Digest Journal of Nanomaterials and Biostructures Vol. 19, No. 4, October-December 2024, p. 1835-1845

Study on the surface sizing of modified chitosan and its effect on the properties of dialysis paper

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In order to improve the paper properties and enhance the utilization efficiency of functional chemical additives, surface sizing agents were prepared by combining water-soluble maleic anhydride acylated chitosan (MAAC), carboxymethylated chitosan (O-CMCS) and polyvinyl alcohol (PVA), and the effects of sizing process on the surface morphology, physical strength and antimicrobial properties of the dialysis paper were investigated. The results showed that when the coating weight was about 6.5 g/m^2 and the dosage of the modified chitosan was about 1.5% of the paper weight, the dry tensile strength, wet tensile strength and burst strength of paper sized with MAAC/PVA sizing agent increased by 46.5%, 82.2% and 107%, respectively, compared to that of unsized paper, while the dry tensile strength, wet tensile strength and burst strength of paper sized with O-CMCS/PVA sizing agent increased by 41.4%, 53.6% and 107%, respectively. In addition, the paper sized with MAAC/PVA and O-CMCS/PVA sizing agent displayed excellent antibacterial effect, which had the antibacterial rate against E. coli of 94.8% and 92.9%, respectively. In a word, the physical strength and antimicrobial properties of paper could be greatly improved by adding a small amount of modified chitosan (CS) to the surface sizing agent, and the strength improvement and antibacterial effect of MAAC/PVA sizing agent were better than that of O-CMCS/PVA.

(Received September 30, 2024; Accepted November 30, 2024)

Keywords: Dialysis paper, Modified chitosan, Surface sizing, Physical strength, Antimicrobial properties

1. Introduction

Medical dialysis paper is a sterilization protective packaging material for medical devices such as scalpels, tweezers, forceps, masks, medical protective clothing, etc., which must have good physical strength to ensure that it is not damaged during the process of the sterilization, transportation, storage and use [1, 2]. In order to improve the physical strength and other properties of medical dialysis paper, various functional chemical additives such as dry strength agents, wet strength agents, sizing agents and antibacterial agents were added into papermaking

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https://doi.org/10.15251/DJNB.2024.194.1835

pulp or applied to paper surface. Chitosan (CS) is a natural biopolymer material obtained from chitin by deacetylating with concentrated alkali solution [3-5]. It has important application value in biomedicine, environment, food, papermaking and other fields due to its good biocompatibility, biodegradability, antibacterial and antioxidant properties [6-8]. CS and its derivatives have the similar structure to that of plant cellulose, and its molecule contains active hydroxyl and amino groups [9-11], which can form hydrogen bonds with the hydroxyl groups of paper fibers. Moreover, CS also has good film-forming properties, so it is a potential reinforcing agent, surface sizing agent and antibacterial agent for paper [12]. However, CS is insoluble in water and can only be dissolved in dilute acid solution, which limits its application in the field of papermaking to a certain extent [13].

In our previous study, CS was modified by maleic anhydride and chloroacetic acid to prepare maleic anhydride acylated chitosan (MAAC) and carboxymethylated chitosan (O-CMCS), which showed good water solubility than chitosan [14,15]. When the prepared MAAC and O-CMCS were added to papermaking pulp, the dry and wet tensile strength of the dialysis paper were significantly improved when the dosage of MAAC was 2.0% and the dosage of O-CMCS was 2.5%, and the antibacterial rate of the dialysis paper against E. coli was more than 80%. MAAC and O-CMCS all had good function of improving the physical strength and antibacterial property of the dialysis paper [2, 16].

In general, functional chemical additives are easily lost with water during the papermaking process when they are added to papermaking pulp before they reach the forming wire of the papermaking machine, thereby reducing their efficiency and increasing their usage and cost. Surface sizing is carried out by applying a suitable coating to the surface of the dried paper, which minimizes the loss of the sizing agent [17]. Therefore, in this study, two kinds of surface sizing agents were prepared by the combination of water-soluble modified chitosan MAAC and O-CMCS with polyvinyl alcohol (PVA), and the effects of the sizing process on the dry and wet tensile strength, burst strength, antibacterial property and surface morphology of the dialysis paper were studied. The results of this study provided theoretical guidance for the application of modified chitosan in the surface sizing of the dialysis paper.

