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 carrier for the delivery of drugs and various macro molecules, storage of H_2 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 $Al_2Si_2O_5(OH)_4 \cdot 2H_2O$. The natural deposits of halloysites nanotubes are found in countries like China, New Zealand, America, Brazil, and France¹. 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 structure². 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 octahedral³. Within the octahedral sheet, only two-third of the presented octahedral sites is filled with aluminium. The crystal structure of halloysites is described as 1:1 dioctahedral layer silicate⁴. The variations in the symmetry of the finishing structure of halloysites are due to the water molecules present between two consecutive layers. Halloysites may be platy, fibers tubular or cylindrical particles of different dimentions⁵.

Fig- 1: Structural forms of HNTs.

The existence of tubular or cylindrical particles is the indication of halloysites but if the samples are with platy particles then they are named as kaolinite. HNTs are used as a stencil in nanotechnology⁶.

Chemistry

HNTs are chemically related to kaolin. HNTs hold two types of hydroxyl groups, inner hydroxyl groups, which are between layers and outer hydroxyl groups which are present on the surface of nanotubes. The surface of HNTs is essentially poised of SiO_2 groups and the siloxane⁷.

Kinds of HNTs

Single walled and multi-walled HNTs are used in field of nanotechnology⁸.

APPLICATIONS

Halloysite clay nanocomposites, nanotubes, nano powders, etc. now are rising fashion setters in olive nanotechnology. HNTs have copious commercial applications in various fields.

Fig- 2: Kinds of HNTs.

HNTs for mechanical reinforcement

The improved mechanical properties of HNTs polymer composites is due to the transfer of applied load from matrix to nanotubes⁹. The tensile properties of a HNTs-PA6 nanocomposite increased by filler loadings¹⁰. The tensile strength and Young's modulus of PA6 improved with HNTs loadings. The mechanical properties of the carboxylated butadiene-styrene rubber (xSBR), considerably improved after loading the HNTs¹¹. The impact strength of the HNTs-epoxy nanocomposite^{2,12} and HNTs-vinyl-ester composites also improved appreciably after loading of HNTs. HNTs also improved the tensile strength and Young's modulus of the chitosan^{13,14} and PVA¹⁵ nanocomposites films. The mechanical properties of PCL¹⁶, PLGA nanofibers^{17,18} and EPDM¹⁹⁻²¹ also improved by the addition of HNTs. HNTs-PLA bionanocomposites have better properties with HNTs contents^{22,23}. The degree of dispersion of HNTs showed the final properties of composites. At higher HNTs contents uniform dispersion is difficult²⁴⁻²⁶. Ball mill homogenization and intercalated treatments can be used for well dispersion in epoxy matrices^{27,28}. A water-assisted extrusion with a PP-graft-maleic anhydride (PP-g-MA) compatibilizer is developed for good dispersion of HNTs in HNTs-PP nanocomposites²⁹. By surface grating PBA, HNTs' dispersion and in the PVC matrix was enhanced³⁰. Surface modified HNTs have improved dispersion in EPDM, PLA/PCL blends, unsaturated polyesters and HNTs-epoxy resin nanocomposites². It is a crucial factor for mechanical properties. HNTs have inherent hydrogen bond interactions therefore, the interface in the HNTs-polar polymers is generally justified^{22,31-35}. The hydrogen bonding should be strengthen otherwise opposite affect will be seen. Such as the tensile strength of PVDF decreased when the HNTs concentration increased³⁶. A method to increase the interfacial interactions is to incorporate compatibilizer³⁷. Quaternary ammonium salt treated HNTs have a better reinforcing effect on PLA²³. Benzoalkonium chloride-treated HNTs showed a better reinforcing effect to plasticized starch film³⁸. Using electron transferring modifiers also increased the interfacial adhesion in the HNTs-non polar polymer nanocomposites. Some electron-transferring modifiers are included BBT^{39,40}, N-cyclohexyl-2-benzothiazole sulfonamide (CBS)⁴¹, and EPB⁴². Methacrylic acid or sorbic acid(SA) were added to HNTs-rubber nanocomposite to improve the interfacial characteristics⁴³⁻⁴⁵. The metal carboxylate-modified HNTs-rubber composites showed improved mechanical strength, heat resistance and lucidity. This approach was efficient for reinforcing NBR and SBR. MAH-g-EPDM compatibilized HNTs-

EPDM nanocomposites showed much higher tensile properties compared²¹.

