Progress in Polymer Science 38 (2013) 1690–1719

Contents lists available at ScienceDirect

Progress in Polymer Science

journal homepage: www.elsevier.com/locate/ppolysci

Functional polymer–clay nanotube composites with sustained release of chemical agents

Yuri Lvov*, Elshad Abdullayev

Institute for Micromanufacturing, Louisiana Tech University, Ruston, LA 71272, USA

ARTICLE INFO

Article history:
Received 31 March 2012
Received in revised form 30 April 2013
Accepted 6 May 2013
Available online 14 May 2013

Keywords:
Halloysite nanotubes
Nanocomposites
Drug delivery
Biopolymers
Anticorrosion
Imogolite

ABSTRACT

Natural halloysite clay nanotubes are described as inorganic reinforcing materials for polymers. Loading these tubes' 15-nm diameter lumens with chemical agents, including bioactive molecules (self-healing, anticorrosion, antimicrobial agents, proteins, DNA, drugs, etc.), and doping them into polymers allows a controlled sustained release, providing these nanocomposites with new smart properties. Typically, addition of 5% halloysite synergistically increases polymer strength on 30–70%, enhances composite adhesivity and adds new functions due to triggered release of needed chemicals. Halloysite is biocompatible "green" material and its simple processing combined with low cost make it a perspective additive for polymeric biocomposites. Comparison of halloysite with other tubule clay – imogolite – is given; these tubes have smaller diameter and much lower loading capacity for macromolecules.

Contents

1. Introduction ... 1691
2. Halloysite structure ... 1692
3. Halloysite biocompatibility ... 1695
4. Encapsulation and sustained release of biomolecules and salts ... 1696
   4.1. Wall intercalation ... 1696
   4.2. Lumen loading ... 1697
   4.3. Release characteristics of drugs ... 1697
   4.4. Release of proteins and DNA ... 1699
   4.5. Shell and tube-stopper formation to extend release ... 1700
   4.6. Polymeric shells ... 1700
   4.7. Metal-imidazole and metal triazole shells ... 1701
   4.8. Enhanced lumen capacity ... 1702
   4.9. Selective modification of halloysite lumen: new inorganic tubular micelle ... 1702
5. Halloysite–polymer nanocomposites ... 1702
   5.1. Bulk polymer composites ... 1704
   5.2. Halloysite–polymer composite coatings ... 1705
   5.3. Halloysite–wax composites ... 1705

* Corresponding author. Tel.: +1 318 257 5144; fax: +1 318 257 5104.
E-mail address: ylvov@coes.latech.edu (Y. Lvov).

0079-6700/$ – see front matter
http://dx.doi.org/10.1016/j.progpolymsci.2013.05.009

6. Halloysite–biopolymer composites 1706
6.1. Layer-by-layer (LbL) assembly of halloysite-polycation multilayers 1706
6.2. Bulk halloysite–polymer composite casting from solution 1707
7. Halloysite–polymer composite drug delivery systems 1709
8. Halloysite–PMMA bone cement 1710
8.1. Mechanical properties 1711
8.2. Adhesion of PMMA–halloysite composites to bone 1711
8.3. Gentamicin release from PMMA–halloysite composite 1712
8.4. Antibacterial effect of gentamicin loaded halloysite–PMMA 1713
9. Protective coating with self-healing 1713
10. Other applications of halloysite 1714
11. Imogolite clay nanotubes as compared with halloysite 1714
12. Conclusions 1716
Acknowledgements 1717
References 1717

1. Introduction

Halloysite is tubule alumosilicate clay with external diameter of 50–80 nm, lumen of 10–15 nm and length of about 1000 nm. Chemically, halloysite is similar to well-known and commonly used platy clay kaolin but its alumosilicate sheets are rolled into tubes [1–19]. Due to the tubular shape and less abundant surface hydroxyl groups, halloysite is readily dispersed in polymers without need for the exfoliation, contrary to the case of platy clays – kaolin and montmorillonite. Interestingly, halloysite–polymer composites are transparent in wide range of wavelengths including near-ultraviolet [4,8]. Polymeric composite materials may be doped with these tiny tubule containers that release application-specific chemical inhibitors (anticorrosion, antimicrobial, drugs, flame-retardant, microcrack self-healing) in a sustained fashion. Halloysite lumen loading capacity is 15–20 wt% and chemical agents release time may vary from 5 to 10 h to days [5–7,20–23]. Tubes admixed in polymers allow much slower release (months) enhanced closer to the sample surface, in microcracks and defect points. An elongated tubule shape of halloysite with length/diameter ratio of 20–50 could provide orientation in polymer microfibers significantly increasing tensile strength along the fiber axis and providing optical and mechanical anisotropy.

Tubule halloysite clay is “green” material, which is not hazardous for the environment, and these clay nanotubes are available inexpensively in thousands of tons from natural deposits. Doping loaded clay nanotubes into polymeric matrix provides a kind of ceramic “skeleton” within the material. These “skeleton bones” are loaded with functional chemicals, like real bones loaded with marrow [24]. Halloysite tube outermost is silica and innermost is alumina, both are polar compounds providing good hydrophilicity (water contact angle on halloysite tablet is below 5°) and consequently good dispersion in polar polymers such as epoxy [20], polyamides [24], polyethyleneimine [25], polyvinyl alcohol [26], polyacrylates [27] and biopolymers such as polysaccharides (pectin, starch) [28], chitosan [29], and humic acid. Surprisingly, halloysite admixes well to medium polarity polymers such as polyvinylchloride and even with low polar polymers, like polyethylene, polypropylene [30–33].

Environmental pollution caused by non-degradable synthetic polymers urged to find replacement with natural biopolymers composed of nontoxic components and degradable by micro-organisms. Extensive research has been done on materials derived from starch, cellulose, chitosan, polycaprolactone, polyvinyl alcohol, etc. for applications in agriculture, food packaging, biomedicine and construction. Often an efficient way to improve mechanical and thermal properties of biopolymers is loading them with inorganic dopants (carbon black, silica, titania, clays and others) [34–41]. The best composite characteristics are obtained when these dopants are well dispersed micro and nano-size particles. Such composites benefit from polymeric biocompatibility and improved mechanical and thermal properties. Nanoparticles with various shapes: platy, spherical, and fibers have been studied as fillers for polymeric composites. Fiber and tubular additives have gained particular interest due to drastic improvement of the composite mechanical properties. Carbon nanotubes have been extensively studied for fabrication of polymer composites with superior tensile strength to replace steel and aluminum in aviation [39]. However, no material with carbon nanotubes was produced for consumer products (cloth, food, and medicine). The problems associated with the utilization of carbon nanotubes include high manufacturing costs and difficulty in dispersing them in biocompatible often polar polymeric matrices [40]. Another limitation is their toxicity which may have adverse effects on human health. Recent works in which carbon nanotubes were injected intratracheally have shown their pulmonary toxicity. Comparative toxicity studies revealed that carbon nanotubes are more toxic than quartz dust, which is considered a serious occupational health hazard if it is chronically inhaled [42]. Cellular studies also indicated that carbon nanotubes are cancerogenic [43].

Natural halloysite clay nanotubes recently introduced in polymer composites offer many benefits not only due to their elongated shape but also due to the cylindrical pore (lumen) that can be loaded with chemically and biologically active substances [7]. Halloysite was named after O. d’Halloy who analyzed the mineral first time [1]. It is two-layered aluminosilicate clay ($Al_2Si_2O_5(OH)_4 \times nH_2O$ which exhibits a predominant form of hollow tubes, and