2. Experimental

2.1. Experimental materials

Maleic anhydride acylated chitosan (MAAC, Degree of substitution: 2.48, water solubility: 5.0 g/L, Laboratory self-made), carboxymethylated chitosan (O-CMCS, Degree of substitution: 0.57, water solubility: 12.4 g/L, Laboratory self-made), Polyvinyl alcohol (PVA, Degree of alcohololysis: 98.0-99.0 mol%, Shanghai Aladdin Biochemical Technology Co., LTD.), Bleached softwood kraft pulp (Moisture: 10.0%, Arauco, Chile), Bleached hardwood kraft pulp (Moisture: 10.0%, Aracruz Celulose S.A., Brazil), LB broth (Haibo Biotechnology Co., LTD., Qingdao High-tech Industrial Park.), LB agar (Hangzhou Base Biotechnology Co., LTD.), E. coli (China Institute of Veterinary Drug Control.).

2.2. Experimental method

2.2.1. Preparation and viscosity determination of surface sizing agent

A certain amount of PVA was mixed with deionized water to prepare a PVA solution with a concentration of 6%, stirred at 95°C for 2 h, then cooled to 50°C and set aside.

A certain amount of MAAC (or O-CMCS) was dispersed in PVA solution according to the mass ratio of 1:6, then a certain amount of water was added to make MAAC/PVA or O-CMCS/PVA surface sizing agent with a concentration of 3.5%, stirred at 60°C for 2 h and kept at 60°C for later use.

An NDJ-8S digital rotational viscometer was used to determine the viscosity of the PVA, MAAC/PVA and O-CMCS/PVA surface sizing agents at 25°C, the No. 1 rotor was chosen at a speed of 30 r/min.

2.2.2. Preparation of dialysis paper base paper

The softwood and hardwood pulp were mixed at a ratio of 6:4, and was beaten to 31±2 ºSR in a Valley beater. Paper with a basis weight of 60±2 $g \cdot m^{-2}$ was made in a laboratory standard paper former. The paper was processed at constant temperature and humidity according to the TAPPI T402 standard for 24 h and set aside.

2.2.3. Surface sizing process

The prepared surface sizing agent was applied to the surface of the dialysis base paper using a size press coater with a size roll at speed of 60 m/min. After surface sizing, the paper sample was placed in a plate dryer and dried at 105°C for 4 min, and the coating weight was measured after the paper was cooled. For each sample, surface sizing agent was applied to the surface of paper for four times to increase the total coating weight.

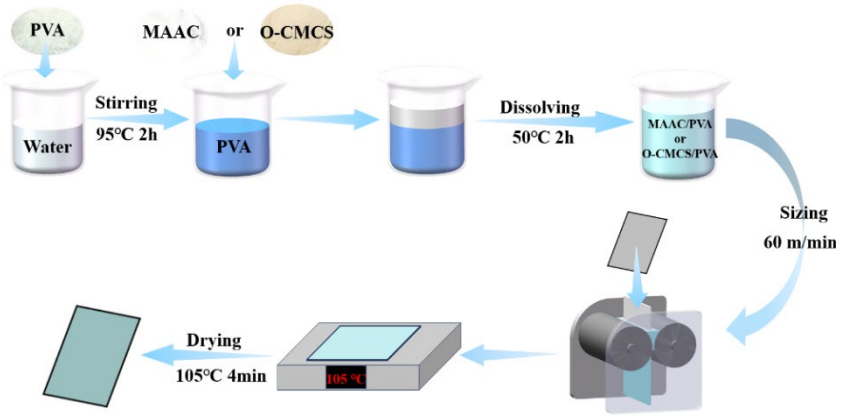


Fig. 1. Schematic diagram of surface sizing.

2.2.4. Scanning Electron Microscopy (SEM)

The SEM analysis of surface sized paper samples was performed using an SEM (SU1510, Hitachi, Japan) at an accelerating voltage of 15.0 kV, and the samples were sputter-coated with a thin layer of gold under vacuum to avoid charging during the examination.

2.2.5. Determination of physical properties

The dry and wet tensile strength of the paper samples were determined according to TAPPI 404 and TAPPI 456 protocols. The burst and tear strength of the samples were determined according to TAPPI 403 and TAPPI 414 protocols [2]. All these tests were repeated in triplicate.

