

# Hydrophobic Noncrystalline Porous Starch (NCPS): Dispersed Silver Nanoparticle Suspension as an Antibacterial Coating for Packaging Paper

Chao Dang,<sup>a</sup> Yihui Yin,<sup>a</sup> Ming Xu,<sup>a,b</sup> and Junwen Pu<sup>a,\*</sup>

Hydrophobic noncrystalline porous starch (NCPS) containing microporous and amorphous structures was prepared from native corn starch *via* heat treatment, solvent exchange, and alkyl ketene dimer (AKD) modification. Then, antibacterial packaging was produced by combining silver nanoparticles with the hydrophobic NCPS (hydrophobic NCPS/Ag) and employing this biobased coating as a layer on the base paper. The antibacterial activity, strength, and barrier properties of the hydrophobic NCPS/Ag-coated paper were measured. In addition, the fine porous surface of NCPS, the distribution of the silver nanoparticles in hydrophobic NCPS as well as the network structure of uncoated paper and coated paper were characterized by scanning electron microscopy. Meanwhile, the hydrophobicity of the corn starch, hydrophobic NCPS, uncoated paper, and coated paper were determined using water contact angles. The silver nanoparticles had a positive effect on the antibacterial activity against *Escherichia coli* and *Staphylococcus aureus*. The air permeability, oil resistance, water vapor transmission rate, water absorption, whiteness, tensile strength, and burst strength improved compared to the uncoated paper.

*Keywords:* Hydrophobic noncrystalline porous starch; Silver nanoparticles; Coating; Antibacterial packaging; Antibacterial property; Barrier property; Strength property

*Contact information:* a: MOE Engineering Research Center of Forestry Biomass Materials and Bioenergy, Beijing Forestry University, Beijing, 100083, P R China; b: Beijing Zhongke Audible and Ultrasound Technology Institute, 100083, P R China; \*Corresponding author: jwpu@bjfu.edu.cn

## INTRODUCTION

Consumers are paying an increasing amount of attention to antibacterial, biodegradable, and lightweight food packaging materials that could better preserve the quality of the food and improve its shelf-life and safety (Lavoine *et al.* 2015). Consequently, antibacterial packaging paper has attracted much attention in the food and packaging industries, which are aiming to replace conventional food packaging to inhibit microbial spoilage (Chung *et al.* 2001; Bagamboula *et al.* 2004; Miltz *et al.* 2006). Food packaging performs three functions: protection, providing of information, and ease of use. Among these functions, the protection of food from the invasion of undesirable pathogenic or spoilage microorganisms is the most important (Makwana *et al.* 2015). Antibacterial cellulosic paper, as a biodegradable, recyclable, and lightweight material, is considered to be one of the most promising candidates for replacing conventional packaging materials (Liu *et al.* 2016). However, plain paper is not applied to protect foods for long periods because of its poor antibacterial and barrier properties. To enhance the antibacterial performance, antibacterial materials are commonly incorporated directly into paper to prevent microbial contamination. Thus, various antibacterial materials have been

investigated and incorporated into food packaging to prevent microbial adhesion, extend shelf-life, and maintain or increase the product quality (Amini *et al.* 2016). Many of these materials are various synthetic materials that have demonstrated an inhibitory activity against different microorganisms and include sodium benzoates, propionates, potassium sorbates, sulfites, chlorides, and various polysaccharides, including chitosan and its derivatives (Devlieghere *et al.* 2000; Cooksey 2001; Zheng *et al.* 2013; Yin *et al.* 2017). Other antibacterial agents, such as metallic ions (silver and copper nanoparticles) (Fayaz *et al.* 2009) and metal oxides (titanium dioxide and zinc oxide) (Chawengkijwanich and Hayata 2008; Tayel *et al.* 2011), have also been proven to resist bacterial growth. Several researchers have studied the possibility of introducing silver nanoparticles into polymer films for enhancing the antimicrobial property. These studies suggested that silver nanoparticles are effective killers of pathogenic bacteria, such as *Escherichia coli* and *Staphylococcus aureus* (Rai *et al.* 2009; Li *et al.* 2010).

Biopolymers, which originate from naturally renewable resources, combined with antibacterial materials have the potential to be used as biobased coatings to prevent food deterioration by acting as a sufficient barrier to oxygen, water vapor, and oil (Hernez-Izquierdo *et al.* 2008; Marcos *et al.* 2010). Biopolymer-based materials with antibacterial materials, particularly starch-based ones, have been studied extensively for food packaging applications (Salleh and Muhamad 2010; Guazzotti *et al.* 2015; Liu *et al.* 2015; Koivula *et al.* 2016). However, the application of starch-based materials to improve chemical and mechanical properties of packaging has been challenging because of certain limitations, including poor processing, fragility, low whiteness, and high hydrophilicity (Lacroix and Le Tien 2005; Olivas and Barbosa-Cánovas 2008). Antimicrobial biobased coatings with improved properties can be prepared from starch that has been physically and chemically modified with other compatible materials that are incorporated with antibacterial materials (Flores *et al.* 2007).

Researchers have produced several starch derivatives through physical and chemical modifications. Examples of starches that have undergone physical modification include noncrystalline granular starch and microporous starch. In recent studies, noncrystalline granular starch that has a granular shape without a crystalline area has been produced by using heat treatment with aqueous ethanol. This type of starch with a mostly amorphous character could accelerate the chemical reaction rate (Liu *et al.* 2010; Zhang *et al.* 2012). In contrast, because of its non-toxicity, biodegradability, high specific surface area, and high whiteness, starch with a porous structure has a broad range of current and potential applications, including fillers, coatings, and wood adhesives. Several researchers have modified native starch by means of a solvent exchange technique to give it a porous structure (El-Tahlawy *et al.* 2007; Patel *et al.* 2010; Wang and Yang 2011). In terms of chemical modification, starch, which shares a similar chemical structural unit to cellulose, could also be reacted with alkyl ketene dimer (AKD) to generate  $\beta$ -keto esters that are fixed on the starch surface to improve the water resistance of the starch. Thus, in a previous work of the authors, it was attempted to combine these three approaches to develop a hydrophobic noncrystal microporous starch (NCPS), which is more stable, and convenient for storage and use in the paper making industries. The results from the experiment indicated that physically and chemically modified starches could remarkably increase the hydrophobicity, mechanical properties, and whiteness of paper (Dang *et al.* 2017). However, there have been minimal reports on the application of hydrophobic NCPS with silver nanoparticles as a coating in food packaging.

Hydrophobic NCPS combined with silver nanoparticles was used as a biobased coating applied onto the base paper surface with the aim of achieving improved antibacterial and barrier properties, as well as whiteness. The base paper of antibacterial packaging paper must have adequate mechanical properties. Ultrasonic-assisted wheat straw pulp (UWP) is produced by ultrasonic pulping, which integrates pulping and bleaching within a reactor to eliminate soda recovery, bleaching, bleaching solution preparation, and a coal-fired steam supply system. This group of authors has conducted a series of experiments on UWP, and the material has exhibited superior strength and optical properties compared with traditional wheat straw pulp and aspen alkaline peroxide mechanical pulp (Xing *et al.* 2017). In this work, because of the interest of the authors in this material, UWP and softwood kraft pulp (SKP) were used to make the base paper.

