Original Article

Nano Composite - Applications For Halloysite Nanocomposite

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Abstract

Halloysite is a naturally occurring nanoclay that attracts attention as a flexible and significant component of biomaterials because of its distinctive properties, including its nanometric size range, tubular structure, excellent biocompatibility, low cost, and opposing charges on its surface. In order to achieve improved and desirable qualities including mechanical strength, barrier properties, and regulated pore size, functionalized Halloysite nanotubes (HNT) are added to the cellulose biopolymer. Bio-nano composites, which have improved qualities, are used in a variety of industries, including food packaging, the car sector, medicine delivery, and many more. Extended research on several HNT-cellulose-based bio-nanocomposites is presented in this chapter, together with information on their structural and functional characteristics and applications.

INTRODUCTION

Nano science, which applies small-scale science, is the study of atoms, molecules, and other entities with sizes measured in nanometers (1–100). It is interdisciplinary, including the collaboration of physicists, chemists, and biologists to analyze, study, and develop ever-smaller structures. Physics differs at the nanoscale. It is becoming more important to consider thermodynamic and quantum mechanical properties that cannot be seen on a macroscopic scale. One works with specific atoms and molecules rather than bulk materials [1-2].

"A material with two phases, one of which is evenly distributed into the second phase at the Nano scale level" is how a nano composite is defined. A unique product called Nano-composite material includes nanoscale (one billionth of a metre) fillers dispersed throughout the matrix. The structure is frequently composed of a matrix and filler, where the fillers, such as particles, fibres, or fragments, surround and attach to one another as discrete units in the matrix. Nano-composite materials' characteristics are influenced by the characteristics of their individual parents as well as by their form and interfacial characteristics. Some nanocomposites may be a thousand times stronger than their bulk constituents. A fast-growing area of research is the general class of Nano composite organic and inorganic materials. Inorganic layered materials come in a variety of varieties [3-5].

Researchers have been interested to develop such composites since 1960 because syntactic foam is composed of hollow particles, such as tiny balloons. In the aerospace and submarine industries, syntactic foams are used in a variety of applications. Such composite materials may be made for mechanical roots by mixing a resin matrix with hollow micro balloons. In sea buildings, where bouncy could be raised to a greater extent, higher concentrations of micro balloons in a matrix provided for makeable weight reductions. They improve the system's capacity to support loads in aeronautical structures. This is because syntactic foams are brittle in tension and ductile in compression.

It has been shown that the tensile strength of syntactic foam is reduced and increased by the volume fracture ion of micro balloons. The failure of syntactic foam under tensile and shear fracture circumstances is well-documented in the open literature, as demonstrated by a microstructure analysis using scanning electron microscopy. Additionally, the significance of compressive, tensile, and shear characteristics in foam core sandwich systems is frequently ignored. Since failure might result in loss of life or property, the strength and dependability of syntactic foam are crucial for aircraft applications. As a result, there is now much more interest in training using syntactic foam that is lighter. The researcher has spent a lot of money on this endeavour [6-7].

NANOTUBES MADE OF ALLOY

Many successful nanotechnology outputs, such as carbon nanotubes, nano fluids, nanoparticles, nano emulsions, nano capsules, and so on, are not viewed as safe for humans or the environment due to their toxicological potencies. Nanotubes made of halloysite are cheap, environmentally friendly, and safe for use by people. Unique and multipurpose nanomaterials known as halloysite nanotubes (HNTs) are comprised of double-layered aluminosilicate minerals and have a hollow tubular structure with a submicron diameter. They have rapid adsorption rates, tunable release rates, and are

harmless. These nanotubes may be used for many different things, such as the treatment of cancer, the extended delivery of certain medications, the creation of biocatalysts using them as templates or nano reactors, personal care and cosmetics, and even environmental protection [8-9].

Fig. 1 shows powdered halloysite nanotube material.

