



Effect of isolation methods of chitin nanocrystals on the properties of chitin-silver hybrid nanoparticles

Ahmed A. Oun^a, Jong-Whan Rhim^{b,*}

^a Food Engineering and Packaging Department, Food Technology Research Institute, Agricultural Research Center, Giza, Egypt

^b Center for Humanities and Sciences, Bionanocomposite Research Center, Department of Food and Nutrition, Kyung Hee University, 26 Kyungheedaero, Dongdaemun-gu, Seoul 02447, Republic of Korea

ARTICLE INFO

Keywords:

Chitin nanocrystal
Acid hydrolysis
TEMPO-oxidation
Ammonium persulfate
Silver nanoparticle
Hybrid nanomaterials

ABSTRACT

Chitin nanocrystal (ChNC) was isolated using sulfuric acid hydrolysis (ChNC^{H2SO4}), TEMPO-oxidation (ChNC^{TEMPO}), and ammonium persulfate (ChNC^{APS}) methods, and used for the preparation of hybrid nanoparticles of ChNC/silver nanoparticles (AgNP). The ChNC exhibited a needle-shaped structure with a sulfate group content of 135 μmol/g for ChNC^{H2SO4} and carboxyl content of 0.71 and 1.42 mmol/g for ChNC^{TEMPO} and ChNC^{APS}, respectively. ChNC worked as a reducing and stabilizing agent for the production of AgNP and reduced the size of AgNP from 23.9 nm to 6.3 nm in the ChNC/AgNP hybrid. The carboxyl content of ChNC played a significant role for the nucleation, size distribution, and antibacterial activity of ChNC/AgNP. ChNC/AgNP hybrid, especially ChNC^{APS}/AgNP, exhibited strong antibacterial activity against food-borne pathogenic Gram-negative (*E. coli*) and Gram-positive (*L. monocytogenes*) bacteria. The prepared ChNC/AgNP hybrid nanomaterials have a high potential for the application to be used as a nanofiller to improve the properties of food packaging materials to extend the shelf-life of packaged food.

1. Introduction

Nanocomposites with improved properties have attracted various industries with a vast number of potential applications such as electronics, cosmetics, paints, medical devices, catalysts, antimicrobial fabrics, water treatment membranes, and food packaging (Jo, Choi, Lee, & Hong, 2012; Rhim, Park, & Ha, 2013). The properties of nanocomposites are strongly dependent upon the type of nano-fillers, their size, and shape, as well as their interfacial characteristics (Xu et al., 2013). Homogeneous dispersion of nano-fillers in polymer matrices is a key factor affecting the functional properties of the polymer nanocomposites. Metallic nanoparticles, such as silver, zinc oxide, copper, and titanium dioxide nanoparticles, are most widely used nanomaterials for the preparation of multifunctional nanocomposites due to their large surface area, high specificity, unique optical, and functional properties (Gong et al., 2007). Silver nanoparticles (AgNP) are reported to have good chemical stability and effective antimicrobial property against different bacteria (Shankar & Rhim, 2015; Xiu, Zhang, Puppala, Colvin, & Alvarez, 2012). Metal nanoparticles including AgNP may aggregate, undermining their unique property and applicability. One strategy to prevent aggregation of AgNP is to produce them in the presence of nanomaterials, so that the produced AgNP is deposited onto

the nanomaterials, which function as carriers/dispersants to the AgNP. The hybrid materials obtained from metallic or bimetallic nanoparticles with organic nanomaterials showed novel physicochemical properties compared with their individual counterpart to improve the properties of composite films (Darroudi, Ahmad, Shamel, Abdullah, & Ibrahim, 2009; Elayaraja, Zagorsek, Li, & Xiang, 2017; Solairaj, Rameshthangam, & Arunachalam, 2017; Thatoi et al., 2016). Among organic nanomaterials, chitin nanocrystal (ChNC) composited with AgNP has recently generated extensive interest due to the novel properties of the hybrid (Solairaj & Rameshthangam, 2017). ChNC/AgNP hybrid nanomaterials have been widely used as multifunctional materials for biomedical applications. For example, hybrid ChNC/AgNP exhibited potent antimicrobial activity against *E. coli*, *P. aeruginosa*, and influenza A virus with a potential application for anti-infectious wound dressings (Nguyen et al., 2014) and scaffolds applications (Madhumathi et al., 2010; Tang et al., 2013), and the ChNC/AgNP hybrid nanomaterials showed anticancer activity against human breast cancer cell (Solairaj et al., 2017). However, a very few reports are available on the application of ChNC/AgNP hybrid nanomaterials as a reinforcing agent for the preparation of food packaging films (Oun & Rhim, 2017b). The morphology and antimicrobial properties of ChNC/AgNP hybrid nanomaterials are known to be greatly influenced by the surface structure

* Corresponding author.

