ESCALATING APPLICATIONS OF HALLOYSITE NANOTUBES

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ABSTRACT

In nanotechnology different nano materials are used like carbon nanotubes, nanofluids, nanoparticles, nanoemulsions, nanocapsules, etc. Due to their toxic effects the results of these nano materials are not considered safe for humans and for the environment as well. Halloysite nanotubes (HNTs) having low cost are naturally occurring environmental friendly nanotubules. These are distinctive and handy materials formed by face weathering of aluminosilicate minerals having definite ratio of aluminum, silicon, hydrogen, and oxygen. HNTs have high mechanical strength and modulus. Due to these properties it is ideal for various applications; remediation of ecological contaminants, these are acting as a career for the delivery of drugs and various macro molecules, storage of H₂ gas, for catalytic conversions and for the processing of hydrocarbons. These are also used in anticancer therapy, sustained delivery for certain agents, as a template or nanoreactor for biocatalyst, in personal care, cosmetics and as environment caring. They are also used in the fabrication of high quality white-ware ceramics, nanotemplates and nano scale reaction bottles. Due to easy dispersability in polymer matrix, abundant availability and biocompatibility, HNTs are also used in different epoxy (EP) composites. In this review, we have tried to recap the different aspects of halloysites nanotubes for their use in different research fields.

Key words: Halloysite nanotubes; composites; reinforcement; adsorbent

INTRODUCTION

The halloysite nanotubes (HNTs) is a kind of aluminosilicate clay with a chemical formula Al₂Si₂O₅(OH)₄.H₂O. The natural deposits of halloysites nanotubes are found in countries like China, New Zealand, America, Brazil, and France. Halloysite nanotubes are naturally formed in the earth over millions of years, halloysite nanotubes are unique and versatile nanomaterials that are formed by surface weathering of aluminosilicate minerals and are composed of aluminum, silicon, hydrogen and oxygen. Halloysite is a fine clay mineral consisting of tubular particles with multi-layered wall structure. It has been reported that HNTs have distinctive dimensional structure and these are formed by two building blocks; one is the tetrahedral and the second is octahedral. Within the octahedral sheet, only two-third of the presented octahedral sites is filled with aluminium. The crystal structure of halloysite is described as 1:1 dioctahedral layer silicate. The variations in the symmetry of the finishing structure of halloysite are due to the water molecules present between two consecutive layers. Halloysites may be platy, fibers tubular or cylindrical particles of different dimentions.

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Halloysite clay nanocomposites, nanotubes, nano powders, etc. now are naturally occurring environmental friendly nanotubules. These are distinctive and handy materials formed by face weathering of aluminosilicate minerals having definite ratio of aluminum, silicon, hydrogen, and oxygen. HNTs have high mechanical strength and modulus. Due to these properties it is ideal for various applications; remediation of ecological contaminants, these are acting as a career for the delivery of drugs and various macro molecules, storage of H₂ gas, for catalytic conversions and for the processing of hydrocarbons. These are also used in anticancer therapy, sustained delivery for certain agents, as a template or nanoreactor for biocatalyst, in personal care, cosmetics and as environment caring. They are also used in the fabrication of high quality white-ware ceramics, nanotemplates and nano scale reaction bottles. Due to easy dispersability in polymer matrix, abundant availability and biocompatibility, HNTs are also used in different epoxy (EP) composites. In this review, we have tried to recap the different aspects of halloysites nanotubes for their use in different research fields.

