Fully Bio-Based Chitosan/Sodium Alginate Coating for Flame Retardant Xuan Paper

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The development of bio-based flame retardants has received increasing attention. In this study, fully bio-based chitosan/sodium alginate (CS/SA) coating was applied by layer-by-layer (LbL) assembly on Xuan paper to improve its flame retardancy. The LOI value of Xuan paper reached 33.3% after 20 BLs CS/SA coating. Its char length was reduced to 8.8 cm with no after-flame and after-glow. These results showed that the flame retardancy of Xuan paper was greatly improved by LbL assembly CS/SA coating. Thermogravimetry results revealed that CS/SA coating on Xuan paper slowed down the thermal degradation process and promoted the char formation both under nitrogen and air atmosphere. The stable char layer formation by CS/SA coating covered on the Xuan paper inhibited the heat transfer and diffusion of combustible gases, showing obvious condensed phase flame retardant action. Scanning electron microscopy confirmed that CS/SA coating on paper fiber promoted the char formation to form the stable covering layer. Furthermore, the CS/SA coating formed non-flammable gases to enhance the flame retardancy of Xuan paper, showing a certain gas phase flame retardant action. This research provides a new approach for fire-resistant Xuan paper by using fully bio-based compounds.

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Keywords: Xuan paper; Fire-resistant; Bio-based; Chitosan; Sodium alginate

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INTRODUCTION

As a famous traditional Chinese handmade paper, Xuan paper is widely used for Chinese calligraphy and painting (Gao *et al*. 2016; Wu *et al*. 2016). Xuan paper has the reputation of being the “paper king lasting over a thousand years”, and it is the preferred paper type for conservation of precious paper-based artifacts (Tang and Smith 2013; Luo *et al*. 2021). The traditional handicraft of making Xuan paper was included in the UNESCO Intangible Cultural Heritage of Humanity in 2009 (UNESCO 2009).

Unfortunately, the high flammability of Xuan paper makes it a potential fire hazard. Numerous precious paper-based art treasures have been destroyed by fire (Dong and Zhu 2018). The Brazil National Museum Fire in 2018 and the huge fire at Paris Notre Dame Cathedral in 2019 brought about huge losses. Therefore, it is important to improve the flame retardancy of paper. Xuan paper with inherent flame retardancy would reduce the fire hazards of precious artworks (Xu *et al.* 2019; Zhang *et al.* 2020a,b).

At present, many methods have been used to improve the flame retardancy of paper, including impregnation, surface coating of paper with flame retardants, and adding flame retardants to paper stock (Sha and Chen 2016; Yang *et al.* 2017; Pan *et al.* 2018). However, the impregnation method reduces the mechanical strength, dimensional stability, and moisture resistance of paper. The surface coating method influences the hand feel of the paper due to the large amount of organic adhesives that are used (Wang *et al.* 2017a). Thus, adding flame retardants into paper stock during the paper making process is the most widely used way to improve the flame retardancy, and inorganic flame retardants are the most widely used for this method. Wang *et al*. (2019a) used Mg-Al hydrotalcites for preparing flame retardant paper by co-precipitation on the paper stock. Nassar *et al.* (1999) investigated the flame retardant treatment of wood pulp paper using inorganic sodium silicate and sodium borate. Ammonium polyphosphate (APP) has been used also (Sha and Chen 2014; Yang *et al.* 2016). Inorganic flame retardants have been studied extensively for fire-resistant paper, but in large amounts, they have adverse effects on the physical properties of paper (Wang *et al.* 2019b).

Flame retardants that are high-efficiency organic halogen-based and phosphorus-based have been used for paper (Gao *et al.* 2005). However, these flame retardants may cause severe environmental pollution and human damage. Halogen flame retardants produce dioxin and other toxic gases during combustion, so they have been forbidden (Fang *et al*. 2017a,b). Therefore, the development of efficient, eco-friendly flame-retardants is urgent.

In response to this need, bio-based flame retardants have received increasing attention. Chitosan (CS) is the second largest bio-based polymer and a renewable natural cationic polysaccharide, and it has been studied extensively in the flame-retardant field (Sheikh and Bramhecha 2018). Cationic CS can be combined with anionic flame-retardant agents such as phytic acid (Laufer *et al.* 2012; Magovac *et al.* 2020), APP (Fang *et al.* 2019), poly(sodium phosphate) (Mateos *et al.* 2014), and poly(vinylphosphonic acid) (Köklükaya *et al.* 2015) to form an intumescent flame-retardant system by the layer-by-layer (LbL) assembly method. The LbL assembly method has been studied for fabricating flame-retardant coating (Qiu *et al.* 2018), due to its cost-effective nature and versatile qualities. In addition, this method has a smaller influence on the substrate than other methods. Sodium alginate (SA) is a bio-based anionic polysaccharide that is widely used in the field of food, textile printing, and biomaterials (Xu *et al.* 2021). SA possesses inherent flame retardancy (Liu *et al.* 2016). The positively charged CS can combine with negatively charged SA through electrostatic attraction as a polyelectrolyte complex to form coating on the matrix surface (Kundu *et al.* 2017).