Halloysite nanotubes are rare and versatile nanomaterials produced naturally in the Earth over millions of years in powder form, as seen in fig. 1. They are constructed of two layers of silicon, hydrogen, oxygen, and aluminium. Small hollow tubes called halloysite nanotubes range in length from 500 nanometers to more than 1.2 microns and have a diameter of less than 100 nanometers (100 billionths of a metre) (millionths of a meter). Lattice mismatch between neighbouring silicon dioxide and aluminium oxide layers leads to the formation of halloysite nanotubes [10].

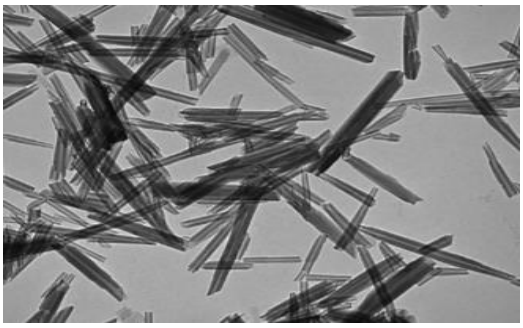

Figure 2. Halloysite nanotubes.

Halloysite nanotubes (HNTs) were added to epoxy composites to increase their mechanical properties, as illustrated in fig. 2. In particular, the fracture toughness and flexural strength of the prepared HNTs reinforced epoxy composites were improved. A Nano composite containing 6% mHNTs had a flexural modulus that was 11.8% higher than that of a pure epoxy resin. The Nano composites also showed improved dimensional stability. The developed epoxy composites with halloysite reinforcement were characterized by thermal gravimetric analysis (TGA). The improved attributes result from interfacial contact, homogenous reinforcement dispersion, and special characteristics of HNTs [11-14].

APPLICATIONS

Halloysites were primarily used as a kaolinite-alternative ceramic raw material up until about 2005. However, the amount of study into the applications of halloysite nanotubes, also known as HNTs, has increased exponentially. Halloysite's readily available and reasonably priced nanotubular forms have potential uses in nanocomposites with polymers, as carriers for active ingredients in products used in medicine, food, cosmetics, and environmental remediation, as well as in notifying, as supports for catalyst immobilization, and as heterogeneous catalysts. They also have the potential to be used for medicinal purposes other than medication delivery, including as water filtration, tissue engineering scaffolds, and wound dressing. Halloysite does have a variety of specialized uses, especially given how well it works with other materials [15-16].

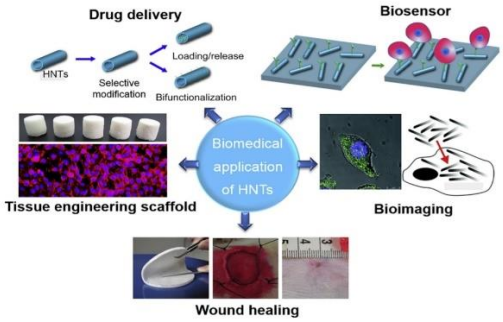

Fig. 3: Halloysite nanotube uses in biomedicine.

The effectiveness of medicine and therapy is crucial in the pharmacy and healthcare industries; failure or disadvantage in drug therapy may lead to ineffectiveness or side effects that are hazardous to human health. Green nanotechnology seeks to produce Nano products that are less harmful to the environment. Nanotubes made of halloysite clay, nanocomposites, nano powders, and other trend-setters in green nanotechnology are being developed. Compared to carbon nanotubes, halloysite nanotubes are less costly and more ecologically friendly. Carbon nanotubes have recently raised growing concerns about their effects on human health and the environment due to their possible toxicity. Electrical parts, drug delivery systems, cosmetics, and home and personal care goods are just a few of the many industrial applications for halloysite nanotubes [17-20].

