Original Article

Preparation of Flame Retardant and Antibacterial Wood with Composite Membrane Coating[1]

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ABSTRACT

A novel flame retardant and antibacterial composite membrane coating for wood surfaces was prepared by adding POSS-based phosphorous nitrogen flame retardant (later referred to as NH_2-POSS) and silver nanoparticles (Ag NPs) to chitosan (CS). The effects of NH_2-POSS content (mass fractions of CS 0%, 0.5%, 1%, 3%, 5%, and 7%) on the structure and properties of the composite membrane coating on wood were investigated. The composite film was prepared by the method of blending and ducting. Contact angle, tensile property and antibacterial effects of the composite film were measured, and infrared spectroscopy was used. The results show that the addition of NH_2-POSS can not only improve the toughness of the membrane, but also the flame retardancy of the membrane, which improves the application of the membrane in wood products. However, with the addition of NH_2-POSS, the transparency of the composite membrane was weakened. The inhibitory effect of the composite membrane on the growth of *Escherichia coli* was enhanced with the increase in Ag NPs. This research provides a foundation for the application of functional wood.

Keywords: nano-silver, chitosan membrane, POSS-based phosphorous nitrogen flame retardant, antibacterial properties

1. INTRODUCTION

Plywood is widely used in furniture manufacture, residential and commercial interior finish and case-work applications (Park *et al*., 2021). In the process of making Asian string instruments like Korean geomungo and gayageum, Chinese zheng, and Japanese koto, the surface of paulownia wood is often finished by scorching with a hot iron of over 1000℃ (Lee *et al*., 2021). But, wood has high hydrocarbon content and is a flammable material. Wood flame retardancy is the process of reducing the burning rate of wood and accelerating the carbonization of the burning surface in order to win rescue time. The mechanism of

action of flame retardants is to form a protective layer on the wood surface to isolate or dilute the oxygen supply. In the case of decomposition at high temperature, a large amount of non-flammable gas or water vapor is released, diluting the flammable gas released during wood pyrolysis. The temperature of retarded wood decreases, which makes it difficult to reach the temperature required for pyrolysis. The flame retardant treatment improves the formation ability of charcoal, reduces the heat transfer rate and cuts off the burning chain to quickly extinguish a fire (Park *et al*., 2020, 2021). In order to improve the flame retardancy of the wood composites, studies on the development of flame retardant epoxy and isocyanate adhesives have also been conducted (Li, 2019; Wen *et al*., 2020). Also, Chitosan is known to have a flame retardant effect, but its effect is weak (Zhao *et al*., 2021; Liu *et al*., 2020; Ren, 2020). The unique inorganic Si-O-Si structure of POSS has outstanding thermal stability and flame retardancy, which can improve the flame retardant performance of chitosan. In addition, its kernel class inorganic flame retardant of silica and the R group structure design make POSS important in flame retardant polymer (Li *et al*., 2019; Yuan *et al*., 2016). Chitosan is safe and nontoxic, and its unique molecular structure makes its chemical properties stable, and it has good biocompatibility, degradability, film formation, adsorbability and antibacterial properties and chitosan is widely used in the food packaging industry (Caz *et al*., 2017). However, chitosan also has many shortcomings in structure and performance, such as: it does not completely dissolve in water and alkalisolution, is insoluble in ordinary organic solvents, and only soluble in dilute acid and weak acid. Chitosan matrix materials are brittle, fragile and have poor water vapor barrier performance (Phil *et al*., 2017). These weaknesses of chitosan affect its practical application in industrialization to a great extent. In order to improve the properties of chitosan and meet the needs

of practical application in wood products, chitosan should be modified. Moreover, as interior decoration material, wood products are often in contact with human body, and there will be bacteria on the surface of wood (Guan *et al*., 2020; Hao *et al*., 2019; Xing *et al*., 2018). Therefore, it is very necessary to give wood coatings antibacterial properties (Li *et al*., 2019). The selection of nano silver (Ag NPs), can enhance its antibacterial effect (Hu *et al*., 2020) and expand its antibacterial spectrum on the one hand, while on the other hand, it can be used to improve the strength and other properties of composite coatings (Liu *et al*., 2010; Liu *et al*., 2019; Yu *et al*., 2019). In this paper, a novel flame retardant and antibacterial wood coating preparation method was developed with the composite membrane system of chitosan, POSS-based new phosphorus, nitrogen and silicon flame retardant and nano silver. It is hoped that this composite membrane can provide wood with more functional properties and thus widen its application as an interior decoration material.