In the present study, NCPS was prepared by heat treatment and solvent exchange, which was followed by modification with AKD. Finally, the authors attempted to functionalize hydrophobic NCPS with silver nanoparticles and coating them onto a base paper surface to produce a material with useful properties for food packaging. The antibacterial activity, air permeability, oil resistance, water vapor transmission rate (WVTR), water absorption, whiteness, tensile strength, burst strength, and morphology of the coated papers were thoroughly characterized.

## EXPERIMENTAL

### Materials

Corn starch, the amylose content of which was analyzed by the supplier and was 26.3%, was supplied by Kangpuhuiwei Technology Co., Ltd. (Beijing, China) Country). The AKD and silver colloid solution were purchased from Kebaiao Co., Ltd. (Beijing, China). The UWP was supplied by Huasen Paper Co., Ltd. (Anyan, China). The SKP was supplied by Sun Paper Co., Ltd. (Yanzhou, China). All of the other chemicals were of analytical grade and used without further purification.

### Methods

#### *Preparation of the base paper*

The base paper (50 g/m<sup>2</sup>), which consisted of 60% ultrasonic-assisted wheat straw pulp (40° SR) and 40% bleached softwood kraft pulp (40° SR), was formed using a KRK semi-auto sheet machine (KRK Corp., Kyoto, Japan).

#### *Preparation of the hydrophobic NCPS*

Ten grams of corn starch were suspended in 300 mL of deionized water. The solution was then heated to 80 °C with continuous stirring for 20 min. The suspension was filtered to collect the noncrystalline starch. Briefly, 100 mL of anhydrous ethanol were added to 5 g of noncrystalline starch, which was stirred for 30 min at room temperature, and then the precipitated starches were filtered out *via* suction. After the precipitate was transferred to a glass beaker, 100 mL of anhydrous ethanol were added, and the mixture was stirred for 60 min, which was then filtered again. The precipitated NCPS was dried under ambient conditions overnight before further characterization. The following day, 80% AKD was dissolved completely in 50 mL of anhydrous ethanol with continuous stirring, and then 12 g of NCPS were added to the solution. The reaction mixture was allowed to sit at 55 °C with continuous stirring for 3 h. After the reaction, the resultant

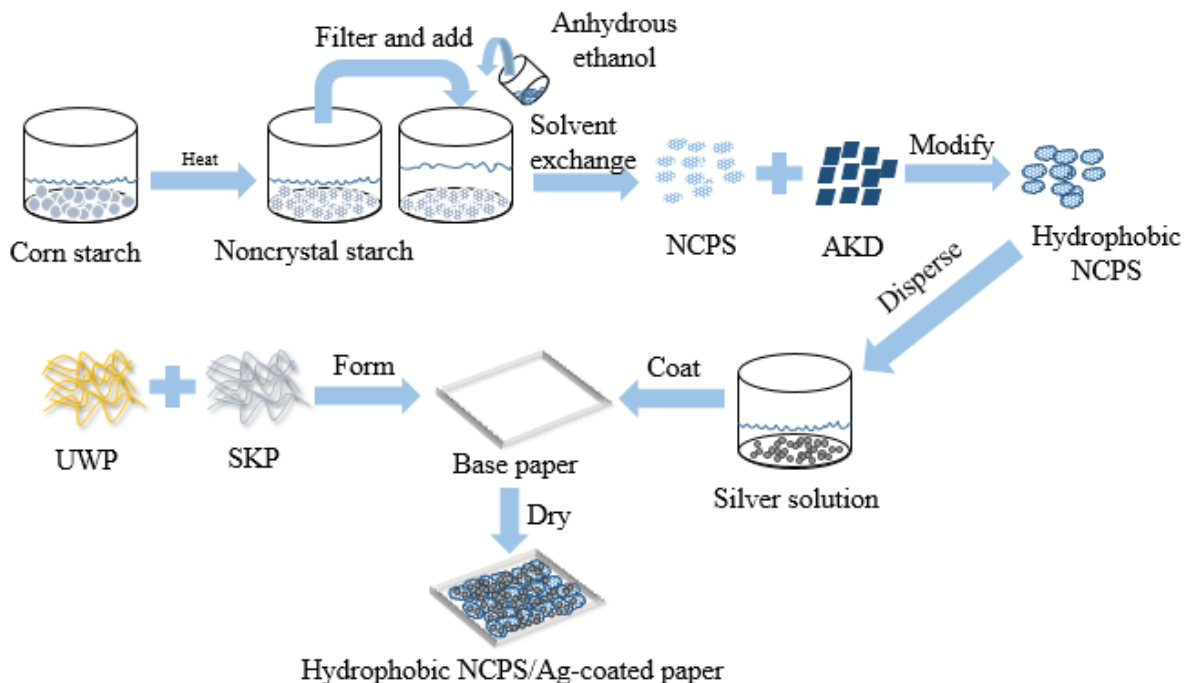
mixture was filtered, and the solid was freeze-dried to collect the hydrophobic NCPS after it was washed with anhydrous ethanol five times.

#### *Dispersion of hydrophobic NCPS into silver nanoparticles solution (hydrophobic NCPS/Ag)*

Five grams of hydrophobic NCPS were dispersed into solutions with different concentrations of colloid silver, which were 5 mg/L, 15 mg/L, 25 mg/L, 35 mg/L, and 45 mg/L. The mixtures were then stirred at 1000 rpm and room temperature for 1 h.

#### *Paper coating*

Hydrophobic NCPS/Ag was coated onto the surface of the base paper using a KRK ST-1 type machine (KRK Corp., Kyoto, Japan) with coat weights of 0.5 g/m<sup>2</sup>, 1 g/m<sup>2</sup>, 1.5 g/m<sup>2</sup>, and 2 g/m<sup>2</sup>. Then, the coated paper was allowed to dry at 23 °C and 50% relative humidity (RH) for 24 h until further analysis. Figure 1 shows the process for preparing the hydrophobic NCPS/Ag-coated paper.



**Fig. 1.** Preparation process of hydrophobic NCPS/Ag-coated paper

#### *Antibacterial activity*

The test method GB/T 20944.3 (2007) was used to determine the antibacterial activity of hydrophobic NCPS/Ag-coated paper with 5 mg/L, 15 mg/L, 25 mg/L, 35 mg/L, and 45 mg/L colloid silver solution and coat weights of 0.5 g/m<sup>2</sup>, 1 g/m<sup>2</sup>, 1.5 g/m<sup>2</sup>, and 2 g/m<sup>2</sup>. *E. coli* and *S. aureus* (Beijing Detection Center of Microbiology, Beijing, China) were selected as the test bacteria.

