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HALLOYSITE NANOTUBES AND THEIR APPLICATION AREAS – A REVIEW

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ABSTRACT

The distinctive nanomaterials such as nanopowder,nanofluids,nanotubes,nanorods, nanoparticles, nanofibres and so forth are used in the field of nanotechnology. These nano materials are toxic in nature so not viewed as safe for people and for nature too.Halloysite nanotubes (HNT) are eco-friendly, naturally occurring cheaply available kaolinite group mineral.HNT incorporated materials havegood in strength, thermal resistance and freely available, HNTs have a number of escalating applications such as cosmetics, drug delivery, fire retardant, structural, wear resistant, nanoreactors, nanocontainers and soon. Due tolarge aspect ratio, low density, rich functionality and easilydispersed with any polymer, HNTs are used for high performance polymer composites and multi-functional nanocomposites. In this review, the exciting applications of HNT in different areas of research is discussed.

Key words: *Halloysite nanotubes; Kaolinite; low density; applications*

I. INTRODUCTION

Halloysite is a chemically under the kaolinite group, generallyshape of kaolin particles are platy in nature whereas Halloysite particles are tubular and naturally deposited in earth over a million years of ago and abundantly occurred in the nations likes New Zealand, France, Brazil, China and America [1].Halloysite nanotubes are novel and adaptable materials that are framed by surface weathering of aluminosilicate clay minerals and are made out of aluminium, silicon, hydrogen and oxygen.HNTs are white nanoparticlesas shown in figure 1, which are odourless with chemical formula $H_4Al_2O_9Si_2{\bullet}2H_2O$ and are more economical than other nanofillers, such as carbon nanotubes [2].It has been accounted that HNTshave low density twin layered tubular structure; one is the tetrahedral and other is an octahedral layer [3,4].

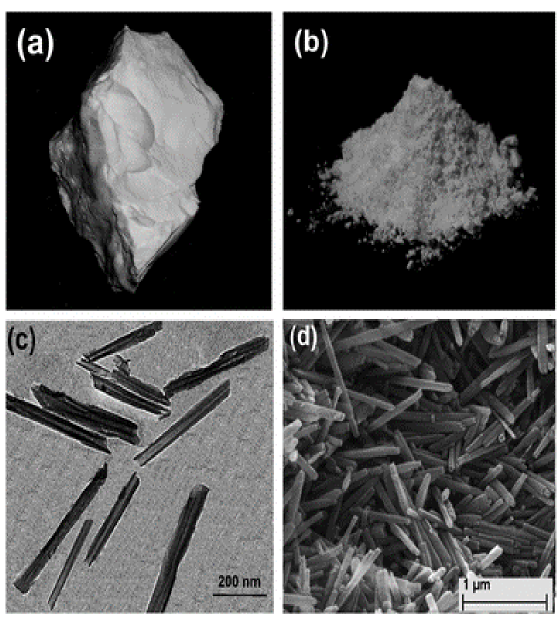

Figure 1: (a) Raw Halloysite (b) Processed HNT
(c) TEM Image of HNT (d) SEM Image of HNT

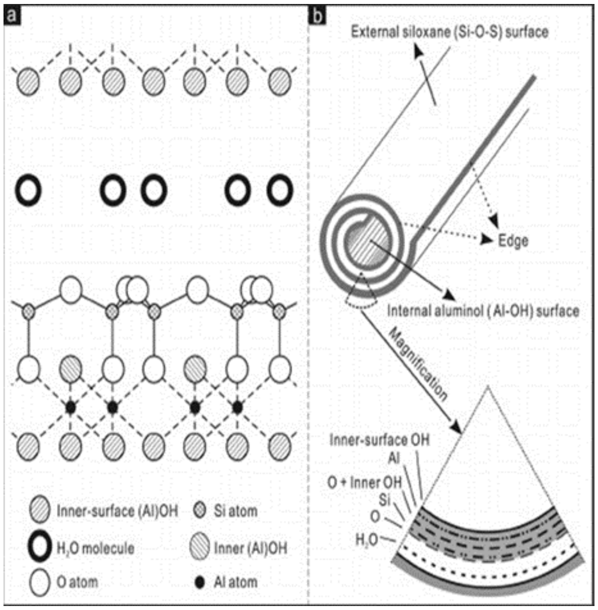

Figure 2: (a) crystal structure of Halloysite. (b) Halloysite nanotube structure.