2.2.6. Determination of antimicrobial properties

2.2.6.1. Preparation of LB culture medium

40 g LB agar was dissolved in 1000 mL deionized water and then 25 g LB broth was added to the solution to prepare LB culture medium. The pH of the LB culture medium solution was adjusted to neutral and then was sterilized in an autoclave at temperature of 121°C for 30 minutes. After the culture medium was cooled to 40~50°C, it was poured into a 90 mm Petri dish, and stored at 0°C for later use [18].

2.2.6.2. Shaking flask test

The antimicrobial performance of the surface sized paper was evaluated by shake flask test using E. coli as a model of biological contamination according to standard WS/T 650-2019. 0.75 g paper sample was cut into 1.0 cm×1.0 cm and placed in a 250 mL conical flask, then 70 mL of LB liquid medium was added and the mixture was sterilized in an autoclave for 30 min. After 24 h, 5 mL E. coli suspension (1×10^4-5×10^4 CFU/mL) was added, then the conical flask was fixed on a shaking table and shaken for 1 h at 250 r/min, and 1 mL of the suspension was taken and dilute 10 times for later use. 40 μL of the diluted suspension was evenly spread on a 90 mm solid medium and incubated at 37℃ for 24 h in a microbiological incubator. Finally, the photographs of solid medium were taken and the number of bacterial colonies were quantitatively analyzed by Colony Counter app (Madison, WI, US). The bacteriostatic rate X of paper samples was calculated according to the formula (1) [19]:

$$X = \frac{A-B}{A} \times 100\% \quad (1)$$

where A was the average number of colonies for unsized paper samples and B was the number of colonies for sized paper samples.

3. Results and discussion

3.1. Effects of sizing agent and times of surface sizing on the coating weight

It can be seen from Fig. 2(a) that the viscosity of PVA sizing agent (6%) was 25.4 mPa·s, while that of MAAC/PVA sizing agent (3.5%) and O-CMCS/PVA sizing agent (3.5%) were 28.2 mPa·s and 31.0 mPa·s, respectively. The combination of PVA and modified chitosan increased the viscosity of the sizing agent, because the viscosity of PVA was lower than that of modified chitosan. The viscosity of O-CMCS/PVA sizing agent was higher than that of MAAC/PVA at the same concentration, this was mainly due to the high solubility of O-CMCS in the compound sizing agent. The size press pickup (coating weight) on paper surface gradually increased with the increase of the times of surface sizing, and the coating weight of pure PVA was generally higher

than that of compound sizing agent, which was mainly caused by the high solid content in PVA sizing agent. The coating weight of first coat of O-CMCS/PVA was higher than that of PVA and MAAC/PVA, because O-CMCS/PVA had the greater viscosity than PVA and MAAC/PVA, more sizing agent was adhered to the surface of paper due to its strong adhesion. It should be noted that the coating weight did not increase proportionally with the times of surface sizing, because that the prime coat changed the state of the paper surface and affected the adsorption and fixation of sizing agent.