#### *Oil resistance*

The oil resistance measurements were conducted based on the method used by Jiao *et al.* (2015). Castor oil was used for sample testing in accordance with TAPPI T507 (1999). First, Sudan III (Kebaiiao Co., Ltd, Beijing, China) was used to change the colors

of the oil to red. Then, according to the schematic diagram given in Jiao *et al.* (2015), ten-layer arrangements, including the test samples, were stacked. A flat panel with a mass of 720 g was placed on the top of the stacks. Finally, the whole set was kept in an oven at 60 °C for 4 h. The area of the blotters stained with oil was determined by a point-counting method. The results were calculated as the average of five measurements.

#### *Air permeability*

Air permeability tests were performed using a KRK No. 2486-3 Air Permeability Tester (KRK Corp., Kyoto, Japan) in accordance with ISO 5636.5 (2013). In this method, the time (s) it took air to pass through coated paper with a settled area was determined. The longer it took air to move through the coated paper, the better the air permeability resistance of the coated paper. Five measurements from each sample were taken.

#### *Water vapor transmission rate*

The WVTR was determined by a gravimetric method based on the procedure used by Amini *et al.* (2016). Hydrophobic NCPS/Ag-coated papers were placed in a petri dish containing calcium chloride (CaCl<sub>2</sub>) salt, which were then properly sealed using solid silicone oil to avoid air penetration. The initial weight of the entire set was measured, and then the set was air-dried at 23 °C and 50% RH for 18 h. After this period, the weight of the dish containing the coated paper was measured. The WVTR (g/m<sup>2</sup>d) was calculated with the following equation,

$$WVTR = 24x / Ay \text{ (g/m}^2\text{d)} \quad (1)$$

where  $x$  is the sample weight (g) after time  $y$  (d), and  $A$  is the area of the paper tested (m<sup>2</sup>). The measurements were conducted five times.

#### *Water absorption (Cobb test)*

In the water absorption tests, the apparatus used was a ZZ-100 Cobb Tester (Paper Test Instruments Co., Ltd., Changchun, China). The Cobb value was calculated in accordance with GB/T 1504 (2002). The results were reported as the average of five measurements.

#### *Whiteness*

The whiteness of the coated paper was measured using a YQ-Z-48B whiteness tester (Qintong Co., Ltd., Hangzhou, China). The tests were performed in accordance with GB/T 7974 (2002). The reported results were the average of five measurements.

#### *Tensile and burst strengths*

The base papers that had been treated with hydrophobic NCPS/Ag were air-dried at 23 °C and 50% RH for 24 h prior to testing. The coated papers were tested in terms of the tensile and burst indices according to the ISO standard methods GB/T 453 (2002) and GB/T 454 (2002), respectively. The results were reported as the average of five measurements.

#### *Scanning electron microscopy (SEM) analysis*

Scanning electron microscopy analysis was used to investigate the surface morphology of the NCPS, hydrophobic NCPS/Ag, uncoated paper, and hydrophobic NCPS/Ag-coated paper.

Pieces were cut from the films, coated with gold by a spraying instrument (Yulong Co., Ltd., Beijing, China), and observed with a scanning electron microscope (S-3000N, Hitachi, Tokyo, Japan) at an acceleration voltage of 10 kV.

#### *Contact angle measurement*

Five microliters of deionized water were dropped onto the surface of the paper, and the water contact angle for the hydrophobic NCPS/Ag-coated paper was measured with an optical contact angle apparatus (OCA 20, Data Physics Instruments GmbH, Filderstadt, Germany) equipped with a video measuring system and high-resolution CCD camera.

## RESULTS AND DISCUSSION

Starch is a semi-crystalline plant polymer composed of amylose and amylopectin. Amylose is localized in the amorphous regions of the starch granule, while the crystalline regions are largely comprised of amylopectin (Shamekh *et al.* 1999; Glenn *et al.* 2008). In the authors' previous study, the XRD spectra of the corn starch and NCPS were detected. The XRD profiles showed that the intensity of the diffraction angle of NCPS was obviously weakened compared with that of corn starch. The results illustrated that the crystalline structure was destroyed entirely during the heat treatment (Dang *et al.* 2017).

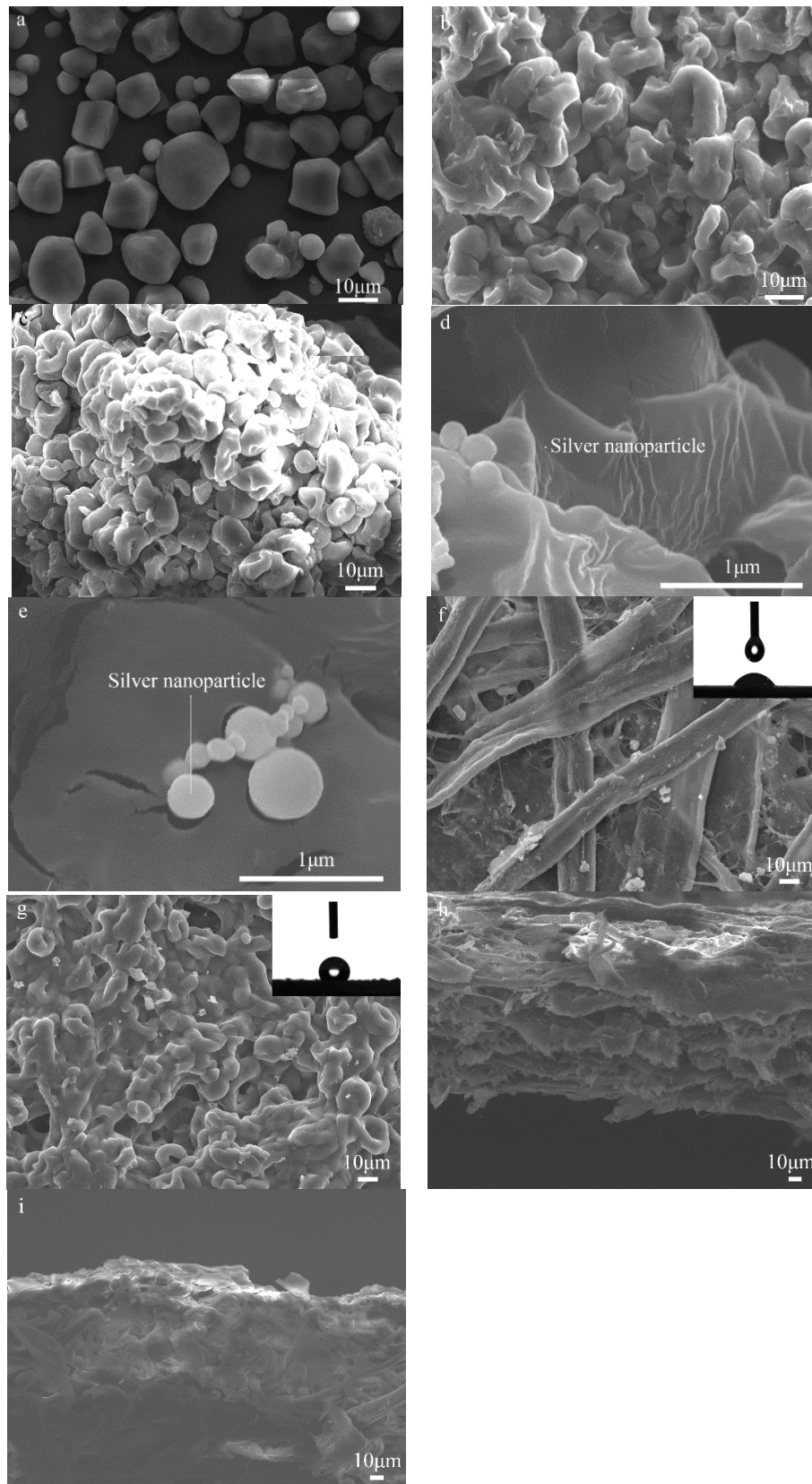
### **SEM Analysis and Contact Angle Measurement of the Corn Starch, NCPS, Hydrophobic NCPS, Hydrophobic NCPS/Ag, Uncoated Paper, and Coated Paper**