HNTs for thermal stability

HNTs generate a barrier effect toward both mass and heat transports, improving the thermal stability. Polymer chains and decomposition products can enter the lumens of the HNTs, slowing mass transport and considerably improving the thermal stability. The thermal stability of HNTs-PP nanocomposites was improved⁴⁶. HNTs can also appreciably improve the decomposition temperature of PVA⁴⁷, PLA, VER³², chitosan¹³, EPDM¹⁹, starch³⁸ and apple pectin⁴⁸. The degradation temperature depends on HNTs loadings^{49,50}.

HNTs and crystallization behavior

HNTs can affect the crystallization behavior of polymers by acting as heterogeneous nucleation points. HNTs can affect the crystallization behavior of PVA^{15,51}, PLA^{22,23}, PP⁵², PA6, PVDF³⁶, and PCL¹⁶. The crystallization temperature of the HNTs-PVA initially increased but further loading decreases the improvement in the crystallization temperature⁵¹. In HNTs-PP nanocomposites there is increase in crystallization temperature⁵². The crystallinities of the HNTs-PLA composites were significantly superior to neat PLA. The HNTs- PCL nanocomposites showed higher crystallization temperatures¹⁶.

Halloysite nanotubes for flame resistance

The following polymers have been selected for flame resistance LLDPE⁵³, PP⁴⁶, PBT, ABS⁵⁴, PES⁵⁵, NBR⁵⁶, and soy protein⁵⁷. HNTs exhibited a decline of flammability of the related polymers appreciably without loss of mechanical properties. It was seen that HNTs have a synergetic effect with other halogen-free flame retardants like magnesium hydroxide, antimony trioxide and melamine cyanurate⁵⁶. The thermal stability of 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 flammability⁵⁸. Poly ethylene graft is used as interfacial modifier in the LLDPE/HNTs composites, in this way the mechanical properties, flame retardancy and thermal stability are increased. These properties are enhanced by the addition of graft copolymer, which also increase the interfacial bonding⁵³. 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.%)⁵⁹. Coefficient of thermal expansion of epoxy resin is considerably decreased by the addition of HNTs³¹. The addition of HNTs slightly affected both ϵ and σ at a certain frequency remaining dependable with HNTs polar nature and the increased number of charge carriers in their presence⁴⁹.

Wet ability and self healing properties

HNTs are hydrophilic in nature showing a 10° water contact angle. PP without HNTs forms a water contact angle of roughly 160°. The maximum contact angle for the HNTs-PP composites was near to 170° with 15 wt.%⁵². But in HNTs-pectin and HNTs-PCL nanocomposites water contact angle was decreased by HNTs^{16,49}. For the HNTs-HPC nanocomposite films an increase in the water contact angle was observed⁴⁹. HNTs are a good candidate for self healing anticorrosion coating formulations^{8,60-62}. Polyurethane and acrylic paints doped with HNTs laden with benzotriazole, 2-mercaptobenzimidazole, and 2-mercaptobenzothiazole corrosion inhibitors produce self-healing nanocomposites coatings for copper⁶².

HNTs for tissue engineering scaffolds

HNTs have been loaded to biodegradable polymers like PVA, chitosan¹⁴, PLA⁶³, and PLGA^{17,64} for the preparation of tissue engineering scaffolds. HNTs loaded PVA bionanocomposites films are extremely compatible with the osteoblast and fibroblast cells¹⁵. Mouse fibroblasts can build up on the HNTs-chitosan nanocomposites surfaces. Electrospun HNTs-PLGA nanofibrous mats have outstanding biocompatibility¹⁷. So HNTs polymer composites have great emerging applications in tissue engineering.

HNTs as a potential drug delivery vehicle, bone implants and wound Care

The applications of HNTs as drug release vehicles were broadly reported in publications⁶⁵⁻⁶⁷ and the drug release rate can be further delayed by coating polymers onto the drug-loaded HNTs^{11,68}. HNTs-polymer nanocomposites can be used as drug containers^{69,70}. Coating of PVA on the HNTs can slow down diphenhydramine hydrochloride release¹¹. Furthermore, the chitosan- and PEI-coated HNTs exhibit show a radically reduced release comparatively to the uncoated HNTs. Other active agents like self healing⁶² anticorrosion⁶⁰ and antimicrobial agents and proteins and DNA⁷¹ can be laden for continued release. HNTs are 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-butylcyanoacrylate may also be used. HNTs are ideal for controlled release of hydrophilic as well as lipophilic drugs⁷². PMMA bone cement has fine biocompatibility and mechanical properties for its use in orthopedic renovate. Gentamicin is loaded into the lumen of HNTs and then drug loaded HNTs were⁷³ 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 implants⁷⁴. 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 stimulants 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, were studied by using confocal laser scanning microscopy (CLSM)⁷⁵.