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EPDM nanocomposites showed much higher tensile properties compared to neat PLA. HNTs can be used for persistent release of drugs for example the use of diltiazem HCl as a sculpt drug which is cationic in nature helps in binding with HNTs faces and its high solubility facilitates the filling of drug into lumen of HNTs but due to high diffusion of diltiazem it is hard to gain sufficient prolong delivery. Cationic polymers like polyvinylpyrrolidone, chitosan cross linked with glutaraldehyde in addition to HNTs may be used to get considerable tardy drug discharge. Non aqueous solvents like alkyl-2-cyanoacrylate and poly-iso-butycyanoacrylate may also be used. HNTs are ideal for controlled release of hydrophilic as well as lipophilic drugs. PMMA bone cement has fine biocompatibility and mechanical properties for its use in orthopedic renovate. Gentamycin is loaded into the lumen of HNTs and then drug loaded HNTs were mixed with PMMA to make bone cement. The PMMA/HNTs/gentamicin composite gave a persistent release for up to 300–400 h. Biodegradable PLA-HNTs composites also have good applications for bone implants. HNTs based drug delivery system in cases of burn care can be very useful, because drugs loaded into HNTs and embedded into the base layer of a bandage are released over an extended time period. It increases the duration of drug efficacy and lessened the turns with which a bandage needs to be tainted. Pharmaceuticals loaded into HNTs provide more controlled release. They give low initial concentrations, eliminates high initial delivery rate and improve the safety, mainly with drugs such as stimuliants or hormones, uniform drug release, cost efficiency and less drug loading is required per patch. Due to these properties it is used as a good candidate for domestic materials and medicine. The uptake of HNTs by cells is activated by the blending of HNTs with amino propyl triethoxysilane (APTES) or fluorescently labeled polyelectrolyte layers, well studied by using confocal laser scanning microscopy (CLSM).

Halloysite nanotubes for flame resistance

The following polymers have been selected for flame resistance LLDPE, PP, PB, PBST, ABS, PEI, NBR, and soy protein. HNTs exhibited a decline of flammability of the related polymers appreciably without loss of mechanical properties. It was seen that HNTs have an amagnetic effect with other halogen-free flame retardants like magnesium hydroxide, antimony trioxide and melamine cyanurate. The thermal stability of the HNTs based polypropylene nanocomposites is highly increased due to the presence of HNTs and iron in HNTs. Because of barriers present between heat and mass transport as well as the iron in HNTs significantly increase the thermal stability and reduce the flammability. Poly ethylene graft is used as interfacial modifier in the LLDPE/HNTs composites, the improvement in the mechanical properties, flame retardancy and thermal stability are increased. These properties are enhanced by the addition of grafted copolymer, which also increase the interfacial bonding. Nylon 6 has inherent property of flame retardancy which is due to the presence of nitrogen but this retardancy is not favorable so to increase retardancy we add HNTs due to low surface hydroxyl groups and tubular nature it is easily dispersed into the nylon 6 matrices and its retardancy ability is increased as comparative to other nanoclays. High concentration of additive is required for adequate retardancy (15 wt.%)\(^{19}\). Coefficient of thermal expansion of epoxy resin is considerably decreased by the addition of HNTs\(^{41}\). The addition of HNTs slightly affected both @ and @ at a certain frequency remaining dependable with HNTs polar nature and the increased number of charge carriers in their presence\(^{19}\).

Wetability and self healing properties

HNTs are hydrophilic in nature showing a 10\(^{4}\) water contact angle. PP with HNTs form a water contact angle of roughly 160\(^{\circ}\). The maximum contact angle for the HNTs-PP composites was near to 170\(^{\circ}\) with 15 wt.\%\(^{62}\). But in HNTs-pectin and HNTs-PCL nanocomposites water contact angle was decreased by HNTs\(^{46,47}\). For the HNTs-HPC nanocomposite films an increase in the water contact angle was observed\(^{46}\). HNTs are a good candidate for self healing anticorrosion coating formulations\(^{46,47}\). Polyurethane and acrylic paints doped with HNTs laden with benzotriazole, 2-mercaptobenzimidazole, and 2-mercaptobenzothiazole corrosion inhibitors produce self-healing nanocomposites coatings for copper\(^{62}\).