2. MATERIALS and METHODS

2.1. Materials

CS (deacetylation≥95%, viscosity 100,000-200,000 cps), NH$_2$-POSS (synthetic in laboratory), NaOH, anhydrous calcium chloride, silver nitrate, and glacial acetic acid are all analytically pure. *Escherichia coli*: ATCC8099 was produced by Nanjing Becheng Biotechnology Co., Ltd.

2.2. Preparation of Experiment

2.2.1. Preparation of NH$_2$-POSS

KH550 40.628 g was added to a 500 mL three-necked flask and magnetically stirred. After mixing 118.96 g of tetrahydrofuran with 28.414 g of distilled water, slowly added to the flask, heated to 60°C and refluxed, then added 10-12 drops of HCl, and reacted

at a constant temperature for 72 hr. The orange-yellow product was filtered with suction and dried at 60°C to obtain NH$_2$-POSS powder.

2.2.2. Preparation of composite membrane

A certain amount of CS was weighed in a glacial acetic acid solution with a volume fraction of 1% and stirred until it was completely dissolved to prepare the CS solution with a mass fraction of 1%. A certain amount of silver nitrate was added and it was stirred well. Then, 0%, 0.5%, 1%, 3%, 5% and 7% of dissolved NH$_2$-POSS solution were added to the CS/Ag NPs solution. After magnetic stirring for 20 hr and ultrasonic treatment for 20 min, a film forming solution was prepared. Waiting for 24 hr, the film was formed by flow extension and then dried in an oven at 40°C for 16 hr to form the film. The membrane was taken out and soaked in 1 mol/L sodium hydroxide solution for 20 min, and then cleaned repeatedly with pure water. The membrane was dried at room temperature and then put into a drying dish for later use.

2.3. Performance and test of composite membrane

2.3.1. Infrared spectroscopy characterization

The composite membrane was scanned by a Fourier transform infrared spectrometer (FTIR) with a scanning range of 400-4,000 cm^{-1} and the number of infrared scanning was 32 times, and the resolution was 4.00 cm^{-1}. The infrared test used the FTIR-650 Fourier transform infrared spectrometer.

2.3.2. Test of contact angle

The effect of NH$_2$-POSS concentration on the hydrophobic properties of composite films was tested. The test liquid was deionized water. Each membrane group was tested three times, and the average value was taken as the result. The contact angle test uses the water drop angle tester (model HD-U805) of Dongwan City Haida Instrument Co., Ltd.

2.3.3. Test of tensile strength

Refer to GB/T 1040.3, membrane mechanical properties of the determination of tensile strength. The sample width was 10 mm, the fixture spacing was 50 mm, and the stretching speed was 50 mm/min. Each sample test was repeated at least 10 times. The tensile performance test uses the electronic tensile testing machine (model WDD-100) of Beijing Guance Jingdian Instrument Equipment Co., Ltd.

