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Research paper

Physicochemical characterization of halloysite/alginate bionanocomposite hydrogel

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ABSTRACT

Bionanocomposite beads of halloysite/alginate have been recently studied as a medium for drug delivery and adsorption or absorption due to their biocompatibility, renewability and ease of preparation. However, there is no dedicated work on extensive characterization of this bionanocomposite material to provide further understanding on the material properties. In this work, the mechanical, chemical, and mass transfer properties of halloysite/alginate bionanocomposite are investigated. The incorporation of halloysite nanotubes has no effect on the size and on the shape of the alginate beads. Fourier transform infrared spectroscopy (FTIR) spectra show no chemical interaction between the halloysite nanotubes and the alginate polymers. Energy dispersive X-ray analyzer (EDX) shows that the halloysite nanotubes are embedded within the layers of Ca-alginate hydrogel networks but they are not present in the pores between the matrices. This finding is confirmed by the field emission scanning electron microscopy (FESEM) images which further show that the halloysite nanotubes are well dispersed within the alginate matrix. The Young's modulus of the halloysite/alginate bionanocomposite beads, determined using uniaxial compression test and Hertz's model, increased by 35% at 100 g/L halloysite nanotube loading compared to that of blank alginate beads. Despite this, the elastic limit of the beads with halloysite nanotubes is only slightly lower than the blank beads. Moreover, the diffusion coefficient of glucose molecules into the halloysite/alginate bionanocomposite beads is in the same order of magnitude with that of the blank alginate beads. The enhanced mechanical properties without severely compromising other physicochemical properties make halloysite/alginate bionanocomposite a more promising material for a variety of applications including bioprocessing and tissue engineering.

1. Introduction

Bionanocomposite, inspired by shells of marine animals in the natural world is currently attracting a great deal of interest due to its potential applications ranging from materials science, life science and nanotechnology (Darder et al., 2007). Taking advantage of the synergistic interaction between the biopolymer matrix and an inorganic nanofiller, bionanocomposite has shown remarkable physicochemical properties by exhibiting improved mechanical properties, thermal stability and swelling behavior.

Alginate, a linear polysaccharide with homopolymeric blocks of (1,4)-linked β-D-mannuronate and α-L-guluronate, is mainly extracted from brown seaweed. Alginate is one of the most commonly used biopolymers that are widely researched as encapsulant for applications in drug delivery, bioprocessing, adsorption and tissue engineering. The extensive use of alginate is derived from its ability to form hydrogel beads via the ionic interaction with divalent cations such as Ca^{2+} and Ba^{2+} at room temperature. Besides the mild fabrication condition, the beads formed are highly permeable to solute transfer, thus rendering them popular for applications involving cell (or enzyme) biocatalysis or adsorption of pollutants. Despite these advantages, alginate hydrogel beads typically contain over 95% water and they are soft. Therefore, they may fail prematurely when subjected to compression force during processing or application (Tal et al., 1997; Leung et al., 1998).

Halloysite (Hal) nanotube, a natural tubular nanomaterial with a chemical composition of $Al_2Si_2O_5(OH)_4 \cdot nH_2O$, consist of a tetrahedral (Si – O) sheet forming the outside and an octahedral (Al – OH) inside with a void or lumen at the center (Churchman et al., 1995). Hal nanotubes have been extensively studied in the recent years due to its attractive characteristics such as naturally abundant, light, mechanically strong, non-toxic, and inexpensive. As recently reviewed by Liu et al.

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(2014), these properties promote the potential use of Hal nanotubes as a nanofiller for polymer, encapsulating agent for drugs or biomaterials, and adsorbent.

Recently, the Hal nanotubes have been incorporated into alginate hydrogel beads to remove dye and heavy metals in wastewater (Liu et al., 2012a; Cavallaro et al., 2013), as well as for controlled-release of drugs (Fan et al., 2013; Tu et al., 2013). These works mainly focused on the respective application without comprehensively characterizing the intrinsic material properties such as the Young's modulus, the elastic limit, and the diffusivity. Insights from characterization results are useful to provide in-depth explanation or interpretation for the observed phenomena in targeted application. For example, Hal/alginate bionanocomposite beads showed better reusability compared to blank alginate beads as reported by Liu et al. (2012a). This could be related to the enhanced mechanical properties and/or chemical stability of the Hal/alginate bionanocomposite beads which had not been quantified before. Hence, there is a need to characterize the Hal/alginate bionanocomposite to establish a correlation between the structure and component composition with their physicochemical properties.