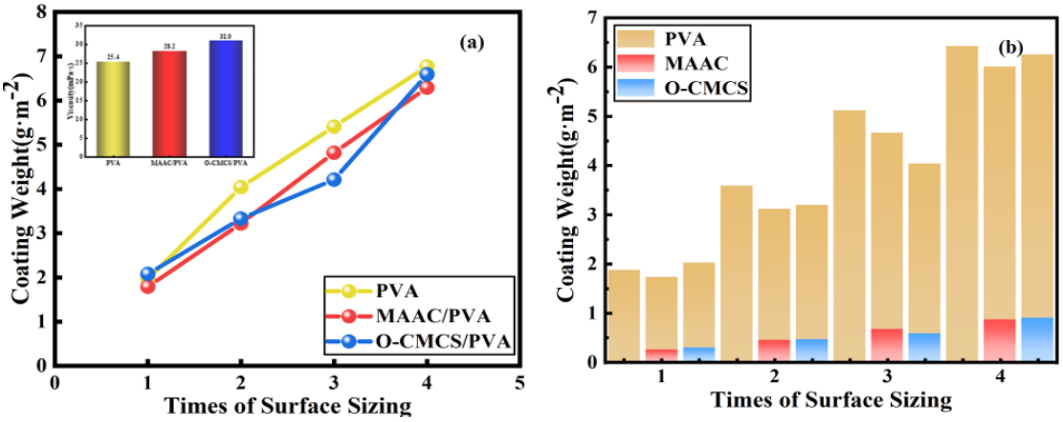
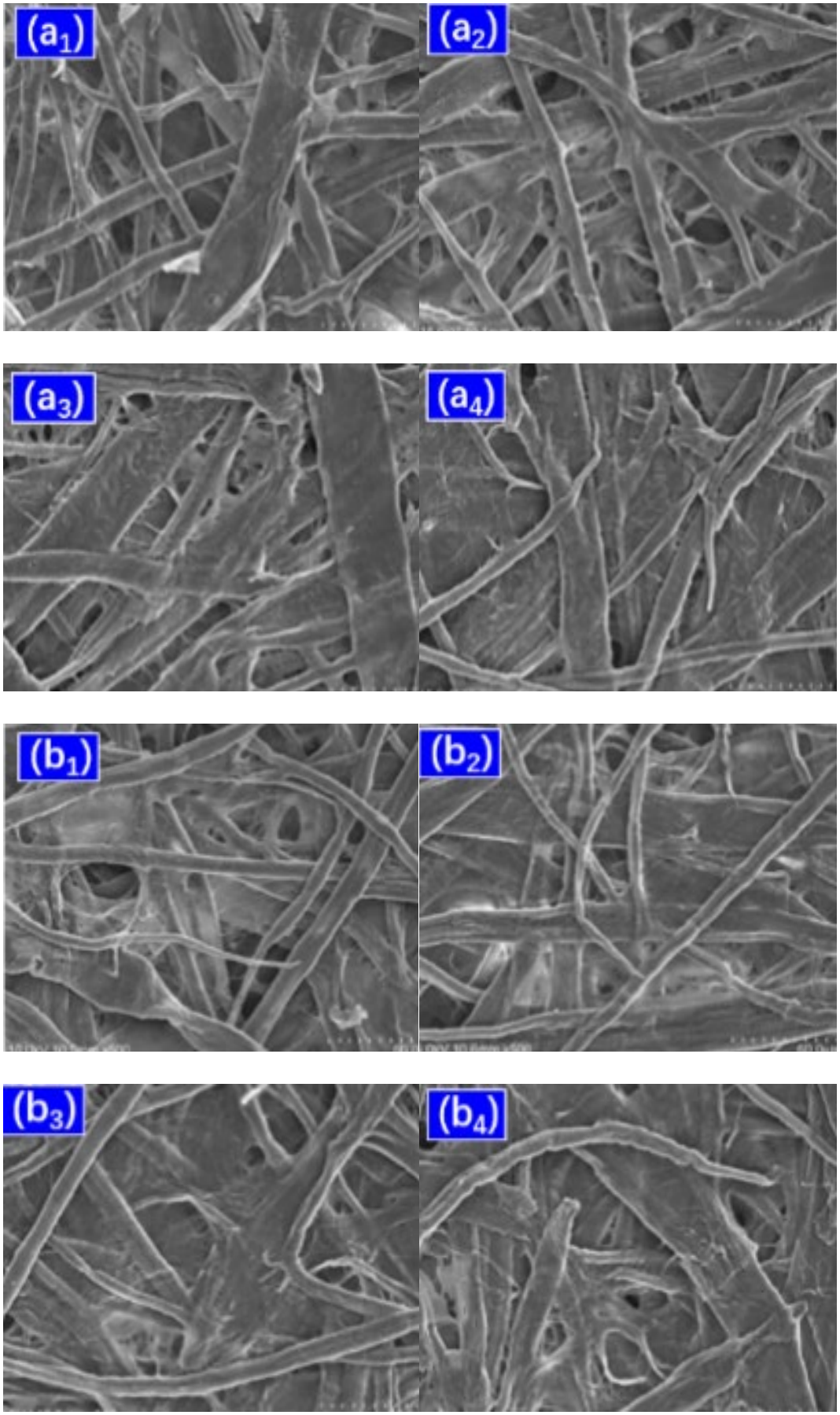


Fig. 2. The effect of sizing agent viscosity and times of surface sizing on the size press pickup (a) coating weight，(b) coating components.