2.3.4. Antibacterial property test of composite membrane

The concentration of *Escherichia Coli* solution was 1.5 × 107 CFU, and 100 μL of the activated *Escherichia Coli* solution was added to a solidified agar medium plate and evenly coated. The film was sampled with a perforator with a diameter of 6 mm, and the circular diaphragm obtained was sterilized under a UV lamp for 30 min. After sterilizing, sterile tweezers were used to clip the membrane onto the surface of the medium plate, and three diaphragms were evenly distributed on each plate. Then the plate was cultured in a constant temperature incubator at 37°C for 24 hr and then taken out. The results of the bacteriostatic experiment were recorded by photos. *Staphylococcus Aureus* (ATCC29213) was activated. The NH$_2$-POSS/CS-nano silver film was cut into a wafer with a diameter of about 0.5 cm. *Staphylococcus Aureus* was inoculated in a shaking flask, cultured at 37°C and 200 RPM for 2 hr, then 100 μL of bacterial solution was removed and evenly applied on the agar plate. The mixed film samples were separately placed on the agar plate and cultured at 37°C for 24 hr, and the bacteriostatic experiment results were recorded by photos. Activation of *Bacillus Subtilis* strains: LB medium (tryptone 10.0 g, yeast extract 5.0 g, NaCl 10.0

g dissolved in 1.0 L distilled water) was prepared and autoclaved (121°C, 15 min.) after pH 7.0 was adjusted. *Bacillus Subtilis* (about 108 Cfu/mL) was inoculated into LB medium at 100 μL and incubated at 37°C for 24 hr. The results of antibacterial experiments were recorded by photos. And the ratio of the membrane of each plate was CS+0.5%NH$_2$-POSS, CS+0.5%NH$_2$-POSS+1%Ag, CS+1%NH$_2$-POSS+1%Ag.

2.3.5. Flame retardant performance test

The sample was made into 100 mm × 100 m × 1 mm by using the butane spray gun of a calorific value meter. The sample was burned through three times for each sample. The thermal imager uses the German Testo 865 infrared thermal imager, the original infrared thermal imaging thermometer. Infrared thermometer; The use of butane spray gun: The spray gun was Ignited and aimed at the center of the sample, and the sample was burn every half a minute. When the sample burns through, the spray gun was stopped and a photo was taken to record the temperature.

3. RESULTS and DISCUSSION

3.1 Infrared spectrum of membrane
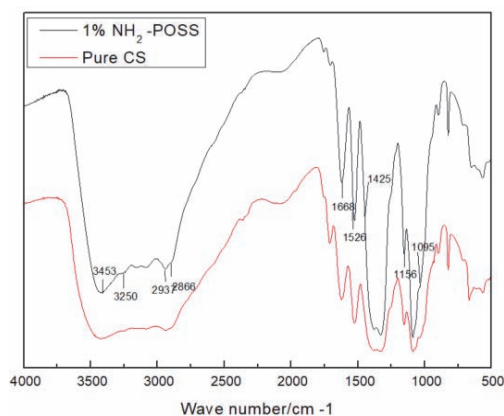
According to the infrared characterization in Fig. 1,

Fig. 1. Infrared characterization.

3,453 cm^{-1} and 1,526 cm^{-1} are the characteristic absorption peaks of −NH$_2$, 3,250 cm^{-1} is the absorption peak of −NH^{4+}, 1,065 cm^{-1} is the absorption peak of Si-O-Si, 2,866-2,937 cm^{-1} is the absorption peak of C-H, 1,425 cm^{-1} is the absorption peak of -CH$_2$ and −CH$_3$, 1,156 cm^{-1} is the absorption peak of C-O-C, 896-1,095 cm^{-1} is the absorption peak of the chitosan ring, and 1,029 cm^{-1} is the absorption peak of chitosan C-O. In the infrared image of 1% NH$_2$-POSS-based phosphorous nitrogen flame retardant, the absorption peak of chitosan C=O appeared at 1,639-1,668 cm^{-1}, which can prove that NH$_2$-POSS-based phosphorous nitrogen flame retardant was successfully grafted onto chitosan.