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

of chitin as well as the size and concentration of AgNP (Nguyen et al., 2013). Though the influence of carboxyl charge density of TEMPO-oxidized nanocellulose (Hoeng, Denneulin, Neuman, & Bras, 2015; Uddin et al., 2014), and the role of sulfate groups of nanocellulose on the size and nucleation of AgNP of nanocellulose/AgNP hybrid nanomaterials have been investigated (Uddin et al., 2014), to the best of our knowledge, no research works have been published about the influence of isolation methods of chitin on the morphology and antimicrobial properties of ChNC/AgNP hybrid nanomaterials.

Therefore, the objective of the present study was to investigate the effect of ChNC prepared with three different methods, acid hydrolysis method (H₂SO₄), TEMPO-oxidation method (TEMPO), and ammonium persulfate method (APS), on the properties of ChNC/AgNP hybrid nanomaterials. The prepared ChNC/AgNP hybrid nanomaterials were characterized using various analytical techniques and their antibacterial activity was determined.

2. Materials and methods

2.1. Materials

Chitin (α -chitin, viscosity: 800–940 cPs in 0.5% ascorbic acid at 20 °C; degree of deacetylation: 6.4%; ash < 5%; particle size: 3 mm) obtained from crab shell was procured from YB Bio Co., Ltd. (Youngduk, Kyungbuk, Korea) and used without any modification. Silver nitrate (AgNO₃) was obtained from Daejung Chemicals & Metals Co., Ltd. (Siheung, Gyeonggi-do, Korea). TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) and ammonium persulfate (APS, 98% + A.C.S. Reagent) were obtained from Sigma-Aldrich Co. (St. Louis, MO, USA). Sulfuric acid, brain heart infusion broth (BHI), tryptic soy broth (TSB), agar power were procured 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). The *L. monocytogenes* and *E. coli* were grown on BHI and TSB agar plates, respectively, and stored at 4 °C for further test.

2.2. Isolation of chitin nanocrystals

Chitin nanocrystals (ChNC) were isolated from α -chitin of crab shell using three different methods, i.e., acid hydrolysis, TEMPO-oxidation (TEMPO), and ammonium persulfate (APS) methods. Firstly, the acid hydrolysis of chitin was performed following the method of Oun and Rhim (2015b). For this, 5 g of chitin was added to 100 mL of 64% H₂SO₄ solution and heated at 60 °C for 90 min with vigorous agitation. The reaction was quenched by adding abundant distilled water and centrifuged and followed by repeated washing with distilled water, neutralization, and sonication to get a sulfonated-ChNC suspension. Secondly, TEMPO-oxidized ChNC were prepared using a TEMPO-oxidation method following the method of Ifuku, Hori, Izawa, Morimoto, and Saimoto (2015). Briefly, 10 g of chitin powder was added to 500 mL of distilled water with stirring, and 0.16 g of TEMPO and 1.0 g of sodium bromide were added to the suspension. Oxidation of chitin was started by adding NaClO (10 mmol/g chitin). Thirdly, oxidized-ChNC were prepared using an APS method (Leung et al., 2011; Oun & Rhim, 2017a). For this, 10 g of chitin powder were dispersed in 1000 mL of APS (1 M) with vigorous stirring at 75 °C for 16 h, followed by washing until the pH reached around 4, then redispersed in water with sonication using a high-intensity ultrasonic processor (Model VCX 750, Sonics & Materials Inc., New-Town, CT, USA) for 15 min at 70% amplitude with pulses (5 s on and 2 s off). All the ChNC suspensions prepared as above were neutralized with 0.1 M NaOH solution and stored in a refrigerator at 4 °C before further use. The three different types of ChNC have been designated as ChNC^{H₂SO₄}, ChNC^{TEMPO}, and ChNC^{APS}, depending on the preparation method.