HNTs for tissue engineering scaffolds

HNTs have been loaded to biodegradable polymers like PVA, chitosan, PLA, and PLGA for the preparation of tissue engineering scaffolds. HNTs loaded PVA biocomposites films are extremely compatible with the osteoblast and fibroblast cells. Mouse fibroblasts can build up on the HNTs-chitosan nanocomposites surfaces. Ecteins can build up on the HNTs-PLGA nanofibrous mats have outstanding biocompatibility\(^{77}\). So HNTs polymer composites have great emerging applications in tissue engineering.

HNTs as potential drug delivery vehicle, bone implants and wound care

The applications of HNTs as drug release vehicles were broadly reported in publications\(^{19,60-62}\) and the drug release rate can be further delayed by coating polymers onto the drug-loaded HNTs\(^{19,68}\). HNTs-polymer nanocomposites can be used as drug containers\(^{19,69}\). Coating of PVA on the HNTs can slow down diphenylhydramine hydrochloride release\(^{61}\). Furthermore, the chitosan- and PEG-coated HNTs exhibit a radically reduced release comparatively to the uncoated HNTs. Other active agents like self healing\(^{62}\) anticorrosion\(^{96}\) and antimicrobial agents and proteins and DNA\(^{13}\) can be laden for continued release. HNTs are used for persistent release of drugs for example the use of

ES-PEG L-DXR can enhance CTC recruitment for chemotherapeutic delivery, whereas preventing healthy cell adhesion and uptake of therapeutic intended for CTCs\(^{61}\).

Use of HNTs as nanoreactors and nanocontainers

HNTs are used as nanoreactors for the fabrication of nanoparticles, nanowires and such purposes. HNTs can amplify the arrest ability of HNTs toward leukemic cells during flow; however also notably decrease the number of captured CTCs in the bloodstream. ES-PEG L-DXR can enhance CTC recruitment for chemotherapeutic delivery, whereas preventing healthy cell adhesion and uptake of therapeutic intended for CTCs\(^{61}\).
pot for benzotriazole which is a corrosion inhibitor. HNTs can be used as an additive in paints to form a useful composite coating material\(^9\). Hybrid sol–gel films doped with HNTs are able to liberate entrapped corrosion inhibitors in a controllable way. They have long term corrosion protection as compared to undoped sol–gel films due to self-controlled discharge of corrosion inhibitor\(^{20}\). HNTs can be used as protective coatings to load metal and plastic anticorrosion agents\(^{32}\). HNTs can entrap active agents within its lumen core and also in any empty spaces present in the multilayered walls of the tubule.

**Use of HNTs in synthesis of silver nanorods and gold nanoparticles**

Silver acetate from its aqueous solution is loaded into the lumen of HNTs and by thermal decomposition silver nanorods were synthesized. Then copper(II) ions in aqueous acidic medium. This method increases the catalytic activity in acidic media and is completed in minimum steps\(^{37}\). Halloysites for the atom transfer radical polymerization (ATRP)

Economy and controllability of reactions can be optimized by Immobilization of the catalysts on HNTs\(^{24}\). In supported catalyst matrix CuBr complex with pyridyl methanamine ligand which is absorbed on support physically or covalently. Polymers with narrow polydispersities are produced by physical adsorption than by covalent adsorption. The disadvantage of this method is failure of immobilization of the catalyst on the support\(^{17}\).

**Halloysite for immobilization**

Due to specific nature of Halloysite nanotubes these can be used for immobilization matrices. To reuse silver nanoparticles they are immobilized onto the different supports like clay minerals, carbon nanotubes, HNTs and polymeric materials. The silver nanoparticles were immobilized onto the HNTs by in situ reduction of AgNO\(_3\) by the polyol process. This immobilized matrix of silver nanoparticles was used for the reduction of aromatic nitro compounds\(^25\). Macro cyclic complexes like Iron (III) and manganese (III) metalloporphyrins are important. HNTs due to their crystal shape and geometry are good candidate for immobilization of metalloporphyrins. Immobilization of metalloporphyrins on HNTs can be done by stirring/reflux or by under pressure\(^{26}\).

