Applied Clay Science 150 (2017) 138–146

Contents lists available at ScienceDirect

Applied Clay Science

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

Research paper

# Functionalization of halloysite nanotubes for the preparation of carboxymethyl cellulose-based nanocomposite films

Long-Feng Wang[a], Jong-Whan Rhim[b,*]

[a] College of Food Science, Heilongjiang Bayi Agricultural University, Daqing 163319, People's Republic of China
[b] Center for Humanities and Sciences, Department of Food and Nutrition, Kyung Hee University, 26 Kyungheedae-ro, Dongdaemun-gu, Seoul 02447, Republic of Korea

A R T I C L E I N F O

*Keywords:*
Halloysite
Functionalization
Metal ions
CMC
Nanocomposite films

A B S T R A C T

Halloysite nanotubes (Hal) were treated with acid to prepare uniformly charged acid treated Hal (Hal-A). After acid treatment, the surface charge (zeta potential) of Hal changed from +0.08 mV to −32.65 mV. Functionalized Hal-A were prepared through adsorbing metal ions by immersing the Hal-A into saturated solutions of three different metal salts, silver nitrate, zinc nitrate, and copper acetate. The number of metal ions attached to the Hal-A and their functionality were dependent on the type of metal ions. The functionalized Hal-A exhibited strong antimicrobial activity against food-borne pathogenic bacteria, *L. monocytogenes* and *E. coli*. The CMC-based film showed a significant increase in mechanical, water vapor barrier, and thermal stability properties after forming a composite with Hal. In particular, CMC-based films incorporated with the functionalized Hal-A showed strong antimicrobial activity against both L. *monocytogenes* and *E. coli*.

## 1. Introduction

Biopolymers derived from animal and plant resources have been regarded as an alternative to the non-biodegradable petroleum-based plastics (Rhim et al., 2013). As one of such biopolymers, carboxymethyl cellulose (CMC) has attracted great interests for the preparation of environmentally-friendly packaging materials since it is biodegradable, biocompatible, and abundantly available with good film forming property (Oun and Rhim, 2016). CMC, one of the most common derivatives of cellulose, is an anionic, linear, water-soluble polymer (Dashipour et al., 2015). CMC has been used in the food processing and cosmetics industries as a thickener, edible film and coating agents, emulsion stabilizer, and a carrier of functional materials (Kono, 2014; Oun and Rhim, 2015). Though CMC has been widely used for the preparation of biodegradable packaging films, the application of CMC-based films is limited owing to their hydrophilic nature and rather inferior mechanical properties (Yadollahi et al., 2014). To solve such problems, the CMC-based films have been reinforced with nano-sized fillers such as nanoclays (Shin et al., 2014; Ebrahimzadeh et al., 2016), nanometals (Kanmani and Rhim, 2014), and cellulose nanocrystals (Oun and Rhim, 2016). In particular, when nano metal or metallic oxides such as Ag, ZnO, and CuO were incorporated into biopolymers, they exhibited additional functional properties such as antimicrobial and UV-light absorption properties (Shankar and Rhim, 2016).

Recently, halloysite nanotubes (Hal) have attracted great attention as a reinforcing nanofiller for the preparation of nanocomposite materials due to their large surface area, high surface reactivity, high mechanical strength with a relatively low cost (Liu et al., 2014; Yuan et al., 2015; Zhang et al., 2016). The Hal, belonging to the kaolin group of minerals, are morphologically similar with multiwalled carbon nanotubes. It is a kind of layered alumino-silicate with a molecular formula of $Al_2Si_2O_5(OH)_4{\cdot}nH_2O$ (Joussein et al., 2005). It is one-dimensional nanoparticle with hollow tubular structure with an inner diameter of 10–30 nm and an outer diameter of 50–70 nm, and the length varies in the range of 0.5–1.5 μm. In particular, the structure of inner and outer surface with positively and negatively charged Hal makes it a potential ideal carrier for loading and sustained release of functional compounds (Ward et al., 2012; Lvov et al., 2016). The Hal has been incorporated into various polymers such as poly(butylene succinate) (PBS) (Wu et al., 2014), poly(ε-caprolactone) (PCL) (Bhagabati et al., 2015), polyethylene (PE) (Qiao et al., 2017), poly(vinyl alcohol) (PVA) (Gaaz et al., 2015), and chitosan (Liu et al., 2012), and they showed significant increase in the toughness, mechanical strength, and thermal stability. However, to take full advantage of the Hal in the preparation of nanocomposite, dispersion of the Hal and stress transfer must be optimized; otherwise, poor load transfer between the Hal and polymer matrix may cause interfacial slippage to decrease in the mechanical strength of the composites (Liu et al., 2014). Therefore, functionalization of Hal is required for processing and enhancing the properties of the nanocomposites. Abdullayev et al. (2012) proposed a method for