Halloysite for osteoblasts and fibroblasts response

Polyvinyl alcohol (PVA) is a biodegradable and biocompatible synthetic polymer. Due to hydrophilic nature it has some drawbacks which can be minimized by the use of HNTs as filler. A number of nanoclays were used for this purpose but HNTs having hydroxyl groups on the chain edges are ideal filler which easily forms the hydrogen bond between HNTs and PVA. Cell studies have revealed that modified film enhance the cell adhesion. On nanotubes ends surface cells show a considerably higher level of adhesion comparative to neat PVA film, while neat PVA revealed higher degree of osteoblast propagation than PVA/HNTs⁷⁶.

HNTs for remediation and cosmetics

Clays are good adsorbents because of their convenience, high surface area and high adsorption capability. Clays like perlite, dolomite, nontronite, montmorillonites, bentonite, zeolites, and sepiolite are used as adsorbents. Among these halloysites is ideal one⁷⁷. HNTs can also be used in cosmetics due to their absorptive nature as a cleansing mask that deeply purifies and refines facial pores. HNTs are also used as nanocontainer during loading and extended release of glycerol for cosmetic applications⁷⁸. HNTs loaded glycerol has extended release rates which are necessary for cosmetic applications⁷⁹. Due to absorptive nature of the HNT it serves as a hypoallergenic skin cleanser. It also acts as an exfoliator which draws dead skin cells away from the surface to keep it fresh and healthy⁸⁰.

Cancer cell isolation

HNTs have been coated with a layer of poly-L-lysine onto their surfaces and functionalized with recombinant human selectin protein. This technique can amplify the arrest ability of HNTs toward leukemic cells during flow⁸¹. Circulating tumour cells present in blood can be arrested by assimilation of HNTs onto the surface of instruments. It is shown that HNTs content and selectin density are important keys for controlling cell capture⁸¹. The mean purity of captured primary CTC samples was 0.660 (0.039) on the nanotube surface and 0.372 (0.030) on the smooth surface, demonstrating a significant benefit provided by the nanotube coating⁸². Selectin functionalized microtubes for cancer cell isolation were prepared by coating halloysite nanotubes⁸³. HNTs-coated microtube devices immobilized with nanoscale liposomes appreciably improved the targeting, capturing and killing of cancer cells. This work provides a novel approach to selectively target and deliver chemotherapeutics to CTCs in the bloodstream⁸⁴. Microtube surfaces with immobilized HNTs and E-selectin functionalized liposomal doxorubicin (ESPEG L-DXR) considerably enlarged the number of breast adenocarcinoma MCF7 cells captured during flow; however also notably decrease the number of captured neutrophils. This shows that nanostructured surfaces composing of HNTs and ES-PEG L-DXR can enhance CTC recruitment for chemotherapeutic delivery, whereas preventing healthy cell adhesion and uptake of therapeutic intended for CTCs⁸⁵.

Use of HNTs as nanoreactors and nanocontainers

HNTs are used as nanoreactors for the fabrication of nanoparticles, nanowires and such purposes. HNTs lumen can act as biomimetic nanoreactor to carry enzyme-catalyzed inorganic preparations⁸. HNTs are used as a tubular

pot for benzotriazole which is a corrosion inhibitor. HNTs can be used as an additive in paints to form a useful composite coating material⁷⁹. Hybrid sol-gel films doped with HNTs are able to liberate entrapped corrosion inhibitors in a controlled way. They have long term corrosion protection as comparative to undoped sol-gel films due to self-controlled discharge of corrosion inhibitor⁸⁶. HNTs can be used as protective coatings to load metal and plastic anticorrosion agents⁸⁷. 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. The silver nanorods based polymer composite is formed which demonstrated antimicrobial activity and increased tensile strength as well⁷⁹. By using HNTs gold nanoparticles were synthesized by the reduction of HAuCl_4 ⁸⁸.

Use of HNTs in protecting environment

HNTs are also used for the protection of atmosphere for example as nano-adsorbents to remove the cationic dye methylene blue and Zn (II) from aqueous solutions⁸⁹. HNTs which are environmentally safe are used as nanocontainers to load the corrosion inhibitors. These nanocontainers are sensitive to external and internal changes. If the interior of the HNTs is leaked it can be prevented by modifying the outer surfaces of 2-mercaptobenzothiazole-loaded HNTs by changing the polyelectrolyte multilayer (poly (allylamine hydrochloride)/poly (styrene sulfonate). The function of the polyelectrolytes multilayer is to release the inhibitor in a controlled way⁷⁹. Benzotriazole entrapped in HNTs nanoscale coatings significantly increase the anticorrosion activity⁹⁰.

