



Research paper

Halloysite-carboxymethyl cellulose cryogel composite from natural sources

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ABSTRACT

In this work, novel superporous composite cryogel using natural source such as carboxymethyl cellulose (CMC) and halloysite nanotubes (Hal nanotubes) was prepared. The composite was prepared via cryogelation method including the Hal nanotubes within polymeric matrices before cryogelation. A series of the Hal nanotubes/carboxymethyl cellulose composite were prepared by varying the used amounts of crosslinker, and Hal nanotubes amounts. Additionally, Hal nanotubes were modified with different modifying agent such as (3-aminopropyl)triethoxysilane (APTES), (3-chloro-2-hydroxypropyl)trimethylammonium chloride (CHPTACI), polyethylenimine (PEI), epichlorohydrin (ECH), diethylenetriamine (DETA), taurine (TA), and tris(2-aminoethyl)amine (TAEA), these modified Hal nanotubes were used in CMC cryogel composite preparation. Characterization of the synthesized materials was performed by Scanning and Transmission Electron Microscopy (SEM and TEM), Zeta Potential (ZP) measurement, Thermogravimetric Analysis (TGA), Fourier Transform Infrared (FT-IR) spectroscopic measurement and Surface area and Porosity Analyzer.

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1. Introduction

Carboxymethyl cellulose (CMC) is known as a plant based “green” and inexpensive natural polymer consisting of glycopyranose units with non-toxic, biocompatible, and biodegradable nature (El-Newehy et al., 2016). As water soluble polysaccharide CMC possesses both carboxylate and hydroxyl groups. The wide range use of these polysaccharides come from their origin e.g., renewable resources obtained from nature and have habitually more economic, and offers great advantages over synthetic polymers (Liu et al., 2009; Barkhordari and Yadollahi, 2016) in applications such as textile, food, cosmetics, chemical, and pharmaceutical industries (Song et al., 2009; Butun et al., 2011).

Nano sized tubular Halloysites, usually called as Halloysite nanotubes (Hal nanotubes) similar to carbon tube but with a two-layered (1:1, Al:Si) naturally occurring aluminosilicate mineral has attracted considerable interest over the past decade in various fields (Shchukin et al., 2005; Li et al., 2008; Yuan et al., 2015). Hal nanotube formed by kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) scrolling and generally has the formulas as $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$. Anhydrous form is $n = 0$, hydrated form is n value equal 2, and 4 that change with the Hal nanotube's cation exchange capacity. Hal nanotube has positive charge in the inner lumen

and negative charge at outer surface having Al-OH group located at the inner lumen and siloxane group, Si-O-Si at the outer surface. Additionally, there are —OH group at the edges, and a few Si—OH groups become defects at the outer side (Yuan et al., 2008; Zieba et al., 2014; Bhagabati et al., 2015). The lumen diameter of the 1-D channels of Hal nanotube is smaller than 100 nm that can allow for the entrapment and subsequent controlled release of guest molecules. Hal nanotube having submicron hollow tubular structure possess reactive groups and large surface/volume ratio are widely used in the area electronics, catalysis, biological and functional materials (Barrientos-Ramirez et al., 2011; Rawtani and Agrawal, 2012; Liu et al., 2014; Peng et al., 2015; Sahiner and Sengel, 2017). Compared with carbon nanotubes, natural Hal nanotubes are naturally occurring matters and are cheaper and environmentally benign. In the literature, Hal nanotubes can even be reported to load and release behaviors for various pharmaceuticals (Massaro et al., 2016). Even though the biocompatibility of Hal nanotubes was confirmed, their medical use might be restricted due to the non-biodegradability of the aluminosilicate (Lvov et al., 2008).