* Corresponding author.
*E-mail address:* jwrhim@khu.ac.kr (J.-W. Rhim).

http://dx.doi.org/10.1016/j.clay.2017.09.023
Received 17 May 2017; Received in revised form 18 September 2017; Accepted 19 September 2017

surface modification of Hal through a selective etching of the Hal by dissolution of aluminum oxide using acid solution. Once the surface reactivity changed by the acid treatment of the Hal, it is expected to introduce functional materials like metal ions to produce functionalized Hal.

The antimicrobial action of the metal ions has been provided in the literature. Silver ions probably cause shrinking the cytoplasmic membrane of the target microorganism and separation from the cell wall, and then releasing the cellular content and degrading bacterial cell wall, resulting in the inhibition of the bacterial growth (Jung et al., 2008). Zinc ions above certain threshold concentration allows the entry of $Zn^{2+}$ inside the cell to perturb cell homeostasis and being cytotoxic to prokaryotes (Pasquet et al., 2014). Moreover, copper ions were found to enter into the cells leading to changes in ion concentrations and leakage of DNA, RNA, and protein to destroy bacteria (Cai et al., 2015).

Therefore, the main objectives of the present work were to prepare the functionalized Hal through acid treatment of Hal and incorporation of silver, zinc and copper ions. The effect of functionalized Hal on the mechanical, antimicrobial, and other properties of CMC-based nanocomposite films were also evaluated.

## 2. Materials and methods

### 2.1. Materials

Sodium carboxymethyl cellulose (CMC) and halloysite nanoclay were obtained from Sigma-Aldrich (St. Louis, MO, USA). The halloysite nanoclay was in the form of nanotubes with a diameter of 30–70 nm, the length of 1–3 μm with the surface area of 64 $m^2$/g. The halloysite (molecular weight of 258.16 g) contains 20.9% aluminum, 21.1% silica, 1.6% hydrogen, and 55.4% oxygen. Silver nitrate ($AgNO_3$), glycerol and sulfuric acid were purchased from Daejung Chemicals & Materials Co., Ltd. (Siheung, Gyeonggi-do, Korea). Zinc nitrate hexahydrate, copper acetate monohydrate, tryptic soy broth (TSB), brain heart infusion broth (BHI), and agar powder were obtained from Duksan Pure Chemicals Co., Ltd. (Ansan, Gyeonggi-do, Korea). Food-borne pathogenic bacteria, *Listeria monocytogenes* ATCC 15313 and *Escherichia coli* O157: H7 ATCC 43895, were obtained from the Korean Collection for Type Culture (KCTC, Seoul, Korea). Both of these strains were grown in TSA and BHI agar medium and stored at 4 °C for further test.

### 2.2. Functionalization of halloysite

The halloysite nanoclay was used without further purification and the pH value of original halloysite suspension was in the range of 6–7. For the acid treatment, 1 g of halloysite was dispersed into 100 mL of 0.5 M sulfuric acid and stirred continuously using a magnetic stirrer at 60 °C for 5 h. The acid-treated halloysite suspension was washed with deionized water for five times until becoming neutral. The acid-treated halloysite was collected by centrifugation and dried in an oven at 40 °C, and then powdered using a mortar to obtain a white powder, which was assigned as the acid-treated halloysite nanotube (Hal-A).

For the functionalization, the Hal-A was dispersed into saturated solutions of metallic salts, $AgNO_3$, $Zn(NO_3)_2$, and $Cu(COOCH_3)_2$, respectively, for 1 h with stirring. The suspension of Hal-A in the metallic salt solution was filtered and washed with excessive deionized water for three times and dried to obtain the metal ion adsorbed functionalized Hal-A, which were assigned as Hal-$A^{Ag}$, Hal-$A^{Zn}$, and Hal-$A^{Cu}$ depending on the types of metal salt.

