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Effect of chitosan silver nanoparticle coating on functional properties of Korean traditional paper

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ABSTRACT

The effect of chitosan silver nanoparticle (CSN) coatings on functional properties of Korean traditional paper (Hanji) was investigated as a function of dilution. In a typical process, CSN solution was prepared from $AgNO_3$ and chitosan *via* microwave irradiation. The as-prepared CSN solution was diluted to several concentrations (10, 1, 0.1 v/v% of undiluted CSN solution) and also used as prepared for coating Hanji by a dip coating method. The mechanical, oil resistance (TAPPI T559 pm-96), air resistance (TAPPI T 460), and antibacterial properties (JIS Z 2801) against *Escherichia coli* were investigated. Among the various concentrations, the minimum concentration that can positively influence the mechanical, air resistance, oil resistance and antibacterial properties of Hanji was identified as 1, 1, 10, 0.1% of the pure CSN solution, respectively. These findings are significant, since an improvement for a specific property of Hanji can be achieved by coating respective concentration.

1. Introduction

Korean traditional paper, Hanji, is considered to be one of the most stable and durable papers in the world. It is traditionally made of the bast fibers obtained from one-year-old paper mulberry [1]. The cellulose found in the pulp of paper mulberry has a very high average degree of polymerization lying in the range 7000–9000 and a high molar mass that is comparable to that of the celluloses produced by bacteria or tunicates [1]. Currently, Hanji is available in the market with various percentage of mulberry and kraft pulp. As a packaging material, Hanji is used as parcel wrappers, food packing paper, and traditional covering material. However, Hanji possesses poor barrier, mechanical and antimicrobial properties. This restricts its effective usage.

In paper industry, chitosan has been used as an additive for surface treatment to enhance the properties of the paper. Chitosan readily forms hydrogen bonds with cellulose fibres, thereby improves the overall mechanical and barrier properties of the paper [2,3]. In addition, chitosan is a natural and environmentally friendly biomaterial, and possesses antimicrobial properties due to the cationic character of the amino groups that present in its structure [4,5]. Owing to these significant properties, chitosan has become one of the most interesting materials for paper coatings. Chitosan has been tested as a wet end additive in paper board and the mechanical properties of the product were reported to be improved [6]. Recently, Tang et al. reported the improved mechanical, barrier and antibacterial properties of the chitosan/TiO_2 coated cellulose paper [7].

Over the past few years, silver nanoparticles (AgNPs) have gained significance as effective antibacterial agents to combat a broad spectrum of micro-organisms including multidrug resistant bacteria [8]. Ling et al. developed effective antibacterial paper with AgNPs quaternized carboxymethyl chitosan/organic montmorillonite nanocomposite through surface coating [9]. Recently, AgNPs enabled cellulose papers were developed for effective water purification [10–12]. These AgNPs nanoparticles function without bringing the microorganisms resistance [8]. So, the problem of disease transmission and the contamination through various micro-organisms could be greatly eradicated.

Keeping in view the abovementioned points, in this investigation, chitosan silver nanoparticles (CSN) solution was applied to improve the properties of Hanji. The required AgNPs were synthesized by employing the reduction property of chitosan *via* microwave irradiation [13]. The as-prepared CSN solution was diluted to several concentrations (10, 1, 0.1 v/v% of undiluted CSN solution) and also used as prepared for coating Hanji by a dip coating method. The effect of coating on the mechanical, oil resistance, air resistance and antibacterial properties was investigated. The dilution method was employed to find the possible minimum concentration of CSN solution that can improve the intended property of Hanji for its specific application. These findings are expected to benefit economically the pilot scale industrial operations of Hanji industries. More recently, our group has improved the properties of Hanji by applying chitosan silver nanoparticles

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solution prepared *via* ultrasonciation [14]. However, in the current approach, a typical microwave approach was followed. Compared to our previous work, in the current work, the properties of Hanji were improved with a minimum input of time and energy. This is the most significant factor in pilot scale operations for bulk scale production, as it reduces overall cost and labor. Further, in the current investigation, the concept of *'washing effect'* induced by the highly diluted coatings is described. The experimental findings pertaining to the investigation are presented here.

2. Experimental

2.1. Materials

Handmade Hanji manufactured traditionally from 20% mulberry fiber with kraft pulp was obtained from a local company, Wonju, South Korea. Chitosan (DD: 75–85%) of medium molecular weight (Mv = 190–310 kDa) with a Brookfield viscosity of 200–800 cP (CAS 9012-76-4) and silver nitrate ($AgNO_3$) (ACS reagent, ≥99.0%) were purchased from Sigma Aldrich. Acetic acid (10%) was purchased from Duksan Pure Chemical Co. Ltd, Korea. All chemicals were used as received without further purification. Deionized water was used throughout the experiments.