Although nanocomposites with practically all the polymer matrices have been reported with varying degrees of enhancement in properties, some properties compromised by the filler such as diffusivity and elasticity are sometimes overlooked. A detailed characterization is required to determine the relationship between these properties and thus, to optimize them. For example, the alginate–carbon nanotube nanocomposite showed 25% improvement of deformation resistance when subjected to 80 g load but no significant differences in the amount of saline absorption compared to the blank alginate (Kawaguchi et al., 2006). These properties promote the use of alginate–carbon nanotube nanocomposite as drug carrier (Zhang et al., 2010) and scaffold (Kawaguchi et al., 2006). Another study by De Silva et al. (2013) demonstrated that the incorporation of 5 mass/volume (m/v)% of Hal nanotubes into chitosan increased the Young's modulus to 0.52 GPa compared from 0.46 GPa for chitosan alone. However, there is no further improvement with the increment of Hal nanotube concentration up to 10 m/v% and 15 m/v%. On the other hand, Hal/chitosan was cytocompatible even at 10% by mass of Hal nanotube loading (Liu et al., 2012b). These results suggested that Hal/chitosan nanocomposite exhibited great potential for applications in tissue engineering which demonstrated by Liu et al. (2013) later.

To the best of our knowledge, no comprehensive study has been reported on the physicochemical properties of Hal/alginate bionanocomposite beads. To better ascertain the application potential of this material, this study aims at analyzing the key properties of Hal/alginate bionanocomposite bead, i.e. (a) the quality of dispersion of Hal nanotubes in the alginate matrix, (b) the nature of interactions of the Hal nanotubes with the alginate polymer chains, (c) the deformation behavior of Hal/alginate bionanocomposite beads, (d) a protocol to characterize mechanical properties of the composite hydrogel material, and (e) the mass transfer properties.

2. Materials and methods

2.1. Materials

Sodium alginate (Manugel GHB, FMC Biopolymer, UK) with a medium range molecular mass of 37% β-D-mannuronic acid residues (M) and 63% α-L-guluronic acid residues (G) was used in this study because alginate richer in G residues was known to give higher elastic moduli. The Hal nanotubes were supplied by Imerys Tableware, New Zealand. The mineralogical compositions of the Hal nanotubes are 11% of quartz and 1% of feldspar by mass (Pasbakhsh et al., 2013). The specifications of Hal nanotubes are listed in Table 1. Calcium chloride dihydrate and sodium chloride (analytical grade) were purchased from Fisher Scientific, UK. D-(+)-Glucose acquired from Sigma was used as diffuse solute for mass transfer study. All chemicals used in this study were of analytical grade and were used as received.

Table 1
Specifications of Matauri Bay Hal nanotubes (Pasbakhsh et al., 2013).

Length (nm)	100–3000
Inner diameter (nm)	15–70
Outer diameter (nm)	50–200
Wall thickness (nm)	20–100
Aspect ratio	12

2.2. Fabrication of Hal/alginate bionanocomposite beads

The Hal nanotubes were dispersed in 100 mL of distilled water using a magnetic stirrer for 10 min. Subsequently, the dispersion was subjected to ultrasonication (Qsonica Ultrasonic Liquid Processor model no. Q700, USA) for 1 min of continuous sonication with 15 s pause interval for a duration up to 5 min. The sonication was carried out in an ice bath to prevent overheating of the sample. Two grams of alginate powder were subsequently added to the dispersion.

The size measurement of Hal nanotubes was normally carried out by optical microscopy (Luo et al., 2010; Pasbakhsh et al., 2013). However, manual measurement of large number of particles to obtain statistically representative result is troublesome and time consuming. In this study, the dispersion uniformity of Hal nanotubes in alginate solution was studied by measuring the relative size of Hal nanotubes at three different locations of the solution (i.e. top, middle, bottom) using the Malvern Zetasizer Nano ZS. The solution was continually stirred with a magnetic stirrer at 250 rpm during sample collection to mimic the process of bead fabrication to ensure the homogeneity of the solution obtained represented the homogeneity of the bionanocomposite bead. Although the Hal nanotubes are tubular in shape and the zetasizer only produces the radii of the equivalent spheres, the results are used as an indication of the relative size distribution between the samples and they do not represent the real dimensions of the Hal nanotubes.

The 100 mL Hal/alginate solution was sealed with parafilm and aluminum foil and left overnight for debubbling. The solution was then stirred gently at 250 rpm and extruded through a hypodermic needle tip (0.81 mm internal diameter), dripping into a gently stirred calcium chloride (20 g/L) bath for gelation. The beads were cured for 1 h before being triply rinsed with distilled water to remove excess calcium ions. Beads produced were tested in the same day. Identical procedures were used to prepare Hal/alginate bionanocomposite beads with 1 g/L, 10 g/L and 100 g/L of Hal nanotubes.

2.3. Characterization

2.3.1. Thermogravimetric analysis

Samples of blank alginate and Hal/alginate bionanocomposite beads were freeze-dried before undergoing thermogravimetric analysis (TGA). The Hal nanotubes were used as supplied. The TGA Q50 determined the thermal decomposition of the Hal/alginate bionanocomposite beads by heating the samples from 100 °C to 900 °C at a rate of 10 °C/min under nitrogen atmosphere.

2.3.2. Fourier transform infrared spectroscopy (FTIR) analysis

FTIR was performed to determine the chemical interaction between the alginate and Hal nanotubes using a FTIR spectrometer (Nicolet iS10, Thermo Scientific). The obtained spectrum was an average of 16 scans from 525 to 4000 cm^{-1} at a resolution of 4 cm^{-1}. Spectra were registered as the reflection attenuated total reflectance spectra.