite (HT) comprises of two-layered aluminium silicate and presence of water between the layers create a packing engendering causing them to curve because of this Halloysite can be used as an inorganic component to prepare polymeric hydrogel based composite. These polymeric hydrogels used as adsorbents for the removal of hazardous metal ions or ionic dyes. Basically, these hydrogels are hydrophilic in nature but they do not dissolved in water, making them easily separated from the aqueous solution. Furthermore, due to presence of a large number of multi functional ionic groups within these hydrogels give them surprising affinity for pollutants in the surrounding water environment.

Earlier, there was no single evidence available for using this type of hydrogel adsorbent to remove ammonium (NH₄⁺) which is the inorganic ion form of

nitrogen pollution and is one of the responsible factors for causing eutrophication. Nanocomposite based on, chitosan was used as the backbone to graft poly (acrylic acid) to form granular hydrogel composite with halloysite (HT) particles being embedded within the polymeric networks. And this also show by introducing HT particles into the polymeric networks, the resulting composite shows comparable adsorption capacity to that of pure polymer hydrogel for NH_4^+ removal [39].

10. HALLOYSITE NANO TUBE BASED FABRICATION

HNTs have immense biological and non-biological applications. They are being used for storing molecular hydrogen, catalytic conversions, hydrocarbon processing, improvement of dispersion, differentiation studies and as an enzymatic nanoreactor. Mechanistic theories of composite formation explain that high content of clay incorporation is necessary for prominent and heightened mechanical strength of composites. However, incorporation of large amount of clay with polymer in fabrication of nano composites result in poor dispersion and that leads to poor mechanical as well as optical properties. These problem can be minimise by incorporation of Halloysite in fabrication of composites. Naturally occurring, nanotubular Halloysite are used to reinforce the strength of the composite. Studies also proves incorporation of up to 65% nanotubular clay exhibit high mechanical as well as heat resistance [40].

Tubular halloysite also used as a template to fabricate Metallic Ni film or Nanoparticles through the process of electroless plating. Resultant properties of material strongly depend on its micro- and nanostructure. Metallic nanoparticles or wires are having useful electronic, magnetic, and catalytic properties because of their nanoscopic size and shape. These all structures are utilized in template directed synthesis. For the arrangement of nanocluster or wire artificial template like carbon nanotubes, ordered arrays of alumina, and porous polymer membranes are used. Biological templates, like lipids, DNA, protein S-layers and microtubules are used to conduct the nucleation, deposition and assembly of inorganic nanoparticles. These studies focused on the artificial as well as biomolecular templates, but naturally available tubular halloysite is being widely used as template. Halloysite nanotube based templates are requiring activation before electroless plating to perform deposition of Ni nanoparticles on the outer surface and wires on

inner side cavity of the halloysite. This process was initiated by presence of colloidal Sn–Pd acid solution. Pd ions get reduced by methanol at halloysite surface and that causes Ni particle deposited [41].

10.1. Non covalent functionalization of HNT's

Dispersion via non-covalent functionalization of carbon nanotubes and biomolecules like protein, nucleic acid, amylase, starch and gum Arabic have been much explored. This approach is based on direct contact between nanotubes and a biomolecules. Halloysite nanotubes have aluminols inside the tubular structure and siloxane groups outside the nanotubes beside these few silanols and aluminols are exposed on the edges of the rolled sheets of the tubes. Combination of tubular geometry and surface characteristics make the Halloysite nanotubes a good candidate for better dispersivity compared to other clays.

Biocompatibility of Halloysite nanotubes can be improved by non-covalent functionalization of HNTs with biomolecules. In one kind of green approach by application of mechanical force a supramolecular complex of DNA and HNT and amylose and HNT in solid state were prepared. Thus formed DNA or amylose wrapped halloysite nanotubes show better dispersion in the DMSO/ H_2O solution [42,43].

10.2. Layer-by-layer coatings of Halloysites on wood microfibers

Layer-by-layer (LbL) assembly approach used to deposit multilayer of nanoparticles coating on softwood fibres. Basic utility of this method is in the area of pulping, paper processing and paper coating. This approach creates thin film of nano meter dimension on large surfaces as well as on microfibers and cores. Lignocellulosic fibers because of their surface properties are necessary component of paper design as well as their quality enhancement. These fibers are negatively charged fibres but hydrogen bonding between cellulosic fibres provides strength to paper during paper formation and drying. Recently Halloysite nanotubes were coated through controlled layer-by-layer approach on wood fibres by alternating them with oppositely charged polyelectrolytes. By coating on fiber surface with continuous layers of nanoparticles changes their surface properties, and abolish the possibility of hydrogen bond formation at the contact region between neighbouring fibers [44].

In other approach, LbL coating of lignocellulose fibers applied to substitute hydrogen bonding among lignocellulose fibers by electrostatic attractions with simultaneous application of positive and negative polyelectrolyte fiber coatings. Resultant electrostatic bonding between fibers drastically enhances the strength of paper sheets. This LbL based nanoassembly employed in great variety of substances including linear or branched polyelectrolytes, nanoparticles, and proteins.

10.3. Halloysite for differentiation studies

Halloysite are ubiquitous clay which occurs in a variety of particle shapes and hydration states. Halloysite usually found with other clay minerals so they are difficult to differentiate.

Halloysite can intercalate a monolayer of water molecules but this interlayer water is weakly held and giving a basal spacing near 10 Å to resultant nanotubes. Halloysite with $-(10 \text{ \AA})$ form can readily dehydrate to give the Halloysite $-(7 \text{ \AA})$ form and this form is very much similar to kaolinite. In comparison to other clay minerals, Halloysite either hydrated form or dehydrated form has a greater propensity for intercalating organic molecules [45].

Numerous intercalation methods have been developed to identify and quantify Halloysite $-(7 \text{ \AA})$ from other clays as well as kaolinite mixtures. Basis of these methods are differences in the rate and extent of formamide intercalation between Halloysite and kaolinite.

Intercalation of formamide within the Halloysite is conclusive for naturally dehydrated Halloysites but it is inconclusive for Halloysites with prior under gone oven dried at 110 °C.

This also applies to some halloysites that have been dried at 40 °C because some water always remains present in the interlayer space [46].

11. CONCLUSIONS

Halloysite nanotubes are not very common in nature being found in many subtropical and tropical soils, within individual origin and descent, a significant divergence arises in Halloysite morphology, depending on the exact forces of nature involved in their formation. Minerals show silently different properties in terms of size, surface area and porosity and indicating the possibility of potentially different grades of Halloysite available, some of which may be suitable for biological applications and some may be for non biological applications. It is very difficult

to summarize all the applications of Halloysites but few of them are become very important component for fabrication, corrosion prevention, polymerization, immobilization, thermostability, macro molecular delivery etc.

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