2.3. Preparation of ChNC/AgNP

Three different types of ChNC prepared as above were used as a template and stabilizing agents for the preparation of ChNC/AgNP hybrid nanomaterials. For this, silver nitrate (0.085 g) was added to 100 mL of each ChNC suspension containing 0.25 g of ChNC with stirring and heating. When the temperature reached 85 °C, 1.5 mL of 1 M NaOH solution was added dropwise to the suspension. The suspension was heated continuously at 85 °C for 2 h and washed with distilled water several times by centrifugation (4000 rpm/20 min) until the pH became 7–8. The precipitate was collected and dried at 100 °C for 1 h to get ChNC/AgNP hybrid nanomaterials. Additionally, the control AgNP were prepared using the same procedure as above without addition of ChNC (Oun & Rhim, 2017b).

2.4. Characterization of ChNC and ChNC/AgNP

Morphology of ChNC^{H₂SO₄}, ChNC^{TEMPO}, and ChNC^{APS} samples was observed using a scanning transmission electron microscope (STEM) (FE-STEM, S-4800, Hitachi Co., Ltd., Matsuda, Japan). For the determination of size distribution of ChNC samples, each ChNC sample was dispersed into deionized water to make 0.005 wt% suspension, and the size distribution was analyzed using a zeta potential analyzer (Zetasizer Nano ZS90, Malvern Instruments Ltd., Worcestershire, UK).

Sulfate content of ChNC prepared by acid hydrolysis method (ChNC^{H₂SO₄}) and carboxyl contents of the oxidized-ChNC isolated by the TEMPO and APS oxidized methods (ChNC^{TEMPO} and ChNC^{APS}) were calculated from conductivity titration curves obtained using the electric conductivity titration method. Sulfate group content was determined following the method of Lokanathan, Uddin, Rojas, and Laine (2014). For the determination of carboxyl content, oxidized samples (0.05 g) were added to 15 mL of 0.01 M HCl solution and stirred for 30 min at room temperature for complete protonation, then sonicated for 10 min. The suspensions were titrated with 0.01 M NaOH solution. The carboxylic acid content was calculated using the following equation (Zhang et al., 2016):

$$\text{COOH content} = \frac{C(V_2 - V_1)}{w} (\text{mmol/g ChNC})$$

where C was the concentration of NaOH (mol/L), V_2 and V_1 were the volumes of NaOH required to deprotonation of carboxylic acid groups which was calculated from the titration curves (mL), and w was the weight of the dry sample (g). The carboxylic acid content was also calculated using a degree of oxidation method (DO) using the following equation (Habibi, Chanzy, & Vignon, 2006):

$$\text{DO} = \frac{162(V_2 - V_1)C}{w - 36(V_2 - V_1)C}$$

where V_2 and V_1 were the amounts of NaOH (L), 162 and 36 corresponded to the molecular weight of an anhydroglucose unit (AGU) and the molecular weight difference between an AGU and sodium gluconate, respectively.

Optical properties of the control AgNP and ChNC/AgNP hybrid nanomaterials were examined using a UV-vis spectrophotometer (Mecasys Optizen POP series UV/Vis, Seoul, Korea) at the wavelength of 300–600 nm using distilled water as a blank.

The microstructure of the control AgNP and ChNC/AgNP hybrid nanomaterials was observed using a transmission electron microscopy at 120 kV (TEM, JEM-F200, JEOL Ltd. Tokyo, Japan). The average and standard deviation of Ag NPs diameters were calculated from the measurement of over 200 individual NPs using ImageJ software. The presence and intensity of AgNP were evaluated by energy dispersive spectroscopy using SEM instrument (SEM-EDS, S-4800, Hitachi Co., Ltd., Matsuda, Japan).

The chemical structure of ChNC and ChNC/AgNP was studied using Fourier transform infrared (FTIR) spectroscopy (TENSOR 37

Download English Version:

<https://daneshyari.com/en/article/7781785>

Download Persian Version:

<https://daneshyari.com/article/7781785>

[Daneshyari.com](https://daneshyari.com)