3.2. Contact angle of the composite film

Considering that it is a coating film, the hydrophobicity of the coating film should be considered. The contact angle was tested, and the results are shown in Fig. 2. CS film is a super-hydrophilic film. The contact angle with oil makes the difference more distinct. The contact angle with oil is 158°. When NH$_2$-POSS increased to 3%, the contact angle was 90°, which reached the level of being hydrophobic. The phenomenon is explained as the amino group on NH$_2$-POSS is hydrogen-bonded with the main hydrophilic functional groups -OH and -NH$_2$ of the chitosan molecule, so that the free hydrophilic functional groups are reduced, thus improving the hydrophobicity of the surface of the composite film.

3.3. Effect of NH$_2$−POSS−based phosphorous nitrogen flame retardant on tensile properties of composite films.

In order to explore the influence of the addition of NH$_2$-POSS on the tensile properties of the film, the tensile properties of the film were tested. As shown

in Fig. 3, when NH$_2$-POSS is added 5%, the mechanical strength of the film is 30 higher than the average value. But when the amount of NH$_2$-POSS is higher than 5%, the performance of the film is reduced. The reason is that the excessive amount of NH$_2$-POSS leads to agglomeration, resulting in performance degradation.

3.4. Test of antibacterial properties of composite membrane

The test of antibacterial performance is shown in Fig. 4. The antibacterial effect of the three membranes on *Escherichia Coli* was basically the same. The antibacterial effect on *Staphylococcus Aureus* and *Bacillus Subtilis* was obvious. The antibacterial effect of the
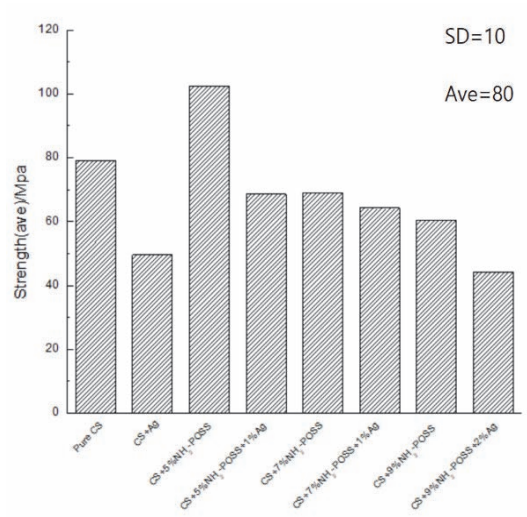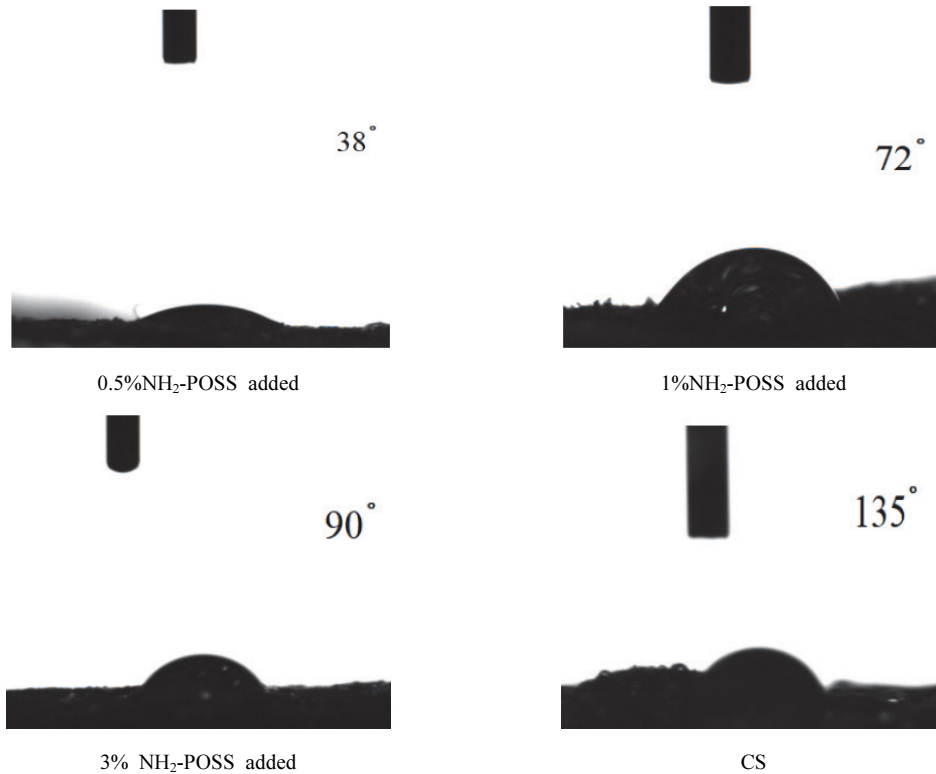
Fig. 3. Elastic performance test results·