Figure 2 shows the SEM morphologies of the corn starch, NCPS, hydrophobic NCPS, hydrophobic NCPS/Ag, uncoated paper, and coated paper. As shown in Figs. 2a and 2b, it was clear that the integrated and smooth surfaces of the corn starch granules were converted to finely porous surfaces by heating and solvent exchange. In addition, the deposition and distribution of silver nanoparticles on the surface of the hydrophobic NCPS are presented in Figs. 2d and 2e.

The hydrophobic NCPS (Fig. 2c) without any silver nanoparticles showed a relatively clean surface with some particle-like defects, which were believed to be some undissolved components in the starch (Wu *et al.* 2009). The hydrophobic NCPS containing 45 mg/L silver nanoparticles exhibited a much rougher surface, and the nanoparticles were obviously aggregated on the starch surface. This behavior was consistent with the results of Li *et al.* (2017).

The SEM micrographs of the uncoated paper and hydrophobic NCPS/Ag-coated paper are shown in Figs. 2f to 2i. The uncoated paper (Fig. 2f) showed a porous structure of randomly interlacing fibers (Zhang *et al.* 2014). Figure 2g showed that the fibers and paper pores of the coated paper became less apparent after being coated with hydrophobic NCPS/Ag at a coat weight of 1 g/m<sup>2</sup>.

These micrographs revealed that the hydrophobic NCPS/Ag coating embedded cellulose fibers and formed a continuous film over the fibers. Meanwhile, the fracture surface images of the coated paper (Fig. 2i) showed an obvious dense structure compared with the loose fracture surface of the uncoated paper (Fig. 2h), which indicated that the hydrophobic NCPS/Ag penetrated the uncoated paper.



**Fig. 2.** SEM images of the corn starch (a), NCPS (b), hydrophobic NCPS (c), hydrophobic NCPS/Ag (d, e), uncoated paper (f, h), and coated paper (g, i). Insets (f and g): images of water droplets

Additionally, the wettability of the paper surface was studied by the contact angle of water droplets, which are shown in Figs. 2f and 2g. The results showed that the coated paper exhibited a higher hydrophobicity compared with the uncoated paper, which could have been because the hydrophobic NCPS/Ag formed a layer on the top of the base papers and penetrated deeply into the core of the papers. Therefore, it was determined that the hydrophobic NCPS/Ag coating is suitable for food packaging materials.

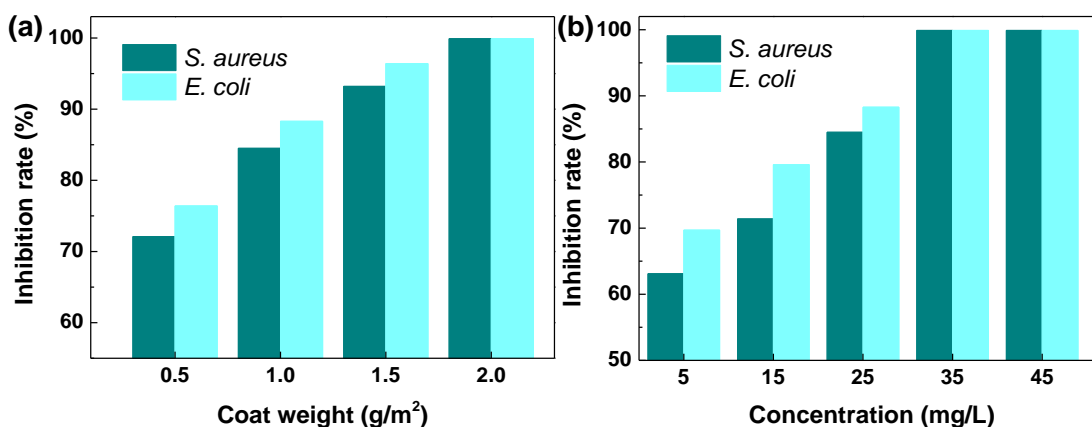
### Antibacterial Activities of the Hydrophobic NCPS/Ag-coated Paper

The antibacterial activities of the hydrophobic NCPS/Ag-coated paper were determined against *E. coli* as a Gram-negative bacterium and *S. aureus* as a Gram-positive bacterium.

Figure 3 shows the inhibition rates of the coated paper with 35 mg/L silver nanoparticles at coat weights of 0.5 g/m<sup>2</sup>, 1 g/m<sup>2</sup>, 1.5 g/m<sup>2</sup>, and 2 g/m<sup>2</sup> for *E. coli* and *S. aureus*. The inhibition rates of *E. coli* and *S. aureus* increased rapidly as the coat weight increased. Additionally, looking more closely at Fig. 3a, the hydrophobic NCPS/Ag coating had a higher antibacterial rate against *E. coli* than *S. aureus* at each coat weight. The antibacterial effect of the hydrophobic NCPS/Ag-coated paper with a 1g/m<sup>2</sup> coat weight at different concentrations of silver nanoparticles on *E. coli* and *S. aureus* was investigated, and is shown in Fig. 3b.

The inhibition rates increased with an increase in the concentration. The coated paper with the highest antibacterial property was obtained at a silver nanoparticle concentration of 35 mg/L. It has been reported that the antibacterial activity of biobased materials increases in the presence of silver nanoparticles (Wei *et al.* 2009; Cano *et al.* 2016). Improvement in the antibacterial performance was explained by the following discussion.

Silver nanoparticles with a high surface area attached to the surface of the cell membrane altered the cell wall permeability and respiration, and penetrated the bacteria to interact with the DNA, which resulted in bacteriostatic and bactericidal effects (Morones *et al.* 2005; Rai *et al.* 2009; Amini *et al.* 2016).