Halloysite nanotubes (HNTs) are 1:1 clay that are found in nature and have nanotubular architectures and chemical compositions that are comparable to kaolin. Numerous fascinating uses have been found for this special, affordable, and abundantly deposited clay because of different features like nanoscale lumens, a high length-to-diameter ratio, a comparatively low hydroxyl group density on the surface, etc. We focus on the uses of HNTs in the creation of polymer nanocomposites after briefly outlining their applications in controlled release, nano templating, and sorption. We discuss the distinctive architectures and functionality of HNT-incorporated polymer nanocomposites produced by diverse methods. According to the findings, these nanocomposites perform very well in terms of reinforcing properties, improved flame retardancy, and decreased thermal expansion [21-22].

Halloysite Nanotubes (HNT), a kind of aluminosilicate clay, have been mixed with natural rubber using a banbury and two roll mill to create natural rubber nanocomposites. The impact of HNT content addition on the morphological, mechanical, and rheological characteristics of the NRHNT nanocomposites was investigated. The mooney viscosity, mooney scorch, and cure index are rheological parameters. Tensile strength, elongation at break, and hardness are the mechanical qualities that are investigated. TGA was used to examine thermal stability in order to examine the impact of adding nanofiller to the rubber matrix. Din abrader was used to study wear characteristics as well. The HNT filler has been well dispersed within NR, according to XRD and SEM measurements. The NR-HNT nanocomposites exhibit better wear, mechanical, thermal, and morphological qualities, according to the results for various attributes [23].

Recent years have seen a lot of interest in polymer composites that feature nano-additive reinforcements because they allow for customizable qualities that are advantageous for specific material applications. Natural halloysite nanotubes were used to create polyurethane-based nanocomposites in this study. Under quasi-static loading and high-strain-rate circumstances, the mechanical characteristics of the polymer nanocomposite system are examined. The nanocomposite exhibits an elastomeric behavior under static loading and a glassy response under dynamic stress. The interference of the nanotubes on the polyurethane matrix's fracture behavior is examined given that halloysite nanotubes may be evenly scattered there. Polypropylene Glycol, a polyurethane based on tolylene 2,4-diisocyanate, was made with halloysite and 4,4'-methylenebis(2-chloroaniline) as a cure. Comparisons between the pristine and nanocomposite polymer's ultimate tensile strength, strain to failure, and spall strength reveal the polymer's reinforcing [24].

- EPA complex classified natural, non-toxic, biocompatible materials
- Large surface area, fine particle size, and effective dispersion
- Keeps release rates constant, maintained, and prevents early overdosage
- Capable of adjustable release rates and preventing discharge unless activated.
- Guards against effective medication inside its lumen during demanding material processing
- Has the ability to load numerous active agents at once.
- Lessens the need of expensive active agents
- Available in many different forms, such as powders, creams, gels, lotions, and sprays

DYE DEGRADATION

Due to its accessibility, simplicity in functionalization, and well-defined structures, halloysite has mostly being researched for usage in novel advanced materials. In particular, for their application as adsorbents, photocatalysts, or photocatalyst supports, their architectures have been changed to provide certain chemical and physical characteristics. HNTs-based nanocomposites have a number of benefits in the area of environmental catalysis, including the use of catalytic amounts, straightforward recovery and high turnover rates, ease of set-up and work-up, mild experimental conditions, high yields, and selectivities, which make them useful building blocks for the development of environmentally friendly technologies [25].

CATALYSIS IN GAS PHASE

Because of its high toxicity and possible harm to human health, toxic waste gas has received a lot of attention in recent years. Both short-term and long-term inhalation exposure to hazardous waste gas can result in inflammation of the gastrointestinal, respiratory, and nervous systems in people and other animals. Due to the high cost and inadequate treatment methods, it has been claimed that many chemical facilities in Asia immediately release harmful waste gas into the atmosphere without complete treatment. As a result, the removal of harmful waste gas released by chemical factories has gained importance. It may be dangerous for both human health and the quality of the atmosphere if poisonous phosphine (PH3) tail gas is not completely removed during the manufacturing process of those compounds in industrial

facilities. In the past, it was necessary to capture the poisonous waste gas and use combustion and oxidation to transform it into other compounds. However, the practical use is constrained by the poor efficiency and potential harmful waste gas leaks during burning. It is customary to use wet scrubbing with calcium hypochlorite, potassium permanganate, or hydrogen peroxide to treat tiny amounts of hazardous waste gas, but due to the high expense, this approach is not appropriate for the removal of industrial waste gas [26].