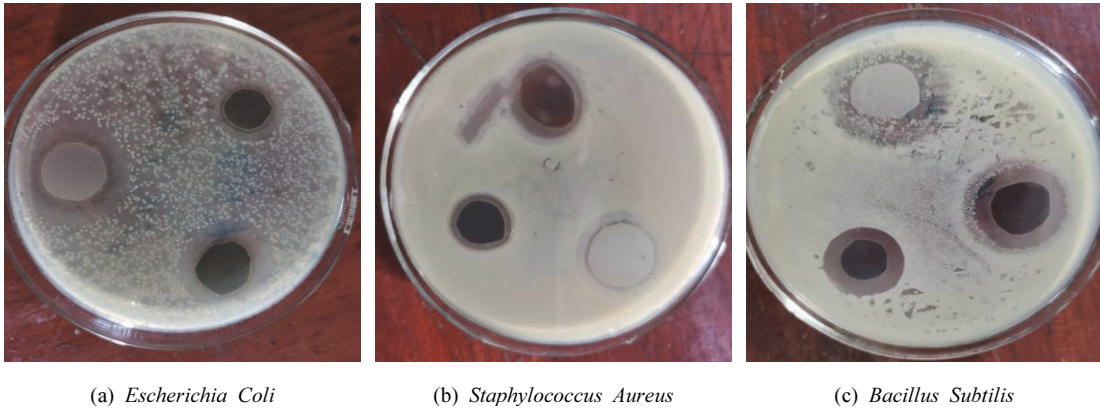**Fig. 2.** Hydrophobic performance test results.

(a) *Escherichia Coli*   (b) *Staphylococcus Aureus*   (c) *Bacillus Subtilis*

Fig. 4. Antibacterial results.