Cryogels are novel polymeric materials prepared via cryopolymerization of gel forming polymers and monomers under freezing conditions. The interesting properties of cryogels such as higher elasticity, flexibility, and high mechanical stability, high porosity (10–100 μm) with sponge-like porous interconnected microstructures (Vi et al., 2003; Shan et al., 2016) make them favorite material as

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multipurpose use for many biomedical applications. Cryogels are widely used as chromatographic materials, tissue engineering scaffolds, and high performance materials. In some applications such as separation of biomolecules can be accomplished very efficiently because of large, tunable and interconnected pore sizes. The adaptability of cryogels with different materials, clays, polymeric particles and with chemical modification with different active agent by embedding or post modification provide increase contact/retention time in bio-separation (cryogel-DNA e.g.) process and augment their application areas (Erturk and Mattiasson, 2014). These types of composites formed by Hal nanotube modified by different functional groups with super porous cryogel prepared from natural sources can be use in various field ranging from environmental to biomedical sciences because of their synergistic effect with biocompatibility and nonhazardous nature. The external surface of Hal nanotube is normally negatively charged, and the charge of the internal surface is pH-dependent. Having both charge in same material provide an opportunity for the interaction/loading/releasing different charged materials such as drugs, bioactive components, bio-macromolecules, antimicrobial agents, growth factors etc. Hal nanotubes have high adsorption capacity because of their high surface area and interesting chemical composition. To render enhance application performance, Hal nanotubes can be incorporated with polymeric materials to prepare composite materials that possesses the properties of each of the components. However, because of organic and inorganic natures of polymeric materials and the Hal nanotubes, respectively, the homogenous distribution of Hal nanotubes within the polymeric matrices cannot be accomplished. To circumvent these problems, the chemical modifications of Hal nanotube are required. Therefore, modified Hal nanotubes with different functional groups on the surfaces can be readily done by employing different chemical modifying agent. This allows the preparation of versatile Hal nanotubes that are homogeneously distributed within polymeric systems as filler. Then the obtained composite system with the little amounts modified inorganic filler such as Hal nanotubes exhibit very effective result about mechanical and physiochemical properties with some additional capabilities.

The aim of this study was to prepare super porous composite cryogel using natural sources, CMC and Hal nanotube. The composite was synthesized via cryogelation method by including the Hal nanotube within polymeric matrices before cryogelation. A series of the Hal nanotube/CMC composite were prepared by varying the used amounts of cross-linker, and Hal nanotube. Additionally, surface modification of Hal nanotube was carried out by using various modifying agents such as (3-aminopropyl)triethoxysilane (APTES), polyethyleneimine (PEI), tris(2-aminoethyl)amine (TAEA), (3-chloro-2-hydroxypropyl)trimethylammonium chloride (CHPTACI), epichlorohydrin (ECH), diethylenetriamine (DETA), and taurine (TA) that were used in cryogel-Hal nanotube composite preparation. All the synthesized materials were characterized by Electron Microscopy (SEM and TEM), Zeta Potential (ZP) measurement, Thermogravimetric Analysis (TGA), Fourier Transform Infrared (FT-IR) spectroscopy and Surface area and Porosity Analysis using BET and BJH methods.

2. Materials and methods

2.1. Materials

Carboxymethyl cellulose sodium (CMC, M_w : 250,000 g mol⁻¹, Degree of Substitution 1.2, Aldrich), Halloysite nanoclay (Hal nanotube, Al₂Si₂O₅(OH)₄·2H₂O, 30–70 nm inner diameter, 1–3 μm length, 8.0 meq/g cation exchange capacity, Aldrich), divinylsulfone (DVS, >98%, Merck), and the modifying agents that were used are (3-aminopropyl)triethoxysilane (APTES, 98%, Sigma-Aldrich), polyethyleneimine (PEI, 50% solution in water, Mn:18,000, Sigma-Aldrich), 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTACI, 65%, Sigma), epichlorohydrin (ECH, 99%, Sigma-Aldrich), glutaraldehyde (GA, 50%, Aldrich), tris(2-aminoethyl)amine (TAEA, 96%,

Aldrich), diethylenetriamine (DETA, 99%, Sigma-Aldrich), and taurine (TA, 99%, Sigma-Aldrich). Sodium hydroxide (NaOH, 98%, Sigma-Aldrich), ethanol (99.8%, Sigma-Aldrich), methanol (99.8%, Sigma Aldrich) and DMF (99%, Merck) were used. Double Distilled water (DW, GFL 2108) was used throughout the experiments.