### 2.3. Preparation of CMC/Hal nanocomposite films

CMC/Hal nanocomposite films were prepared using a solution casting method (Oun and Rhim, 2016). 3 g of CMC was dissolved in 150 mL of distilled water under vigorous stirring with heating on a hot plate at 90 °C for 30 min, and 0.9 g of glycerol (30 wt% of CMC) was added as a plasticizer. Then 0.06 g (2 wt% based on CMC) of Hal (Hal, Hal-A, Hal-$A^{Ag}$, Hal-$A^{Zn}$, and Hal-$A^{Cu}$) were mixed into the above solution with vigorous stirring, and sonicated for 15 min using an ultrasonic bath (FS 149H, Ultrasonic Cleaner, Fisher Scientific, Pittsburg, PA, USA). The film forming solution was cast onto a levelled Teflon film (Cole-Parmer Instrument Co., Chicago, IL, USA) coated glass plate (24 cm × 30 cm) and dried at room temperature (23 ± 2 °C) for 48 h. The dried films were peeled off from the casting plates and conditioned in a humidity chamber controlled at 25 °C and 50% RH for two days before further analysis. For comparison, neat CMC films were also prepared by the same procedure without the addition of Hal.

### 2.4. Characterization

The morphological properties of Hal were evaluated using a transmission electron microscopy (TEM, JEM-F200, JEOL USA, Inc.) at 120 kV. The microstructure of the nanocomposite films was observed using field emission scanning electron microscopy (FE-SEM, S-4800, Hitachi Co., Ltd., Matsuda, Japan) operated at an acceleration voltage of 10 kV and current of 10 μA after coating the samples with platinum (Pt) using a vacuum sputter coater.

Zeta potential of Hal was measured using a Zetasizer (Zetasizer Nano ZS, Malvern Instruments Ltd., Malvern, UK) using a disposable capillary cell (DTS1070) and deionized water as a dispersant. Before each measurement, the operating conditions were calibrated using a standard latex dispersion (zeta potential: −50 ± 5 mV) supplied by the manufacturer.

The concentration of metal ions adsorbed to the Hal-A was determined using an ICP-MS (Nexion 300X ICP-MS, Perkin Elmer, Waltham, MA, USA). The sample transport system utilized a baffled cyclonic spray chamber equipped with a Meinhard nebulizer. Ag, Zn and Cu ions were determined by quantifying isotopes of $Ag^{109}$, $Zn^{66}$, $Cu^{63}$ using $In^{115}$ as an internal standard. Each sample measurement was the average of three replicate readings (20 sweeps each). The samples were prepared by treating the functionalized Hal-A with 50 mL of 1 M nitric acid solution. The suspension was kept in a water bath sonicator for 30 min and then filtered through Whatman No. 541 filter paper. The filtrates were diluted to 10–400 folds with 1 M Optima $HNO_3$ solution so that concentrations would fall within the prepared multi-point calibration curve.

X-ray diffraction (XRD) patterns of Hal, Hal-A and functionalized Hal-A were analyzed using an XRD diffractometer (PANalytical Xpert pro MRD diffractometer, Amsterdam, Netherlands) operated at 40 kV and 30 mA, equipped with Cu Kα radiation at a wavelength of 1.54056 Å and a nickel monochromator filtering wave. The samples were scanned over the range of 2θ = 5–80° with a scanning rate of 0.4°/min at room temperature.

The FTIR spectra of Hal and CMC/Hal nanocomposite films were obtained using an attenuated total reflectance (ATR) model in a FTIR spectrophotometer (TENSOR 37 spectrophotometer with OPUS 6.0 software, Billerica, MA, USA). Sixteen consecutive scans were taken, and their average was stored. Spectra were recorded from 4000 to 400 $cm^{-1}$ with the resolution of 2 $cm^{-1}$.

### 2.5. Light transmittance of film

Light transmittance spectra of CMC/Hal nanocomposite films were collected using a UV/vis spectrophotometer (Optizen POP UV/Vis Series, Mecasys Co., Ltd., Seoul, Korea) in the wavelength of 200–700 nm.

### 2.6. Mechanical properties

Preconditioned film samples were cut into rectangular strips (2.54 cm × 15 cm) using a precision double blade cutter (model LB.02/A, Metrotec, S.A., San Sebastian, Spain). The thickness of each specimen