**Use of HNTs in protecting environment**

HNTs are easily available, economical and have low surface charges as compared to carbon nanotubes and montmorillonites so we use HNTs as nano filler in nanocomposites. The HNTs may be modified before their use in composites so that their tubular structure may remain intact with resulting polymer halloysites composite\(^{27}\). The polymer chains can start from inner or outer surface of the HNTs. Corn starch and a polymer are coated on the surface of composite is formed when the interior of the HNTs is fully covered with polymer matrix\(^{32}\). The tensile strength and tensile modulus of HNTs based nanocomposites are higher than unmodified ethylene propylene diene monomer (EPDM) after the modification of HNTs the elongation at break is little bit decreased\(^{27}\). HNTs are used to get excellent mechanical properties and lower permeability for high performance polymer composites. Sorbic acid (SA) is used to improve the mechanical properties and optical properties. This problem is reduced by using HNTs. Halloysites for the atom transfer radical polymerization (ATRP)

**Halloysite for intercalation**

Due to the presence of organic groups, the dyes are resistant to decomposition, if decompose will cause toxicity. So the dyes such as Neutral Red, Methylene blue, Malachite green and methyl violet are removed from aqueous solution by using HNTs due to their ability to remove cationic dyes. The adsorption potential of HNTs is enhanced with enhancement of adsorbents, dosage, preliminary pH, temperature and preliminary concentration\(^{30}\).

**Halloysite for drug delivery**

The compatibility between PP and HNTs is improved by grafting PP chains between HNTs and rubber matrix is due to SA. SA based rubber composites have high modulus and strength\(^{30}\). HNTs incorporated epoxies have high fracture toughness, strength and modulus without loss of thermal properties. The use of potassium acetate for surface treatment of HNTs is an effective way\(^2\). Nanocomposites having inorganics as fillers show better properties as compared to unfilled composites. Recently we are using HNTs as a nano filler for different composites such as epoxy resin, polypropylene, polystyrene, natural rubber, etc.\(^{27}\) Also shows that higher contents of HNTs promote higher vulcanization and lower contents of HNTs hold up the vulcanization of XSSB/HNT compound. The mechanical properties like modulus and hardness are extensively improved by the filling of HNTs\(^{26}\). HNTs combined with natural rubber increase the mechanical and thermal characteristics of composites. Reinforcing ability of HNTs is superior to commercial silica coupled with the same amount of silane coupling agent. This has been confirmed by (TEM)\(^{29}\).

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**Halloysite based fabrication**

High concentration of clay cause poor dispersion which results in poor mechanical and optical properties. This problem is reduced by using HNTs. Up to 65% nanotubular clay in composites show high mechanical strength and high heat resistance\(^{22}\). HNTs may also be used as a stencil to formulate metallic Ni film or nanoparticles in electroless plating method. HNTs based stencils require activation before electroless plating to deposit Ni nano particles at surface or on the inner cavity of HNTs. Palladium ions can be reduced by methanol on HNTs surface, which cause the Ni particles to deposit.

**Future aspects of nanotechnology**

HNTs have been commercialized as polymer additives in USA under the Dragonite trade name. Now for the reduction of cost the wall thickness is minimized by taking the benefit of improvements in physical properties. The compatibility between PP and HNTs is improved by grafting PP chains at the surface of HNTs which enhance the mechanical performance of nanocomposites. Now research is being concentrated on HNTs added polymer nanocomposites due to their unique properties.

**CONCLUSION**

HNTs are distinctive nanomaterials poised of double layer of aluminium, silicon, hydrogen and oxygen and are non toxic even at high concentrations. HNTs are found in tropical and subtropical soils having variable morphology due to the forces they bear during their formation. Depending upon size, surface area and pore size, HNTs are of different grades which can be used for biological and non biological applications. It is very hard to sum up all the applications of HNTs but some of them are too vital constituent for fabrication, corrosion prevention, polymerization, immobilization, thermostability, macro molecular delivery etc. So it can be derived that HNTs are promising nanomaterials to prepare new structural and functional materials.
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