Colloids and Surfaces B: Biointerfaces 167 (2018) 538–543

Contents lists available at ScienceDirect

Colloids and Surfaces B: Biointerfaces

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

Rhelogical and antibacterial performance of sodium alginate/zinc oxide composite coating for cellulosic paper

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ARTICLE INFO

Article history:
Received 2 February 2018
Received in revised form 26 April 2018
Accepted 27 April 2018
Available online 1 May 2018

Keywords:
Sodium alginate
Zinc oxide
Cellulosic paper
Rheological property
Antibacterial activity
Tensile property

ABSTRACT

Coating of antibacterial layer on the surface of cellulosic paper has numerous potential applications. In the present work, sodium alginate (SA) served as a binder to disperse Zn^{2+} and the prepared zinc oxide (ZnO) particles were used as antibacterial agents. The rheology test revealed that there were cross-linking between Zn^{2+} and SA molecular chains in the aqueous solution, resulting in the viscosity of ZnO/SA composite coating increased in the low shear rate region and decreased in the high shear rate region as compared with pure SA. SEM and EDS mapping images showed that the ZnO particles were prepared successfully at 120 °C and dispersed homogeneously on the surface of cellulose fibers and the pores of cellulosic papers. The thermal stabilities of the coated papers decreased as compared to the original blank cellulosic paper, which was ascribed to the low thermal stability of SA and the catalytic effect of ZnO on SA. The tensile stress and Young's modulus of ZnO/SA composite coated paper increased up 39.5% and 30.7%, respectively, as compared with those of blank cellulosic paper. The antibacterial activity tests indicated that the ZnO/SA composite coating endowed the cellulosic paper with effectively growth inhibition of both Gram-negative bacteria *E. coli* and Gram-positive bacteria *S. aureu*.

1. Introduction

Antibacterial cellulosic paper has drawn growing interest from both engineers and researchers to counteract the surface contamination and disease transmission caused by bacterial interaction. It holds great promise applications for many places, such as food packaging factories, hospitals, restaurants and public places. However, natural cellulosic paper does not have any antibacterial activity. The surface coating is a simple and effective way to incorporate organic and/or inorganic antibacterial agents, rendering cellulosic papers with antibacterial properties.

Zinc oxide (ZnO) is an exceptionally important material, possessing unique optical, electrical, chemical and catalytic properties. In fact, as an effective antibacterial agent, ZnO exhibits good biocompatibility, easy fabrication, less toxicity and heat stability [1–3]. Extensive work has been reported on the antibacterial activity of ZnO against various bacteria, including *E. coli* [4], *C. jejuni* [5], *S. aureus* [6], and *B. subtilis* [7]. It is well known that the dispersion and stabilization of ZnO nanoparticles play very crucial roles in their antibacterial activities, and hence the use of suitable bio-based binders have been investigated. For instance, Cheng et al. [8] prepared carboxymethyl-starch-stabilized ZnO nanoparticles in situ in water, and deposited the ZnO coating on cellulose paper by using aqueous solution. Martinsna et al. [9] used the electrostatic assembly method to fabricate nanofibrillated cellulose/ZnO nanocomposite coating. Pang et al. [7] synthesized the sodium lignosulfonate stabilized ZnO nanoparticles through a two step dip-coating approach. These results showed that the sodium lignosulfonate modified ZnO could be homogeneously dispersed in water.

Sodium alginate (SA) is one of the most widely used natural polysaccharides, which is extracted from brown seaweeds [10]. Owing to its nontoxicity, biodegradability and biocompatibility, SA has been found widespread applications in tissue scaffolds, drug delivery and food industry. Recently, several studies have reported

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https://doi.org/10.1016/j.colsurfb.2018.04.058
0927-7765/

the preparation of SA/ZnO composites by various methods. Baskoutas et al. [11] used zinc nitrate or zinc acetate as the starting material to prepare zinc alginate gels, and subsequently heated the gels at high temperatures (800 °C and 450 °C) to get the ZnO nanocrystals. Trandafilovic et al. [1] showed that the spherical ZnO nanoparticles could be synthesized within the alginate solution by using microwave treatment. Shalumon et al. [12] obtained ZnO nanoparticles by using a wet chemical method, and then developed SA/ZnO/poly (vinyl alcohol) (PVA) nanofibrous mats with the electrospinning of SA/PVA from aqueous solutions. Varaprasad et al. [13] prepared rod-shape ZnO particles with precipitation technique, and deposited on the surface of cellulose fibers through the SA matrix with impregnation. These works proved that the ZnO particles could homogeneously disperse in the SA hydrogel. Therefore, the development of SA/ZnO composite coating as an antibacterial layer on the cellulosic paper has wide application potentials. Moreover, it has been reported that the treatment of ZnO at a lower temperature leads to a higher antibacterial activity [14,15].

In this present work, ZnO nanoparticles were prepared within the SA matrix at 120 °C. In this SA/ZnO composite coating, ZnO nanoparticles were used as antibacterial agents, and SA served as a binder to disperse ZnO nanoparticles. The effect of ZnO concentrations on the rheological behavior of the SA/ZnO composite coating was investigated. Subsequently, the change in thermal stability and tensile property of the modified cellulosic papers was identified. The antibacterial activity of the coated cellulosic paper was further tested by using *E. coli* (Gram-positive bacteria) and *S. aureus* (Gram-negative bacteria).