2.2. Modification of Hal nanotube

Before modification, Hal nanotube was cleaned according to the following procedure: 0.1 g/mL Hal nanotube was dispersed in water-ethanol mixture (50:50, v:v) by stirring about 24 h. Then, the mixture was centrifuged at 10,000 rpm, 10 min at 20 °C. Centrifugation was carried out three times by the removal supernatant by decantation and dispersing Hal nanotubes again in ethanol-water (50:50, v:v) mixture. After the cleaning procedure, Hal nanotubes were dried in freeze dryer (Christ Alpha 2–4 LSC) overnight and stored closed vial for chemical modification.

2.2.1. Modification of Hal nanotube with APTES

APTES was grafted on Hal nanotube by a chemical method. For this purpose, 1.0 g cleaned Hal nanotube was dispersed in 100 mL ethanol stirring at 500 rpm in a polypropylene flask, and 5.0 mL APTES mixed 5.0 mL water in different flask. After 15 min, APTES solution was added dropwise in Hal nanotube containing flask, and stirred for 24 h. After that time, Hal nanotube was centrifuged at 10,000 rpm for 10 min at 20 °C, then the supernatant was removed by decantation and dispersed in ethanol:water (50:50, v:v), and re-centrifugation and washing at least five times. The product was dried in freeze dryer overnight, and stored in a closed vial for characterization and cryogel composite preparation. The product denoted as APTES-Hal nanotube.

2.2.2. Modification of Hal nanotube with PEI and TAEA

Hal nanotube modification with PEI was realized by two methods: physical and chemical modification. The coating of Hal nanotube with PEI (e-PEI-Hal nanotube) was carried out by physical impregnation method as reported in literature (Chanda and Rempel, 1995; Ghouli et al., 2003; Chaikittisilp et al., 2011; Tian et al., 2015; Kim et al., 2016). Briefly, the coating solution was 100 mL 2.0 wt% of the PEI in methanol, and stirred with 1.0 g Hal nanotube for 24 h.

The chemical modification of Hal nanotube with PEI (PEI-Hal nanotube) was done according to the following routes little modification (Ghouli et al., 2003; Tian et al., 2015). In brief, 1.0 g APTES-Hal nanotube powder was immersed in 100 mL methanol solution containing 1.0 mL PEI for 24 h under 800 rpm stirring rate. After that time, the suspension was immediately transferred into 200 mL 0.5% (w/v) glutaraldehyde (GA) solution for 30 min under vigorous stirring. Then, the product washed with DW several times until the dispersion became clear. After last cleaning with water:methanol (50:50 v:v), the modified Hal nanotube centrifuged and dried in freeze dryer.

Modification of Hal nanotube with TAEA is similar to the PEI-Hal nanotube modification procedure. For this purpose, 1.0 g APTES-Hal nanotube powder was immersed in 100 mL 1.0% (w/v) TAEA in methanol solution at a stirring speed of 800 rpm for 24 h. After that time, the dispersion was immediately transferred into 200 mL 0.5% (w/v) GA solution for 30 min under vigorous stirring. Then, the product was washed with DW several times until the dispersion became clear. After last cleaning, the modified Hal nanotube centrifuged and dried in freeze dryer.

2.2.3. Modification of Hal nanotube with CHPTACI

For the modification of Hal nanotube with CHPTACI, the previous reported method was employed (Butun et al., 2011). For this goal, two modification mixtures were prepared. One is 0.2 M, 50 mL NaOH solution containing 0.5 g cleaned Hal nanotube that is stirred at 500 rpm at ambient temperature for 2 h. The second mixture, 1.0 mL of CHPTACI aqueous solution (65 wt%) was added into the 0.2 M 30 mL NaOH

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