Halloysite polymer nanocomposites

HNTs are easily available, economical and have low surface charges as comparative 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 composite⁹¹. The polymer chains can start from inner or outer surfaces of the HNTs. Corn shell coaxial structure of composite is formed when the interior of the HNTs is fully covered with polymer matrix⁹². The tensile strength and tensile modulus of HNTs based nanocomposites are higher than unmodified ethylene propylene diene monomer (EPDM) while after the modification of HNTs the elongation at break is little bit decreased⁹³. HNTs are used to get excellent mechanical properties and lower permeability for high performance polymer composites. Sorbic acid (SA) is used to improve the performance of styrenebutadienerubber SBR/HNTs nanocomposites. Bonding between HNTs and rubber matrix is due to SA. SA based rubber composites have high modulus and strength⁴⁴. 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 way². Nanocomposites having inorganics as fillers show better properties as comparative to unfilled composites. Recently we are using HNTs as a nano filler for different composites such as epoxy resin, polypropylene, polyamide, natural rubber, etc.²⁷ It also shows that higher contents of HNTs promote higher vulcanization and lower contents of HNTs hold up the vulcanization of xSBR/HNT compound. The mechanical properties like modulus and hardness are extensively improved by the filling of HNTs⁹⁴. 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)⁹⁵.

HNTs for in-situ chemical polymerization

Nanocomposites of polyaniline (PANI) are formed to improve its mechanical, physical and electrical properties. The nanomaterials are encapsulated inside the shell of polyaniline. In this technique polyaniline is layered on the surfaces of the HNTs through in-situ soap less emulsion polymerization following the anilinium chloride is adsorbed on the HNTs. HNTs are spread in aqueous acidic solution of aniline with constant stirring and by ultrasonic irradiation by use of ammonium per sulfate (APS) as an oxidant. Morphological properties of PANI/HNTs nanocomposites are affected by the acidity of the polymerizing media and adsorption of anilinium chloride on HNTs⁹⁶.

Halloysites for biomimetic polymerization of aniline

PANI is synthesized by using different chemical and enzymatic polymerization techniques. Enzyme based polymerization is an attractive method due to eco pleasant technique in which H_2O_2 is used as an oxidizer which produces water as a by-product. Hematin is a natural biomimetic catalyst which is not soluble in acidic medium. So it is activated by chemical method which also broadens its pH range. In chemical method hematin is immobilized onto HNTs and is used as biomimetic catalyst for polymerization of aniline in

aqueous acidic medium. This method increases the catalytic activity in acidic media and is completed in minimum steps⁹⁷.

Halloysites for the atom transfer radical polymerization (ATRP)

Economy and rate of reactions can be optimized by Immobilization of the catalysts on HNTs⁹⁸. In supported catalyst matrix CuBr complex with pyridyl methanimine ligand which is absorbed on support physically or covalently. Polymers with narrow polydispersities are produced by physical adsorption than produced by covalent adsorption. The disadvantage of this method is failure of catalytic activity and deprivation of catalyst may occur. HNTs can reduce these shortcomings. Silane is efficient as ligand for ATRP catalyst because silane can improve the physical adsorption of the catalyst on the support⁴.

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 compounds⁷². 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 pressure⁹⁹.

HNTs based hydro gel as adsorbent

HNTs are used for making polymeric hydro gel based composites. The polymeric hydro gels are used as adsorbents to remove harmful metal ions and ionic dyes. HNTs embedded polymer hydro gels have greater capacity for adsorption as comparative to pure polymer hydro gels for the removal of NH_4^+ ions⁵.

HNTs and dyes

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 (NR), 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 concentration¹⁰⁰.

Halloysite for intercalation

HNTs can be intercalated by a number of molecules like amides, dimethyl sulfoxide, potassium acetate, aniline, hydrazine and formamide. The Algerian halloysites were also characterized to study the intercalation of Na^+ , NH_4^+ , and Pb^{2+} acetate and to pertain these solids for removal of copper (II) ions from aqueous solutions. The adsorption of copper ion is explained by electrostatic interaction between the copper (II) ions and negatively charged surface of halloysites and ion-exchange of cations within the acetate interlayer space¹⁰¹.

HNTs based fabrications

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 resistance¹⁰². 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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