**Fig. 3.** (a) Effect of the coat weight on the antibacterial performance of the coated paper with 35 mg/L silver nanoparticles; and (b) effect of the silver nanoparticle concentration on the antibacterial performance of the coated paper with a coat weight of 1 g/m<sup>2</sup>



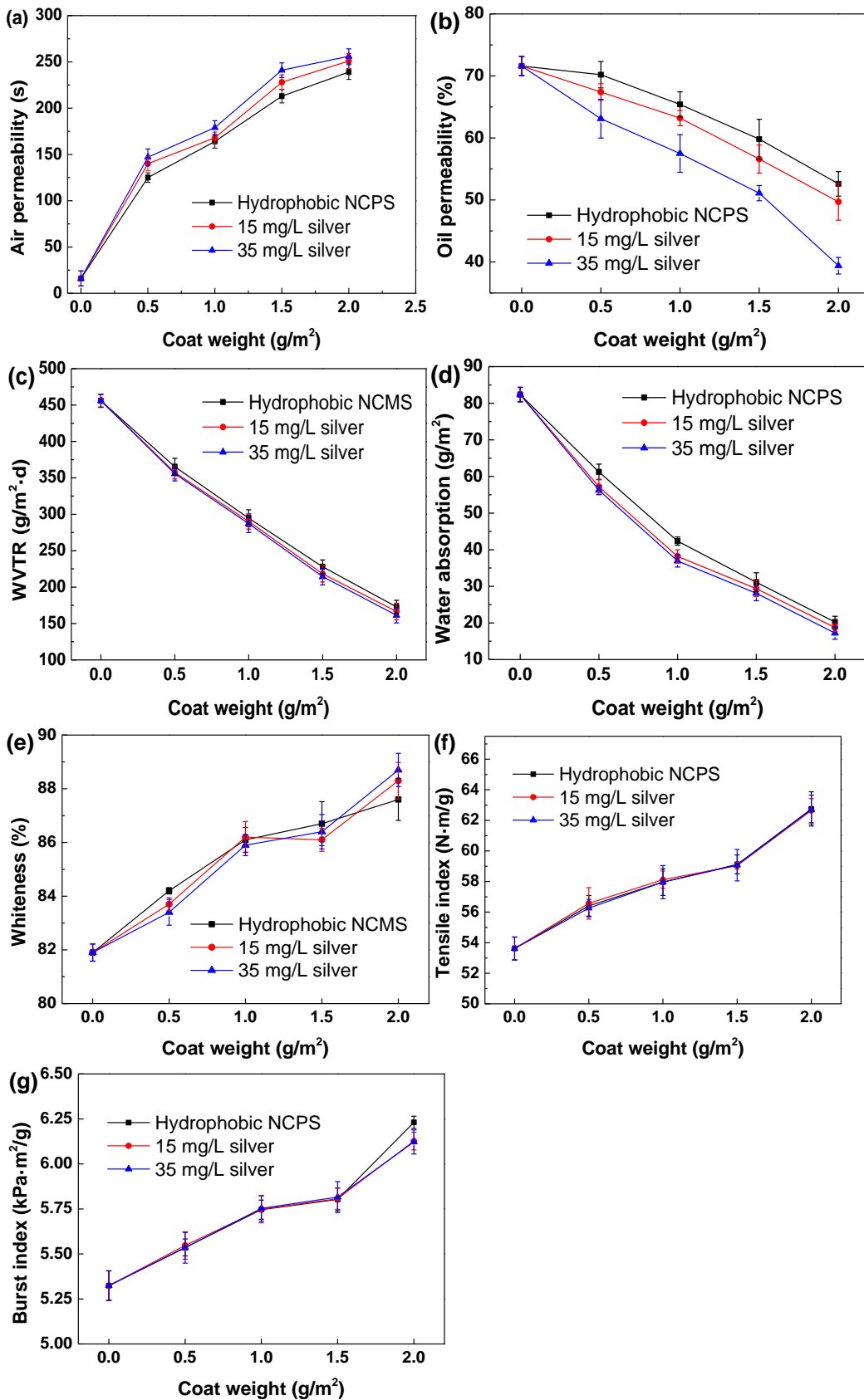


Fig. 4. Properties of the coated paper: (a) air permeability; (b) oil permeability; (c) WVTR; (d) water absorption; (e) whiteness; (f) tensile index; and (g) burst index

### Air Permeability of the Hydrophobic NCPS/Ag-coated Paper

Previous studies have shown that the addition of metal nanoparticles to polymeric matrices affects the gas permeability (Shahverdi *et al.* 2007; Sheikh *et al.* 2011). The air permeability values of the coated paper were measured at different coat weights and are shown in Fig. 4a. As was expected, the coated paper showed decreased air permeability as the coat weight increased. Consequently, the maximum air permeability was 256 s when the coat weight of hydrophobic NCPS/Ag was 2 g/m<sup>2</sup>. With the increased coat weight, the coated paper had an excellent air permeability resistance because the hydrophobic NCPS/Ag absorbed the fibers and formed a film on the base paper surface. It was noteworthy that for the base paper with a coat weight of 1.5 g/m<sup>2</sup>, the air permeability was approximately 228 s and 241 s for the hydrophobic NCPS impregnated with 15 mg/L and 35 mg/L silver nanoparticles, respectively. The reason for this was that the silver nanoparticles acted as a barrier to fill the voids of the fibers and controlled the amount of air transported, which would extend the food shelf life (Abreu *et al.* 2015). These results were in good accordance with the results of the SEM analysis given previously.

### Oil Resistance of the Hydrophobic NCPS/Ag-coated Paper

The effect of the hydrophobic NCPS/Ag on the castor oil resistance is shown in Fig. 4b. The oil resistance of the coated paper was sharply improved with the addition of the hydrophobic NCPS/Ag. The maximum oil resistance was 39.4% when the coated weight was 2 g/m<sup>2</sup>. Additionally, for the paper with a coat weight of 2 g/m<sup>2</sup>, the oil permeability of the coated paper with 15 mg/L and 35 mg/L silver nanoparticles was 49.7% and 39.4%, respectively. This result indicated that an increase in silver nanoparticles may have led to a decrease in the oil permeability. Oil can diffuse into the paper through its pores by capillary action and gradually penetrate the paper (Long *et al.* 2015). Therefore, oil resistance usually results from a relative absence of pores on the paper surface and is mainly determined by the largest paper pore size (Kjellgren 2005). Figures 2g and 2i showed that the relatively smooth surface and tight structure was beneficial in decreasing the surface porosity and preventing the paper from oil wetting.

### WVTR of the Hydrophobic NCPS/Ag-coated Paper

Because of interaction with water or gases, natural deterioration of fresh or processed food can easily happen. Therefore, WVTR is one of the most important properties of food packaging. Figure 4c presents the WVTR for the base paper coated with hydrophobic NCPS/Ag. It was found that the higher the coat weight of the hydrophobic NCPS/Ag, the lower the WVTR of the coated paper. Hence, the coated sample with a coat weight of 2 g/m<sup>2</sup> exhibited the highest barrier properties compared with the lower coat weights.

The cause of this effect may have been because the coating, which has a high hydrophobic property, was able to form an impermeable film on the fiber surface and penetrate through the base paper. This film decreased the penetration of water vapor through the base paper to prevent an increase in the WVTR. Therefore, it was evident that deposition of hydrophobic NCPS/Ag coating onto the paper surface boosted this property. Moreover, there was little difference between the base paper coated with 15 mg/L and 35 mg/L hydrophobic NCPS/Ag at the same coat weights, which was mainly caused by the paper surface pores being filled with silver nanoparticles.