2. Materials and methods

2.1. Materials

Sodium alginate (SA), ammonium hydroxide (NH_4OH) and zinc oxide (ZnO) were obtained from Sigma-Aldrich. The viscosity of 1 wt% SA in water solution was 15–25 cP. Commercially available filter-papers (Double-circle™, Grade 101) were supplied by Whatman-Xinhua Filter Paper Co. Ltd. (Hangzhou, China). All the materials were used as received without further purification.

2.2. Preparation of SA/ZnO composite coatings modified paper sheets

The preparation of ZnO nanoparticles was based on the report [16] with modification. Briefly, different concentration of ZnO powder was firstly dissolved in 3 mL ammonium hydroxide and 3 mL distilled water under continuous stirring to get the zinc tetra-amine complex, $Zn(NH_3)_4^{2+}$ [17]. After completely dissolving, 300 mg SA powder was added into the as-prepared ZnO precursor solution under vigorous stirring to obtain homogenous distribution. The solution coated on glass was dried in an air-blast oven at 120 °C for 30 min to form the SA/ZnO composite film for XRD characterization. The SA/ZnO composite coatings with the ZnO concentrations varying from 0, 3, 6, 9, and 12 wt% with respect to the mass of SA, were labeled as ZnO-0, ZnO-3, ZnO-6, ZnO-9 and ZnO-12, respectively.

The prepared SA/ZnO composite coating solution was coated on a filter-paper sheet using a laboratory coater (MS-XB320D, Beijing Golden Speed Instrument Company) at the sizing speed of 30 cm/min. The thickness of the coating solution was 125 μm, which was decided by the tapes used for fixing the cellulosic papers. The modified paper was dried in an air-blast oven at 120 °C for 30 min to completely remove the ammonium hydroxide and water.

2.3. Characterization

The rheological properties of pure SA and SA/ZnO composite coatings were conducted on a 25 mm parallel plate rheometer (Anton-Paar MCR302). The samples were tested in the gel state under ambient conditions. The gap of parallel plate was fixed at 1 mm. The steady shear rheological curves were collected at the shear rate between 0.1 and 600 s^{-1} under the constant strain of 1%. X-ray diffraction (XRD) patterns were characterized by an X-ray diffractometer (Bruker AXS D2) with Cu-K_α radiation, operated at 30 kV and 10 mA. The scanning range of diffraction angle (2θ) was from 10° to 80° with a fixed interval of 0.02°. A thermogravimetric analyzer (TGA, TA Q50) was used to evaluate the thermal stability of the modified cellulosic papers. The sample was placed in a platinum pan and heated from 30 °C to 700 °C under nitrogen atmosphere with a heating rate of 20 °C/min. The tensile properties of the modified cellulosic papers were examined using a universal testing machine (Instron Model 5567) equipped with a 50 N load. The paper sheets were cut in rectangular shapes with dimensions of 80 mm × 15 mm and tested by maintaining a gauge length of 50 mm at the tensile speed of 1 mm/min. The reported results were average values for five parallel measurements. A field emission scanning electron microscopy (FE-SEM, FEI Quanta 450) equipped with an energy dispersive X-ray spectroscopy (EDX, Oxford Instruments X-Max^N) was employed to observe the surface morphology and analyze the surface elements of the blank and modified cellulosic paper sheets. Before observation, the samples were coated with carbon in an SPI-Module Sputter Coater.

2.4. Antibacterial activity

The antibacterial performance of the coated cellulosic papers against both *E.* coli (Gram-positive bacteria) and *S.* aureus (Gram-negative bacteria) were evaluated according to the standard antibacterial test "SNV 195920-1992" [18]. In brief, nutrient agar was prepared by mixing 1.5 g peptone, 0.5 g plant peptone, 0.5 g sodium chloride and 1.5 g agar in 100 mL of distilled water. The pH of this nutrient agar was 7.2 after adjustment. Then 1 mL of bacterial culture was transferred into a sterilized petri dish which was filled with the agar growth medium. Subsequently, the testing samples, 6 mm diameter circles, were placed over the bacteria colony and incubated at 37 °C for 12 h to observe the inhibition area. The antibacterial property of the samples was graded as "good" (inhibition zone >1 mm), "fair good" (inhibition zone <1 mm), "sufficient" (no bacterial growth on the paper sample), "limited" (limited bacterial growth on the paper sample) or "poor" (the paper sample is rehabitated by the bacteria) according to the dimension of the inhibition zone. The reported results were mean values for five independent experiments.

3. Results and discussion

3.1. Steady shear rheological behavior of SA/ZnO composite coatings

The measurement of rheological properties of composite coatings is crucial to infer the microstructure of the fluid matrix and understand the surface coating processing. Fig. 1a shows the steady shear viscosity of the composite coatings with various ZnO concentrations versus the shear rate. The ZnO-0 exhibited a typical Newtonian behavior at low shear rates, i.e., the viscosity increased slightly in the shear rate range of 0.01 ~ 10 s^{-1} [19]. At the high shear rate regime, the decrease in the state viscosity was more pronounced for ZnO-0, revealing a strong shear-thinning behavior. This tendency indicated that the interjection of SA molecular chains was