Control

CS

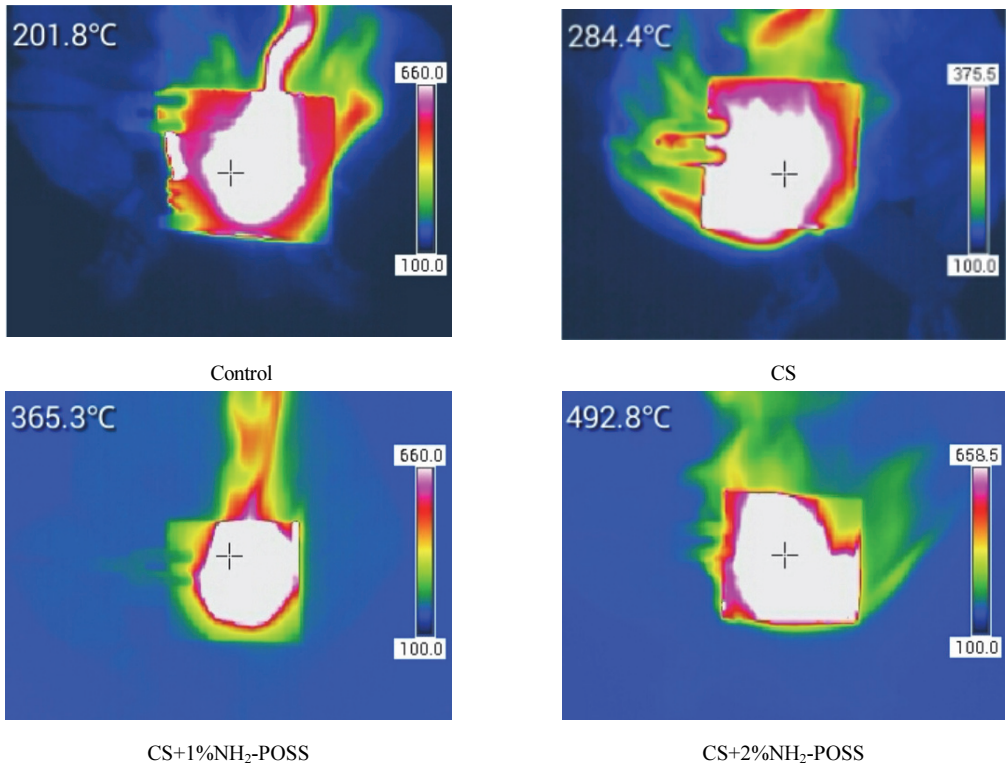CS+1%NH$_2$-POSS

CS+2%NH$_2$-POSS

Fig. 5. Fire performance test.

membrane with Ag was contrasted with that without Ag. The inhibition zone of the membrane without Ag was 13.2 mm, and the inhibition zones of the mem- branes with 0.5% and 1% NH$_2$-POSS were 15.49 mm and 20.3 mm, respectively. For the antibacterial effect of *Bacillus Subtilis*, the comparison of antibacterial ef-

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Table 1. Results contrast

Category	Control	CS	CS+1%NH$_2$-POSS	CS+2%NH$_2$-POSS
Temperature	201.8℃	284.4℃	365.3℃	492.8℃
SD		107.8		

fect between membranes with Ag and without Ag is also distinct. The inhibition zone of the membrane without Ag was 16.7 0mm, and that of the membranes with 0.5% and 1% NH$_2$-POSS were 19.41 mm and 22.39 mm, respectively. It can be concluded from this experiment that the addition of Ag greatly improves the antibacterial performance of the membrane, and the addition of NH$_2$-POSS also improves the antibacterial performance of the membrane. This is because -NH$_2$ is easy to combine with H$^+$ to form -NH^{3+}. With the increase in deacetylation degree, -NH^{3+} increases, and the electrostatic attraction to bacteria (with negative charge) increases, leading to more bacteria being flocculated and concentrated, thus inhibiting the growth and reproduction of microorganisms. This also explains why the concentration of NH$_2$-POSS increases, and the inhibition zone of the membrane becomes larger, and the antibacterial performance becomes stronger.

3.5. Flame retardant performance test

The fire performance was tested by a calorific value meter, and a butane spray gun was used to conduct fire spraying tests on the wood surface with and without the CS membrane coating. The test results are shown in Table 1. The burn-through temperature of the raw wood in the control group (referring to the temperature when the wood is approximately burned through) was 201.8℃, and the burn-through temperature of CS film did not obviously increase. However, the test of the composite coating film was continued. It was found that when NH$_2$-POSS was added to 2%, the burning temperature of the wood increased more

than two times and the burning time was also improved compared with the control group, reflecting the superior flame retardant performance of the coating film.

4. CONCLUSION

Based on the above experiments, the hydrophobic properties and flame resistance of the wood with coating composite CS film with the addition of NH$_2$-POSS are gradually enhanced. These advantages increase the application of composite membranes in the wood products fields. And it was found in the experiment that when the amount of NH$_2$-POSS was higher than 5%, agglomeration would occur, which resulted in poor performance of the composite film. The experiment on antibacterial properties of the CS coating of wood showed that the wood surface has certain antibacterial properties, which can lay a foundation for the next research on functional wood paint.

ACKNOWLEDGMENTS

Forestry Promotion Institute) for its support.

REFERENCES

Caz, N.P., Vela, G., Ram, J.A. 2017. Polysaccharide -based Films and Coatings for Food packaging: A review. Food Hydrocolloids 68: 136-148.