II. CHEMISTRY

HNTs are synthetically identified with kaolin.HNTs had two sorts of hydroxylgroups such as internal hydroxyl groups,which are exist between intermediate layers and external hydroxyl groups were present at nanotube surfaces are as shown in figure2 and their physical characteristics were tabulated in Table 1.The surface of HNT is scrolled by dioctahedralsilicon and siloxane[5].In nanotechnology field both single walled and multi-walled Halloysite nanotubes are used [6].

Table 1: Physical Characteristics of HNT.

Length(µm)	0.5-2
Outside diameter(nm)	50-70
Inside diameter(nm)	15-45
Aspect ratio (L/D)	10-20
Density(g/cm^3)	2.54
Molecular weight(g)	294.19
Specific heat capacity(KJ/KgK)	0.92
Thermal Conductivity(W/m.K)	0.092
Surface area(m^2/g)	65-100
Modulus of single tubular Particle(Gpa)	130

Abbreviations

PLA:Poly Lactic Acid
PP:Polypropylene
PCL:Polycaprolactone
PVA:Polyvinyl Acetate
PVDF:Polyvinylidene Fluoride
PLGA: poly (lactic-co-glycolic acid)
EPDM: Ethylene Propylene Diene Monomer Rubber
PA 6: Polyamide 6

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PEI: *Polyetherimide*
PMMA:Polymethylmethacrylate

III. APPLICATION AREAS

Reinforcement for polymer composites

The both stiffness and strength of the polymer is appreciably increasing with HNTs loadings [7]. The elastic modulus of a HNTs-PA6 nanocomposite were increased by adding different weight percentages of HNT [8]. The impact strength of epoxy improved with HNTs loadings [9]. The tensile properties of a HNTs- vinyl-ester nanocomposite increased after loading of HNTs [10]. EPDM and PLA have better properties with HNTs contents[11,12].The final properties of composites depends on degree of dispersion HNT, at higher loading of HNT very difficult to achieve uniform dispersion hence ball mill homogenization and intercalated treatments can be used for well dispersion especially with epoxy [13-16]. Surface grating technique is employed for HNTs to improved dispersion with PLA/PCL blends, unsaturated polyesters, EPDM, and epoxy resin [17-20]. The elastic strength of PVDF reduced when increased the HNTs concentration due improper strengthening of hydrogen bonds [21]. The metal carboxylate-modified HNTs- Natural rubber composites showed improved mechanical strength and heat resistance [22].

Flame retardant

HNTs loading with polymers exhibited an excellent flame retardant property without sacrificing of mechanical properties [23-26].It is reported that HNT has better resistance to flammability similar to magnesium hydroxide and antimony trioxide[24]. Due to the presence of HNTs in polypropylene significantly increase the thermal stability and reduce the flammability because of barriers occur between heat and mass transport [36]. The presence of nitrogen in nylon 6 exhibits good in fire retardancy and it is further improved by adding HNTs due to easy dispersion with nylon 6 [25].The thermal stability of epoxy is considerably increased by addition of HNT[19].

Cosmetics

Generally clays are excellent adsorbents due to their high absorption capacity, comfort and high surface region. Generally the clays such as perlite, sepiolite, nontronite, montmorillonites, bentonite, zeolites and dolomite are used as adsorbents. HNT is also one type clay, have theabsorption capability and refines facial voids therefore used in beauty care products [26]. HNTs are also used as nanocontainer to release of glycerol in cosmetics applications [27, 28].It is also acts as skin cleanser by removing dead cells from skin and kept as healthy and fresh [29].