2.2. Preparation of CSN solution

Initially, chitosan solution (1.5 wt.%) was prepared from 2.0 v/v% acetic acid solution through vigorous stirring over a heating magnetic stirrer at 60 °C for 6 h. The obtained chitosan solution was cooled to room temperature. Subsequently, $AgNO_3$, previously diluted with 5 mL of distilled water, was added to the solution and stirred for 5 min in order to obtain chitosan $AgNO_3$ (35 mM) solution (experimental solution). The experimental solution was transferred completely to a round-bottom reaction vessel and then subjected to microwave irradiation in a modified microwave oven (MWO-2015, 800 W) for 15 min. The modified microwave oven used for the preparation of CSN solutions was installed with a condenser and teflon-coated overhead stirrer through holes at the top and was operated at 75 rpm during the course of reaction. At the end of the reaction, the color of the contents of the reaction vessel changed from colorless to ruby red, indicating the formation of AgNPs, and hence chitosan silver nanoparticles (CSN) solution is obtained. The as-prepared CSN solution was then allowed to cool to room temperature and utilized for coating Hanji in the subsequent steps.

2.3. Coating of CSN solution on Hanji

The as-prepared CSN solution was diluted to 10, 1, 0.1 v/v% of undiluted CSN solution using deionized water. A dip coating technique was employed to coat the solutions on Hanji. For this, Hanji papers were separately dipped into the solutions for 30 s to obtain various CSN coated Hanji samples. The excess solution was removed by gently press-passing the coated Hanji samples in between two glass rods. Next, the coated Hanji samples were dried in an oven at 90 °C for 10 min and were stored protected from light in air-tight polyethylene covers. Depending on the concentration of the CSN solution, the coated Hanji samples were designated as 100H, 10H, 1H and 0.1H, denoting 100, 10, 1, 0.1% CSN solutions, respectively.

3. Characterization

3.1. UV–vis analysis

UV–vis spectrum of the CSN solution was recorded on a UV–vis JASCO V-650 spectrophotometer (Japan). The reaction solution cooled to ambient temperature was used.

3.2. Transmission electron microscopy (TEM) analysis

The morphological analysis of the CSN coatings was carried out using a TEM (Tecnai G2 Spirit, FEI Company, USA), operating at an accelerating voltage of 120 kV. The TEM samples were prepared by diluting the as-prepared CSN solution and dropping the diluted solutions onto carbon-coated copper grid (400 mesh).

3.3. Coat weight

The CSN coat weight was determined gravimetrically by using a microbalance. The samples with an area of 0.1 × 0.1 m^2 were weighed. For each sample, five specimens were tested.

3.4. Thermogravimetric analysis (TGA)

The thermal characteristics of the samples were recorded on a TGA 4000 thermogravimetric analyzer (PerkinElmer Co., Ltd.,) at a heating rate of 20 °C/min under a nitrogen atmosphere (20 mL/min). Prior to recording, all the samples were thermally treated at 100 °C for 10 min to remove volatile compounds.

3.5. Scanning electron microscopy-energy dispersive spectrum (SEM–EDS)

The morphologies of the samples were analyzed by a Quanta FEG250 scanning electron microscope equipped with an energy dispersive X-ray spectrometer (SEM-EDS, FEI Co., Ltd.,). The top as well as fracture surfaces of all the samples were scanned. Prior to the analysis, the samples were coated with platinum for 60 s in a vacuum chamber.

3.6. Tensile strength

The tensile strength of the samples was evaluated using a universal test machine (UTM, Model QM100T, Qmesys Co., Gun-po, Korea). The test was performed in accordance with ASTM D828-97. Eight measurements were performed on each sample.

3.7. Burst test

The burst strength of the samples was measured by using a burst test machine (Model BT-1000, TM Electronics Inc., USA) as described in ASTM F1140. Eight measurements were performed on each sample.

3.8. Oil resistance

The oil resistance of the samples was evaluated according to TAPPI standard test T559 pm-96 through a Kit test procedure, as followed by other authors [15,16]. The samples were tested with a series of solutions containing specific proportions of three reagents: castor oil, toluene, and *n*-heptane. Depending on the specific proportions of three reagents, each solution was assigned a number ranging from 1 to 12, called Kit numbers (1–12), as shown in Table 1. Kit number 1 is the least aggressive oil, i.e., it has the highest surface energy, and Kit number 12 is the most aggressive oil, i.e., it has the lowest surface energy. To check oil resistance, various solutions were separately dropped onto the sample surface. After 15 s, the solutions were removed with tissue. The highest numbered solution that remained on the surface of the sample without causing staining was reported as the Kit value for the sample. Higher the Kit value indicates the higher oil resistance of the sample, and *vice-versa*. In Table 1, Kit numbers are given based on the weight measurements of castor oil (density, ρ = 969 kg/m^3).

3.9. Gurley permeation

The air permeability of the samples was measured using a Gurley