CONCLUSION

Natural halloysite nanotubes were incorporated into an epoxy polymer matrix as reinforcement. Modified HNTs were created by coupling with silane and then dispensed into an epoxy matrix to improve dispersion and interface contact. In the absence of modification, HNTs appear to be grouped together. The produced Nano composites all have improved flexural properties, dimensional stability, and char yield. In the creation of mechanically improved polymeric composite materials, a low-cost, naturally occurring reinforcing ingredient plays an important role. This study helps us comprehend this role. The mechanical properties of composites can be dramatically changed by proper HNT alignment in polymer matrix due to the peculiar form of HNTs. Enhancing the anisotropic mechanical properties of HNTs reinforced composite materials may be the outcome of further research into surface modification techniques.

REFERENCES

1. Kirkman, J.H. (1977). Possible structure of halloysite disksand cylinders observed in some New Zealand rhyolitic tephras. Clay Miner. 3(12), 199–216.
2. Joussein, E., Petit, S., Churchman, J., Theng, B., Righi, D. & Delvaux, B. (2005). Halloysite clay minerals — a review. Clay Miner. 4(40), 383–426. DOI: 10.1180/0009855054040180.
3. Levis, S.R. & Deasy, P.B. (2002). Characterization ofhalloysite for use as a microtubular drug delivery system. Inter. J. Pharm. 1–2(243), 125–134. DOI: 10.1016/S0378- 5173(02)00274-0.
4. Imai, T., Naitoh, Y., Yamamoto, T. & Ohyanagi, M. (2006).Translucent Nano Mullite Based Composite Ceramic Fabri-cated by Spark Plasma Sintering. J. Cer. Soc. JPN 1325(114), 138–140. DOI: 10.2109/jcersj.114.138.
5. Wilson, I.R. (2004). Kaolin and halloysite deposits of China.Clay Miner. 1(39), 1–15. DOI: 10.1180/0009855043910116.
6. Guo, B., Zou, Q., Lei, Y. & Jia, D. (2009). Structure and Performance of Polyamide 6/Halloysite Nanotubes Nanocom- posites. Polym. J. 10(41), 835–842.
7. Handge, U.A., Hedicke-Höchstötter, K. & Altstädt, V.(2010). Composites of polyamide 6 and silicate nanotubes of themineral halloysite: Influence of molecular weight on thermal, mechanical and rheological properties. Polymer 12(51), 2690–2699. DOI: http://dx.doi.org/10.1016/j.polymer.2010.04.041.
8. Ning, N., Yin, Q., Luo, F., Zhang, Q., Du, R. & Fu,Q. (2007). Crystallization behavior and mechanical properties of polypropylene/halloysite composites. Polymer 25(48), 7374–7384. http://dx.doi.org/10.1016/j.polymer.2007.10.005
9. Oburoğlu, N., Ercan, N., Durmus, A. & Kaşgöz, A. (2011). Effects of Halloysite Nanotube on the Mechanical Properties and Nonisothermal Crystallization Kinetics of Poly (Butylene Terephthalate) (PBT). J. Macromol. Sci., Part B 5(51), 860–879. DOI: 10.1080/00222348.2011.610231.
10. Szczygielska, A. & Kijeński, J. (2011). Studies of propertiesof polypropylene/halloysite composites. Pol. J. Chem. Technol.3(13), 61. DOI: 10.2478/v10026-011-0039-0.
11. Vahdat Vahedi, Pooria Pasbakhsh, Siang-Piao Chai, "Toward high performance epoxy/halloysite nanocomposites: New insights based on rheological, curing, and impact properties". Materials and Design 68 (2015) 42–53.