### Water Absorption of the Hydrophobic NCPS/Ag-coated Paper

Data on the water absorption of the base paper made from UWP and SKP coated with hydrophobic NCPS/Ag are presented in Fig. 4d. At a coat weight of  $2 \text{ g/m}^2$ , the water absorption of the coated paper decreased 65.12% compared with the uncoated paper. This suggested that the coat of hydrophobic NCPS/Ag could effectively improve the hydrophobicity of the base paper. Because of the large surface pores and high swelling potential of the highly beaten fibers, the base paper was prompted to absorb water. After the use of hydrophobic NCPS/Ag, the coating formed a highly hydrophobic film on the base paper surface to resist water, which was in accordance with the water contact angle tests. Additionally, the coated paper with 35 mg/L silver nanoparticles exhibited higher water resistance than those with a concentration of 15 mg/L silver nanoparticles. This interesting result was probably because of the use of more silver nanoparticles that filled the paper network pores. The data obtained for the hydrophobic NCPS/Ag-coated paper was also in agreement with the SEM results.

### Schematic of the Common Barriers

The schematic of common barriers is shown in Fig. 5. First, the hydrophobic NCPS/Ag was coated onto the fiber. After the paper was dried, the hydrophobic NCPS/Ag coating formed a layer with improved water and air resistances. Silver nanoparticles dispersed on the surface of the hydrophobic NCPS provided an antibacterial activity and extra improvement to the water, air, and oil resistances.

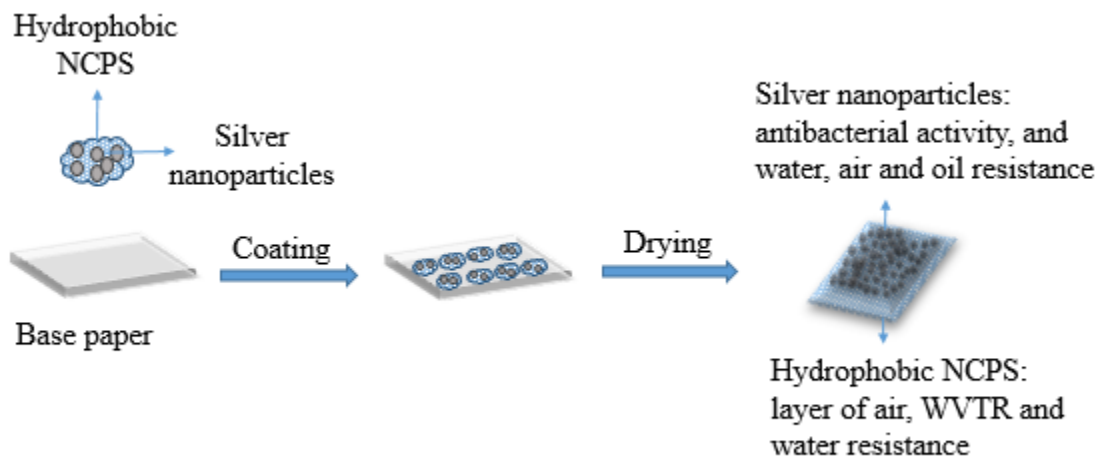


Fig. 5. Schematic of the common barriers

### Whiteness of the Hydrophobic NCPS/Ag-coated Paper

Antibacterial food packaging paper with high whiteness is helpful in improving the print quality. Figure 4e shows the effect of the coat weight on the whiteness performance of the coated paper. The whiteness increased to 88.7% as the coat weight increased to  $2 \text{ g/m}^2$ . The whiteness of the coated paper was higher than that of the uncoated sample, presumably because of the presence of a porous structure of hydrophobic NCPS (Bolívar *et al.* 2007). Meanwhile, it was observed that there was no difference in the whiteness of the paper coated with 15 mg/L and 35 mg/L silver nanoparticles, which indicated that the silver nanoparticles did not increase the whiteness.

### Mechanical Properties of the Hydrophobic NCPS/Ag-coated Paper

The tensile and burst indices of the paper coated with hydrophobic NCPS/Ag are shown in Figs. 4f and 4g, respectively. It was demonstrated that the tensile and burst indices of the coated paper were improved by the hydrophobic NCPS/Ag. Therefore, the mechanical properties of the coated paper were at their peak when the coat weight of hydrophobic NCPS/Ag was 2 g/m<sup>2</sup>. The results indicated that the coating was effective at improving the mechanical properties of the coated paper. There were many factors behind these improvements. Hydrogen bonds were formed between the hydrophobic NCPS and hydroxyl groups of the fibers (Dang *et al.* 2017). Furthermore, compared with the fracture surface of the uncoated paper, the hydrophobic NCPS/Ag also penetrated into the base paper, which resulted in the dense structure that is shown in Fig. 2i. Among the test samples, the mechanical properties of the coated paper were the same for the 15 mg/L and 35 mg/L silver nanoparticle concentrations. This result suggested that the silver nanoparticles did not increase the mechanical properties, at least for this concentration range.

### CONCLUSIONS

1. Functional antibacterial packaging paper with excellent barrier and mechanical properties was prepared by dispersing hydrophobic NCPS into silver nanoparticles and depositing it as a coating on the surface of a base paper, which consisted of 60% UWP and 40% SKP.
2. A relatively uniform distribution and fine dispersion of silver nanoparticles in the hydrophobic NCPS was evidenced by SEM.
3. The biobased antibacterial coating dramatically increased the antibacterial activity of the base paper against *E. coli* and *S. aureus* bacteria. The coated paper with the highest antibacterial property was obtained at a silver nanoparticle concentration of 35 mg/L.
4. The mechanical and barrier properties of the coated paper increased noticeably with higher coat weights. Additionally, the coated paper with 35 mg/L silver nanoparticles exhibited higher performance than those with a concentration of 15 mg/L silver nanoparticles in each coat weight.
5. All of the results revealed that the hydrophobic NCPS/Ag coating, which had antibacterial features and improved resistances and whiteness, has promising applications as packaging materials.

### ACKNOWLEDGMENTS

This work was sponsored by the Special Fund for Beijing Common Construction Project and Beijing Forestry University, Grant No. 2016HXKFCLXY0016.