Nucleation of polymer crystallization

HNT initiates the heterogeneous nucleation, which influences in the crystallization of polymers. It is reported that HNTs can affect the crystallization behaviour of some of the polymers namely PLA [12, 30], PP [31], PVA [32, 33], PA6 [12], PCL [34], and PVDF [21].HNTs can affect the improvement in the crystallization temperature of polymers [31, 33,34].The crystallinity of polymer composites is improved by addition of HNT.

Corrosion resistance

HNT is used in fabrication of nanoreactors and nanocontainers. HNTs act as an anticorrosion agent so it is used as an additive in paints for coating of defensive components [28, 37]. The sol-gel films doped with HNT behaves as corrosion inhibitors and protects corrosion for long duration [38].

Tissue engineering

HNT have been loaded compatibly with biodegradable polymers namely PLA [39], PLGA [35, 40] and PVA [35] which are used for making of scaffolds for tissue engineering. HNT-PVA bionanocomposites are used for preparation of osteoblast and fibroblast cells [41].The mats made from HNT-PLGA nanocomposites shows outstanding biocompatibility [40]. So HNTs based polymer composites have great emerging applications in the field of tissue engineering.

Drug delivery

It is reported that HNT is used as drug delivery vehicle [37, 42, 43]. Drug loaded HNTs with coating of polymer reduces the releasing rate of drug [42]. Drug containers are manufactured by HNTs-polymer nanocomposites [44, 45]. The chitosan and PEI-coated HNTs shows a delaying in drug release compare to the uncoated HNTs. HNTs are ideal for controlled release of hydrophilic as well as lipophilic drugs [46]. HNTs may be used to get considerable tardy drug discharge. Drug loaded HNTs were mixed with PMMA to make bone cement [47].HNT based PLA composites are used for bone implantation applications [48]. HNTs based drug delivery system also used in cases of burn care applications. HNTs have the characteristics such as low delivery rate, uniform drug release, cost efficiency and less drug loading per patch so it is used for preparation of medicines.

Environmental protection

HNTs were acts as nanoadsorbents to remove the cationic dye methylene blue and Zn (II) from aqueous solutions so used for environmental protections [49]. HNTs which are environmental friendly corrosion inhibitors therefore it is used as nanocontainers, these are very sensitive to external and internal changes. Any leakages in internal surfaces of the HNTs can be prevented by changing outer surfaces of HNT loaded materials with polyelectrolyte multilayers, which releases the inhibitors in controlled manner [28].The anticorrosion property is improved by coating of HNT in nanoscale on Benzotriazole [50].

Separation of cancer cell

HNTs-coated nanotube devices are used for the targeting, capturing and killing of cancer cells [51, 52]. HNTs have been coated with a layer of poly-l-lysine onto their surfaces and functionalized with recombinant human selection protein. This technique can amplify the arrest ability of HNTs toward leukemic cells during flow. Tumour cells present in blood can be settled at HNT loaded instruments. It shows that HNT play an important role in controlling of cell capture [53]. The nanostructured surfaces composing of HNTs can enhance chemotherapeutic delivery, which prevents the adhesion of cancer cells [54].

IV. FUTURE ASPECTS OF HNT

The applications of Halloysite nanotube has been proven in potential areas as mentioned, so it is available commercially with a trade name Dragonite in USA. Nowadays a research is being concentrated on HNTs added polymer nanocomposites due to their unique properties to enhance the mechanical and tribological performance of nanocomposites. HNT assures that replacement for high cost nano materials such as Carbon nanotube and Graphene in upcoming days.

V. CONCLUSION

Halloysite is a unique and rarely available natural nanotubular material and found in tropical and subtropical soils with different morphology. HNTs have the unusual properties like non-toxic, corrosion resistance, good thermal stability, better mechanical strength, low density etc…are interested to use for all aspects of nanotechnology applications. Due to their pore size and surface area the different grades of HNTs are commercially available in market and also derived that promising nanomaterials to fabricate novel structural and functional devices for the usage of mankind.

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