12. Youhong Tang, Shiqiang Deng, Lin Ye, Cheng Yang, Qiang Yuan, Jianing Zhang, Chengbi Zhao," Effects of unfolded and intercalated halloysites on mechanical properties of halloysite epoxy nanocomposites". Composites: Part A 42 (2011) 345–354.
13. Youhong Tang, Lin Ye, Shiqiang Deng, Cheng Yang, Wangzhang Yuan," Influences of processing methods and chemical treatments on fracture toughness of halloysite–epoxy composites". Materials and Design 42 (2012) 471–477.
14. Ravindra Kamble, Manasi Ghag, Sheetal Gaikawad, Bijoy Kumar Panda," Halloysite Nanotubes and Applications: A Review". Journal of Advanced Scientific Research, 2012, 3(2): 25-29.
15. Deepak Rawtani and Y.K. Agrawal," Mmultifarious applications of halloysite nanotubes: a review". Institute of Research & Development, Gujarat Forensic Sciences University, 30 (2012) 282-295.
16. N. Abacha, M. Kubouchi, K. Tsuda, T. Sakai," Performance of epoxy-nanocomposite under corrosive Environment." eXPRESS Polymer Letters Vol.1, No.6 (2007) 364–369.
17. K. Prashantha, M. F. Lacrampe, P. Krawczak," Processing and characterization of halloysite nanotubes filled polypropylene nanocomposites based on a masterbatch route: effect of halloysites treatment on structural and mechanical properties". eXPRESS Polymer Letters Vol.5, No.4 (2011) 295–307.
18. R. Nakamura1, a.n. netravali, m.v. hosur," effect of halloysite nanotubes on tensile properties and interfacial property between carbon fiber and epoxy resin". 18th international conference on composite materials.
19. Zhenqing Wang, Fang Liu, Wenyan Liang, and Limin Zhou," Study on Tensile Properties of Nanoreinforced Epoxy Polymer: Macroscopic Experiments and Nanoscale FEM Simulation Prediction". Hindawi Publishing Corporation Advances in Materials Science and Engineering Volume 2013, Article ID 392450, 8 pages.
20. Michael Russ, Sameer S. Rahatekar, Krzysztof Koziol , Benjamin Farmer, Hua-Xin Peng," Length-dependent electrical and thermal properties of carbon nanotube loaded epoxy nanocomposites". Composites Science and Technology 81 (2013) 42–47.
21. Azeez AA, Rhee KY, Park SJ, Hui D."Epoxy clay nanocomposites–processing, properties and applications: a review". Compos B Eng 2013; 45:308–20.
22. Ragosta G, Abbate M, Musto P, Scarinzi G, Mascia L."Epoxy–silica particulate nanocomposites: chemical interactions, reinforcement and fracture toughness". Polymer 2005; 46:10506–16.
23. Guo B., Lei Y., Chen F., Liu X., Du M., Jia D."Styrene–butadiene rubber/halloysite nanotubes nano- composites modified by methacrylic acid". Applied Surface Science, 255, 2715–2722 (2008).
24. Liu M., Guo B., Zou Q., Du M., Jia D."Interactions between halloysite nanotubes and 2, 5-bis(2-benzoxazolyl) thiophene and their effects on reinforcement of polypropylene/halloysite nanocomposites". Nanotechnology, 19, 205709 (2008).
25. Du M., Guo B., Jia D."Newly emerging applications of halloysite nanotubes: A review. Polymer". International, 59, 574–582 (2010).
26. Velmurugan R, Mohan T. Room, "temperature processing of epoxy–clay nanocomposites". J Mater Sci 2004; 39:7333–9.