3.2. Effect of surface sizing on paper surface micromorphology

SEM images of the surface sized paper with different sizing agents and different times of surface sizing were shown in Fig. 3. The a_1, a_2, a_3, and a_4 were the pure PVA surface sized paper which was sized by once, twice, three and four times, respectively. The b_1, b_2, b_3, and b_4 were the MAAC/PVA surface sized paper, and the c_1, c_2, c_3, and c_4 were the O-CMCS/PVA surface sized paper. It could be seen that the paper samples after the first surface sizing (a_1, b_1, and c_1) were looser and had larger pore sizes, and the surface of the paper samples became denser and the pore size became smaller with the increase of times of surface sizing. When the paper sample was surface sized for four times (a_4, b_4, and c_4), the size press pickup was about 6.5 g/m^2, the surface of paper was very smooth and dense, and there was almost no pore on the surface of paper. A large amount of sizing agent filled the pore between fibers and formed a thin film on the surface of paper [20]. There was no significant difference between the surface sized paper with different sizing agent, because MAAC and O-CMCS had good solubility and formed gels in solution rather than simple precipitation, which made them very effective in improving inter-fiber bonding [21].


(a1)
(a2)
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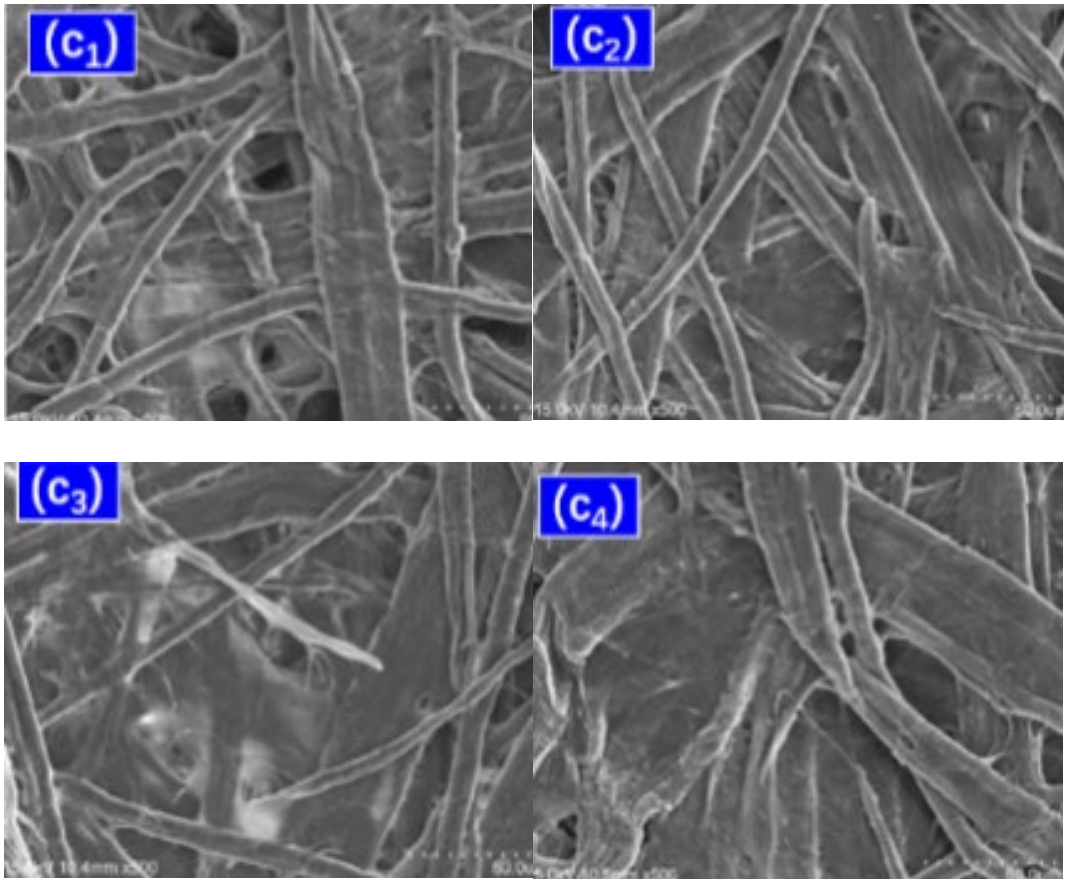

Fig. 3. SEM images of the surface sized paper (×500) a_1, a_2, a_3, a_4 pure PVA surface sized paper; b_1, b_2, b_3, b_4 MAAC/PVA surface sized paper; c_1, c_2, c_3, c_4 O-CMCS/PVA surface sized paper; a_1, b_1, c_1 surface sized once; a_2, b_2, c_2 surface sized twice; a_3, b_3, c_3 surface sized three times; a_4, b_4, c_4 surface sized four times.