Guan, C., Li, Z. 2020. Journal of Fire Science and Technology(in Chinese) 39(10): 1421-1424.

Ham, Y., Yang, J., Choi, W.S., Ahn, B.J., Park, M.J. 2020. Antibacterial Activity of Essential Oils from Pinaceae Leaves Against Fish Pathogens. Journal of the Korean Wood Science and Technology 48(4): 527-547.

Hao, F., Geng, W., Zhang, J., Liu, Q., Ding, B. 2019. Research progress of chitosan based flame retardant. Woolen Textile Science and Technology 47(2): 80-85.

Hu, L., Zhu, X., Yu, S., Jiang, C., Xu, H. 2020. Research progress of antimicrobial application of silver nanoparticles. Chinese Journal of Antibiotics 45(8): 745-750.

Lee, C., Jung, H., Chung, Y. 2021. Functional Characteristics of Nakdong Technique Treated on Paulownia Wood Surface. Journal of the Korean Wood Science and Technology 49(1): 82-92.

Li, S.N. 2019. Application of cage net structure phosphorus-containing POSS reactive flame retardant in epoxy resin. Hebei University.

Li, Z., Yang, L., Du, F., Yu, Z., Li, J. 2019. Preparation of antibacterial paper by chitosan/nano silver and its antibacterial effect. China's Paper Industry 38(8): 22-28.

Liu, C. W., Zhang, H.X. 2020. The effect of chitosan-based intumescent flame retardant/zinc borate on the properties of PE-HD. Plastics 49(6): 9-12.

Liu, L., Wu D., Wang, T. 2010. Research progress on antibacterial properties of chitosan and

development of antibacterial textiles. Acta Textile Sinica 31(7): 145-150.

Liu, Y., Li, M., Zhao, X., Zhang, R., Zhang, Y., Xing, Y. 2019. Preparation of nano-silver particles and its application in antibacterial coatings. New Chemical Materials 47(2): 37-41.

Park, S., Han, Y., Son, D.W. 2020. Flame Retardancy of Wood Products by Spreading Concentration and Impregnation Time of Flame Retardant. Journal of the Korean Wood Science and Technology 48(4): 417-430.

Park, S., Han, Y., Son, D.W. 2021. Flame Retardancy of Plywood Treated with Various Water Glass Concentration and Additives. Journal of the Korean Wood Science and Technology 49(1): 44-56.

Phil, T., Lee, B.H., Fabi, N. 2017. Current Status and New Perspectives on Chitin and Chitosan as Funtional Biopolymers. Applied Biochemistry and Biotechnology 181(4): 1314-1337.

Ren, Y.J. 2020. Preparation of chitosan microsphere bio-based flame retardant and its application in polylactic acid. Beijing University of Chemical Technology 2020.

Wen, M.Y., Zhu, J.Z., Zhu, M., Sun, Y.X, Park, H.J., Shi, J. 2020. Research on Flame Retardant Formaldehyde-Free Plywood Glued by Aqueous Polymer Isocyanate Adhesive. Journal of the Korean Wood Science and Technology 48(5): 755-764.

Xing, Y., Liu, Q., Jiang, Y. Guo, T., Yue, W., Xu, Q., Gou, J. 2018. Antimicrobial and physical properties of chitosan/nano TiO$_2$ composite coatings. Journal Of Xihua University (Natural Science Edition) 37(2): 34-39.

Yu, Z., Chen, F., Dong, W., Du, J. 2019. Research progress of antimicrobial mechanism of silver nanoparticles and its application in food storage. Food Industry Science And Technology 40(19): 305-309.

Yuan, Z.L. 2016. Study on the preparation and application performance of a new type of POSS flame retardant. Shanghai University of Engineering Science 2016.

Zhao, F.Y., Fu, Y.C. 2021. The effect of the number of assembled layers of chitosan/sodium phytate/nano-MgO composite coating on the flame retardant properties of wood. Furniture 42(2): 48-51.