## REFERENCES CITED

- Abreu, A. S., Oliveira, M., de Sà, A., Rodrigues, R. M., Cerqueira, M. A., Vicente, A. A., and Machado, A. V. (2015). "Antimicrobial nanostructured starch based films for packaging," *Carbohydr. Polym.* 129, 127-134. DOI: 10.1016/j.carbpol.2015.04.021
- Amini, E., Azadfallah, M., Layeghi, M., and Talaei-Hassanloui, R. (2016). "Silver-nanoparticle-impregnated cellulose nanofiber coating for packaging paper," *Cellulose* 23(1), 557-570. DOI: 10.1007/s10570-015-0846-1
- Bagamboula, C. F., Uyttendaele, M., and Debevere, J. (2004). "Inhibitory effect of thyme and basil essential oils, carvacrol, thymol, estragol, linalool and *p*-cymene towards *Shigella sonnei*, and *S. flexneri*," *Food Microbiol.* 21(1), 33-42. DOI: 10.1016/S0740-0020(03)00046-7
- Bolivar, A. I., Venditti, R. A., Pawlak, J. J., and El-Tahlawy, K. (2007). "Development and characterization of novel starch and alkyl ketene dimer microcellular foam particles," *Carbohydr. Polym.* 69(2), 262-271. DOI: 10.1016/j.carbpol.2006.10.004
- Cano, A., Cháfer, M., Chiralt, A., and González-Martínez, C. (2016). "Development and characterization of active films based on starch-PVA, containing silver nanoparticles," *Food Packaging & Shelf Life* 10, 16-24. DOI: 10.1016/j.fpsl.2016.07.002
- Chawengkijwanich, C., and Hayata, Y. (2008). "Development of TiO<sub>2</sub> powder-coated food packaging film and its ability to inactivate *Escherichia coli* in vitro and in actual tests," *Int. J. Food Microbiol.* 123(3), 288-292. DOI: 10.1016/j.ijfoodmicro.2007.12.017
- Chung, D., Chikindas, M. L., and Yam, K. L. (2001). "Inhibition of *Saccharomyces cerevisiae* by slow release of propyl paraben from a polymer coating," *J. Food Protect.* 64(9), 1420-1424. DOI: 10.4315/0362-028X-64.9.1420
- Cooksey, K. (2001). "Antimicrobial food packaging materials," *Additives for Polymers* 2001(8), 6-10. DOI: 10.1016/S0306-3747(01)80187-1
- Dang, C., Xu, M., Yin, Y., and Pu, J. (2017). "Preparation and characterization of hydrophobic noncrystal microporous starch (NCPS) and application in food wrapper paper as sizing agent," *BioResources* 12(3), 5775-5789. DOI: 10.15346/biores.12.3.5775-5789
- Devlieghere, F., Vermeiren, L., Bockstal, A., and Debevere, J. (2000). "Study on antimicrobial activity of a food packaging material containing potassium sorbate," *Acta Aliment. Hung.* 29(2), 137-146. DOI: 10.1556/AAlim.29.2000.2.4
- El-Tahlawy, K., Venditti, R. A., and Pawlak, J. J. (2007). "Aspects of the preparation of starch microcellular foam particles crosslinked with glutaraldehyde using a solvent exchange technique," *Carbohydr. Polym.* 67(3), 319-331. DOI: 10.1016/j.carbpol.2006.05.029
- Fayaz, A. M., Balaji, K., Girilal, M., Kalaichelvan, P. T., and Venkatesan, R. (2009). "Mycobased synthesis of silver nanoparticles and their incorporation into sodium alginate films for vegetable and fruit preservation," *J. Agr. Food Chem.* 57(14), 6246-6252. DOI: 10.1021/jf900337h
- Flores, S., Haedo, A. S., Campos, C., and Gerschenson, L. (2007). "Antimicrobial performance of potassium sorbate supported in tapioca starch edible films," *Eur. Food Res. Technol.* 225(3-4), 375-384. DOI: 10.1007/s00217-006-0427-5
- GB/T 453 (2002). "Paper and board determination of tensile properties – Constant rate of loading methods," Standardization Administration of China, Beijing, China.

- GB/T 454 (2002). "Paper – Determination of burst strength," Standardization Administration of China, Beijing, China.
- GB/T 1504 (2002). "Paper and board determination of water absorption," Standardization Administration of China, Beijing, China.
- GB/T 7974 (2002). "Paper and board determination of the brightness (whiteness)," Standardization Administration of China, Beijing, China.
- GB/T 20944.3 (2007). "Textiles. Evaluation for antibacterial activity. Part 3: Shake flask method," Standardization Administration of China, Beijing, China.
- Glenn, G. M., Klamczynski, A., Chiou, B. -S., Orts, W. J., Imam, S. H., and Wood, D. F. (2008). "Temperature related structural changes in wheat and corn starch granules and their effects on gels and dry foam," *Starch-Starke* 60(9), 476-484. DOI: 10.1002/star.200800203
- Guazzotti, V., Limbo, S., Piergiovanni, L., Fengler, R., Fiedler, D., and Gruber, L. (2015). "A study into the potential barrier properties against mineral oils of starch-based coatings on paperboard for food packaging," *Food Packaging & Shelf Life* 3, 9-18. DOI: 10.1016/j.fpsl.2014.09.003
- Hernez-Izquierdo, V. M., Reid, D. S., McHugh, T. H., Berrios, J. D. J., and Krochta, J. M. (2008). "Thermal transitions and extrusion of glycerol-plasticized whey protein mixtures," *J. Food Sci.* 73(4), 169-175. DOI: 10.1111/j.1750-3841.2008.00735.x
- ISO 5636.5 (2013). "Paper and board-determination of air permeance," International Organization for Standardization, Geneva, Switzerland.
- Jiao, L., Ma, J., and Dai, H. (2015). "Preparation and characterization of self-reinforced antibacterial and oil-resistant paper using a NaOH/urea/ZnO solution," *PLOS One* 10(10), 179-183. DOI: 10.1371/journal.pone.0140603
- Kjellgren, H. (2005). *Barrier Properties of Grease Paper*, Master's Thesis, Karlstad University, Karlstad, Sweden.
- Koivula, H. M., Jalkanen, L., Saukkonen, E., Ovaska, S. -S., Lahti, J., Christophliemk, H., and Mikkonen, K. S. (2016). "Machine-coated starch-based dispersion coatings prevent mineral oil migration from paperboard," *Prog. Org. Coat.* 99, 173-181. DOI: 10.1016/j.porgcoat.2016.05.017
- Lacroix, M., and Le Tien, C. (2005). "Edible films and coatings from non-starch polysaccharides," in: *Innovations in Food Packaging*, J. H. Han (ed.), Elsevier Academic Press, San Diego, CA, pp. 338-354.
- Lavoine, N., Desloges, I., Manship, B., and Bras, J. (2015). "Antibacterial paperboard packaging using microfibrillated cellulose," *J. Food Sci. Tech.* 52(9), 5590-5600. DOI: 10.1007/s13197-014-1675-1
- Li, W. -R., Xie, X. -B., Shi, Q. -S., Zeng, H. -Y., Ou-Yang, Y. -S., and Chen, Y. -B. (2010). "Antibacterial activity and mechanism of silver nanoparticles on *Escherichia coli*," *Appl. Microbiol. Biot.* 85(4), 1115-1121. DOI: 10.1007/s00253-009-2159-5
- Li, W., Zhang, C., Chi, H., Li, L., Lan, T., Han, P., Chen, H., and Qin, Y. (2017). "Development of antimicrobial packaging film made from poly(lactic acid) incorporating titanium dioxide and silver nanoparticles," *Molecules* 22(7), 1170. DOI: 10.3390/molecules22071170
- Liu, C., Xiong, H., Chen, X., Lin, S., and Tu, Y. (2015). "Effects of nano-TiO<sub>2</sub> on the performance of high-amylose starch based antibacterial films," *J. Appl. Polym. Sci.* 132(32). DOI: 10.1002/app.42339
- Liu, K., Liang, H., Nasrallah, J., Chen, L., Huang, L., and Ni, Y. (2016). "Preparation of the CNC/Ag/beeswax composites for enhancing antibacterial and water resistance