3.3. Effect of surface sizing on the tensile strength of paper

The effects of surface sizing on the tensile strength of the paper were shown in Fig. 4. It could be seen that the dry and wet tensile indices of papers sized with MAAC/PVA and O-CMCS/PVA all increased with the increase of coating weight. PVA surface sizing improved the dry tensile strength of paper, but it had almost no effect on the wet tensile strength of paper due to the good water solubility of PVA. When the coating weight was about 6.5 g/m^2, the dry tensile index of papers sized with PVA, MAAC/PVA and O-CMCS/PVA increased by 28.4%, 46.5% and 41.4%, respectively, and the wet tensile strength increased by -2.22%, 82.2%, and 53.6%, respectively. The improvement of MAAC/PVA surface sizing agent on the tensile strength of paper was greater than that of O-CMCS/PVA, and this might be due to the lower viscosity of the MAAC/PVA sizing agent, which accelerated its diffusion and deposition between paper fibers, thereby enhancing the fiber-to-fiber bonding strength [21]. Furthermore, the carboxyl groups in the MAAC molecule were esterified with the hydroxyl groups on the fiber to form ester bond, which was stable in water, thereby increasing the wet tensile strength of paper [22].

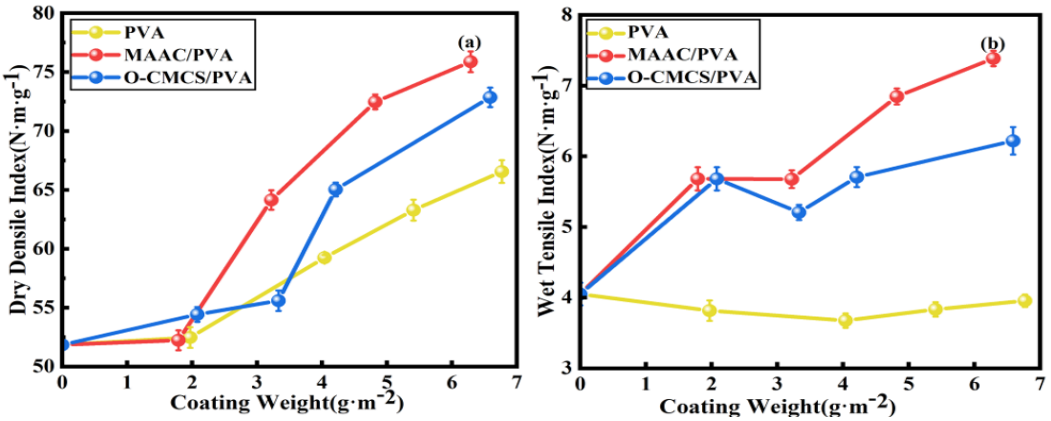

Fig.4. The effect of surface sizing on the tensile strength of paper (a) dry tensile index and (b) wet tensile index.

3.4. Effect of surface sizing on the burst strength and tear strength of paper

As can be seen from Fig. 5(a), the burst index of the papers sized with PVA, MAAC/PVA and O-CMCS/PVA all increased with the increase of coating weight, and the burst strength of the papers sized with MAAC/PVA and O-CMCS/PVA were higher than that of paper sized with the pure PVA. When the coating weight was about 6.5 g/m^2, the burst index of paper surface sized with PVA, MAAC/PVA and O-CMCS/PVA increased by 61.7%, 107% and 107%, respectively. It can be seen from Fig. 5(b) that the tear strength of paper surface sized with PVA, MAAC/PVA and O-CMCS/PVA all decreased to some extent, because that surface sizing increased the stiffness of paper and resulted in the decrease of its tear strength. When the coating weight was about 6.5 g/m^2, the tear indices of papers surface sizing with PVA, MAAC/PVA and O-CMCS/PVA were 14.4 mN·m^2/g, 10.8 mN·m^2/g, and 10.9 mN·m^2/g, respectively.

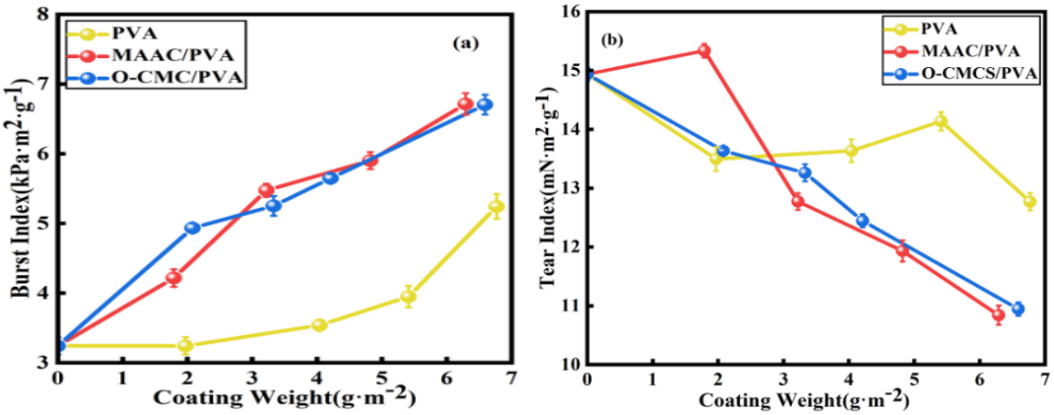

Fig. 5. The effect of surface sizing on the burst strength and tear strength of paper (a) burst index and (b) tear index.

3.5. Effect of surface sizing on the antimicrobial property of paper

In Fig. 6, blank group referred to the unsized paper. The unsized paper and paper sized with 6.5 g/m^2 PVA had no antimicrobial performance. However, when MAAC/PVA and O-CMCS/PVA were used as the surface sizing agents, and the coating weight was about 6.5 g/m^2 (the percent of MAAC to paper weight was about 1.5%), the antimicrobial rate of paper achieved 94.8% and 92.9%, respectively, which were even better than that of papers made from pulp containing 2.0% MAAC and 2.5% O-CMCS. This demonstrated that the antimicrobial performance of paper mainly came from the modified CS, and modified CS used as surface sizing agent was superior to it was used in pulp [23].

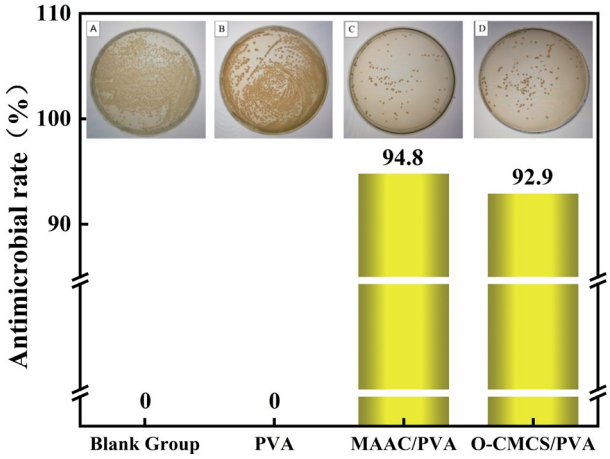

Fig. 6. Antimicrobial rate of papers (Blank Group, PVA sized paper, MAAC/PVA sized paper, O-CMCS/PVA sized paper).

4. Conclusions

The MAAC/PVA and O-CMCS/PVA surface sizing agents were prepared by the combination of MAAC and O-CMCS with PVA according to the mass ratio of 1:6, and the effects of the types of surface sizing agent and the times of surface sizing on the properties of sized paper were investigated. The results showed the surface sizing with MAAC/PVA and O-CMCS/PVA effectively increased the dry tensile strength, wet tensile strength, burst strength and antibacterial property of paper.

When the paper was surface sized for four times, the coating weight reached about 6.5 g/m^2, and the dry, wet tensile and burst strength of the paper surface sized with MAAC/PVA increased by 46.5%, 82.2% and 107%, respectively, while the dry, wet tensile and burst strength of the paper surface sized with O-CMCS/PVA increased by 41.4%, 53.6% and 107%, respectively. Meanwhile, the antibacterial rate of paper surface sized with MAAC/PVA and O-CMCS/PVA achieved 94.8% and 92.9%, respectively. In a word, surface sizing of paper with modified CS is a better way to improve the physical strength and antibacterial property of dialysis paper, and MAAC/PVA surface sizing agent is better than O-CMCS/PVA surface sizing agent overall, and the result of this study provides theoretical guidance for the selection and application of modified chitosan in the preparation of medical dialysis paper.

Acknowledgments

The authors are thankful to the support of the "Pioneer" and "Leading Goose" R&D Program of Zhejiang (Grant No. 2023C01195, 2024C03119), the Fundamental Research Funds for Zhejiang University of Science and Technology (Grant No. 2023QN048, 2023JLZD006).

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