- properties of paper,” *Carbohydr. Polym.* 142, 183-188. DOI: 10.1016/j.carbpol.2016.01.044
- Liu, P., Zhang, B., Shen, Q., Hu, X., and Li, W. (2010). “Preparation and structure analysis of noncrystalline granular starch,” *Int. J. Food Eng.* 6(4), 61-64. DOI: 10.2202/1556-3758.1900
- Long, Z., Wu, M., Peng, H., Dai, L., Zhang, D., and Wang, J. (2015). “Preparation and oil-resistant mechanism of chitosan/cationic starch oil-proof paper,” *BioResources* 10(4), 7907-7920. DOI: 10.15376/biores.10.4.7907-7920
- Makwana, S., Choudhary, R., and Kohli, P. (2015). “Advances in antimicrobial food packaging with nanotechnology and natural antimicrobials,” *International Journal of Food Science and Nutrition Engineering* 5(4), 169-175. DOI: 10.5923/j.food.20150504.02
- Marcos, B., Aymerich, T., Monfort, J. M., and Garriga, M. (2010). “Physical performance of biodegradable films intended for antimicrobial food packaging,” *J. Food Sci.* 75(8), 502-507. DOI: 10.1111/j.1750-3841.2010.01785.x
- Miltz, J., Rydlo, T., Mor, A., and Polyakov, V. (2006). “Potency evaluation of a dermaseptin S4 derivative for antimicrobial food packaging applications,” *Packag. Technol. Sci.* 19(6), 345-354. DOI: 10.1002/pts.738
- Morones, J. R., Elechiguerra, J. L., Camacho, A., Holt, K., Kouri, J. B., Ramírez, J. T., and Yacaman, M. J. (2005). “The bactericidal effect of silver nanoparticles,” *Nanotechnology* 16(10), 2346-2353. DOI: 10.1088/0957-4484/16/10/059
- Olivas, G. I., and Barbosa-Cánovas, G. V. (2008). “Alginate-calcium films: Water vapor permeability and mechanical properties as affected by plasticizer and relative humidity,” *Food Sci. Technol.* 41(2), 359-366. DOI: 10.1016/j.lwt.2007.02.015
- Patel, S. V., Venditti, R. A., and Pawlak, J. J. (2010). “Dimensional changes of starch microcellular foam during the exchange of water with ethanol and subsequent drying,” *BioResources* 5(1), 121-134. DOI: 10.15376/biores.5.1.121-134
- Rai, M., Yadav, A., and Gade, A. (2009). “Silver nanoparticles as a new generation of antimicrobials,” *Biotechnol. Adv.* 27(1), 76-83. DOI: 10.1016/j.biotechadv.2008.09.002
- Salleh, E., and Muhamad, I. I. (2010). “Starch-based antimicrobial films incorporated with lauric acid and chitosan,” *AIP Conference Proceedings* 1217, 432-436. DOI: 10.1063/1.3377861
- Shahverdi, A. R., Fakhimi, A., Shahverdi, H. R., and Minaian, S. (2007). “Synthesis and effect of silver nanoparticles on the antibacterial activity of different antibiotics against *Staphylococcus aureus* and *Escherichia coli*,” *Nanomedicine Nanotechnology Biology & Medicine* 3(2), 168-171. DOI: 10.1016/j.nano.2007.02.001
- Shamekh, S., Forssell, P., Suortti, T., Autio, K., and Poutanen, K. (1999). “Fragmentation of oat and barley starch granules during heating,” *J. Cereal Sci.* 30(2), 173-182. DOI: 10.1006/jcrs.1999.0263
- Sheikh, F. A., Kanjwal, M. A., Saran, S., Chung, W. -J., and Kim, H. (2011). “Polyurethane nanofibers containing copper nanoparticles as future materials,” *Appl. Surf. Sci.* 257(7), 3020-3026. DOI: 10.1016/j.apsusc.2010.10.110
- TAPPI T507 (1999). “Grease resistance of flexible packaging materials,” TAPPI Press, Atlanta, Georgia.
- Tayel, A. A., El-Tras, W. F., Moussa, S., El-Baz, A. F., Mahrous, H., Salem, M. F., and Brimer, L. (2011). “Antibacterial action of zinc oxide nanoparticles against foodborne pathogens,” *J. Food Safety* 31(2), 211-218. DOI: 10.1111/j.1745-4565.2010.00287.x

- Wang, B., and Yang, R. -D. (2011). "Preparation and characterization of starch microcellular foam particles crosslinked with glutaraldehyde using a solvent exchange technique," *Gongneng Cailiao/Journal of Functional Materials* 42(1), 524-528.
- Wei, D., Sun, W., Qian, W., Ye, Y., Ma, X., and Ma, X. (2009). "The synthesis of chitosan-based silver nanoparticles and their antibacterial activity," *Carbohydr. Res.* 344(17), 2375-2382. DOI: 10.1016/j.carres.2009.09.001
- Wu, M., Meng, W., and Ge, M. (2009). "Investigation into the performance and mechanism of SiO<sub>2</sub> nanoparticles and starch composite films," *J. Text. I.* 100(3), 254-259. DOI: 10.1080/00405000701757677
- Xing, L. Y., Xu, M., and Pu, J. W. (2017). "The properties and application of an ultrasonic-assisted wheat straw pulp having enhanced tendency for ash formation," *BioResources* 12(1), 871-881. DOI: 10.15376/biores.12.1.871-881
- Yin, Y., Dang, C., Zheng, X., and Pu, J. (2017). "Synthesis of 2-hydroxypropyl trimethylammonium chloride chitosan and its application in bamboo fiber paper," *BioResources* 12(2), 2899-2911. DOI: 10.15376/biores.12.2.2899-2911
- Zhang, B., Dhital, S., Haque, E., and Gidley, M. J. (2012). "Preparation and characterization of gelatinized granular starches from aqueous ethanol treatments," *Carbohydr. Polym.* 90(4), 1587-1594. DOI: 10.1016/j.carbpol.2012.07.035
- Zhang, W., Xiao, H., and Qian, L. (2014). "Enhanced water vapour barrier and grease resistance of paper bilayer-coated with chitosan and beeswax," *Carbohydr. Polym.* 101, 401-406. DOI: 10.1016/j.carbpol.2013.09.097
- Zheng, X., Zhang, H., She, Y., and Pu, J. (2013). "Composite films of N,O-carboxymethyl chitosan and bamboo fiber," *J. Appl. Polym. Sci.* 131(3), 1082-1090. DOI: 10.1002/app.39851

Article submitted: August 25, 2017; Peer review completed: October 29, 2017; Revised version received and accepted: October 30, 2017; Published: November 8, 2017.  
DOI: 10.15376/biores.13.1.192-207