In this paper, a bio-based CS/SA flame retardant coating was fabricated on Xuan paper surface by the LbL assembly method. The flame retardancy of Xuan papers coated by different BLs of CS/SA coating was determined. The flame retardant mechanism of CS/SA coated Xuan paper was determined by thermogravimetric analysis (TGA) and scanning electron microscopy (SEM).

EXPERIMENTAL

Materials and Chemicals

Xuan paper (38 g/m^2) was purchased from Anhui Yuchen Paper Co., Ltd. (Anhui, China). Chitosan (CS, degree of deacetylation was higher than 90%, viscosity: 50 to 800 mPa·s) and sodium alginate (SA, viscosity: 200±20 mPa·s) were purchased from Aladdin reagent Co., Ltd (Shanghai, China). Concentrated hydrochloric acid (HCl) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

Flame Retardant Treatment of Xuan Paper

A certain amount of CS was put into the deionized water, which was adjusted to pH 4 by concentrated HCl solution, and the mixture was stirred for 24 h to prepare 1 wt% CS solution. A certain amount of SA was added into the deionized water, which was stirred for 2 h to prepare 0.5 wt% SA solution.

Xuan paper was immersed into the CS solution for 5 min, rinsed with deionized water for 1 min, and oven-dried at 60 °C for 1 h. After that, the Xuan paper was immersed into the SA solution for 5 min, rinsed with deionized water for 1 min, and oven-dried at 60 °C for 1 h to finish one bilayer (BL) of CS/SA coating. The Xuan papers were alternately immersed into CS and SA solution to repeat the layer-by-layer assembly process to reach 1, 5, 10, 15, and 20 BL CS/SA coatings, which were named X-CS-1, X-CS-5, X-CS-10, X-CS-15, and X-CS-20, respectively. The LbL assembly process of flame-retardant Xuan paper is shown in Fig. 1. The add-on of Xuan papers with different bilayers CS/SA coating was calculated by Eq. 1,

$$add - on\ (\%) = \frac{m - m_0}{m_0} \times 100\% \quad (1)$$

where the m_0 is the mass of the uncoated Xuan paper, and the m is mass of Xuan paper coated with different CS/SA BLs.

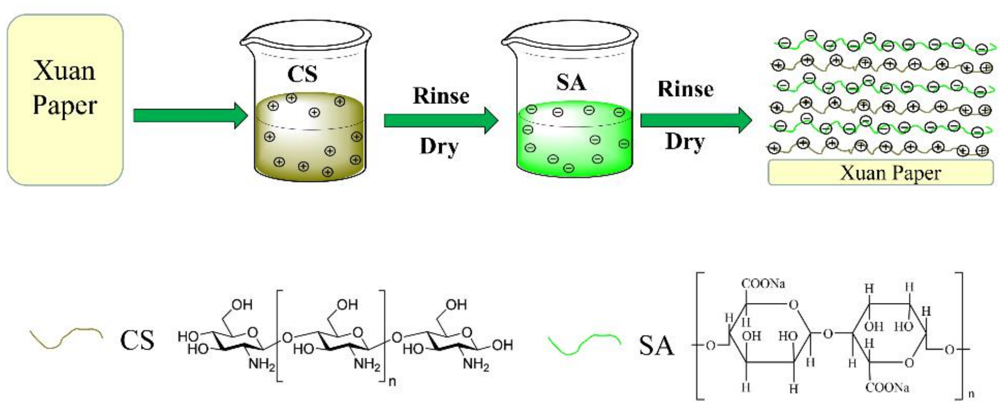

Fig. 1. Schematic representation of the LbL assembly CS/SA coating on Xuan paper

Characterization

The flame retardancy of Xuan paper before and after treatment was determined by the limiting oxygen index (LOI) and the vertical burning test. LOI value was determined according to the ASTM D2863 (2006) on a JF-3 oxygen index instrument (Jiangning Analysis Instrument, Nanjing, China). The vertical burning test was conducted according to ASTM D6413 (2008) on YG(B)815D-I flame retardant performance tester (Wenzhou Darong, Wenzhou, China). Thermal stability of Xuan paper before and after treatment was investigated on a DTG-60H thermal analyzer (Shimadzu, Kyoto, Japan) from room temperature to 700 °C with a heating rate of 10 °C/min under both nitrogen and air atmosphere. The morphology of Xuan paper and char residues were viewed by a Hitachi S-4800 scanning electron microscope (Hitachi Limited, Tokyo, Japan).

RESULTS AND DISCUSSION

SEM Images of Xuan Paper

The surface morphology of the Xuan paper before and after coating of CS/SA was viewed by SEM, as shown in Fig. 2. The surface of coated Xuan papers changed compared with the uncoated one (X-0). The pulp fibers of the uncoated Xuan paper were clearly visible, and the surface of uncoated Xuan paper fiber was clean and smooth. The surface of LbL assembly coated Xuan paper was covered by CS/SA coating, and the area of the coating layer on paper fiber increased with the BLs. The shape of the pulp fibers was obvious when the Xuan paper was assembled by the LbL process and coated by 10 BLs CS/SA. However, the pulp fiber could not been seen when the paper was coated by 20 BLs CS/SA. As shown in Fig. 2d-g, the cross section images of Xuan paper before and after coating with CS/SA showed the layer-by-layer structure. And the thickness of Xuan paper was slightly influenced by the CS/SA coating. Thus, the CS/SA coating had formed on Xuan paper fibers surface.

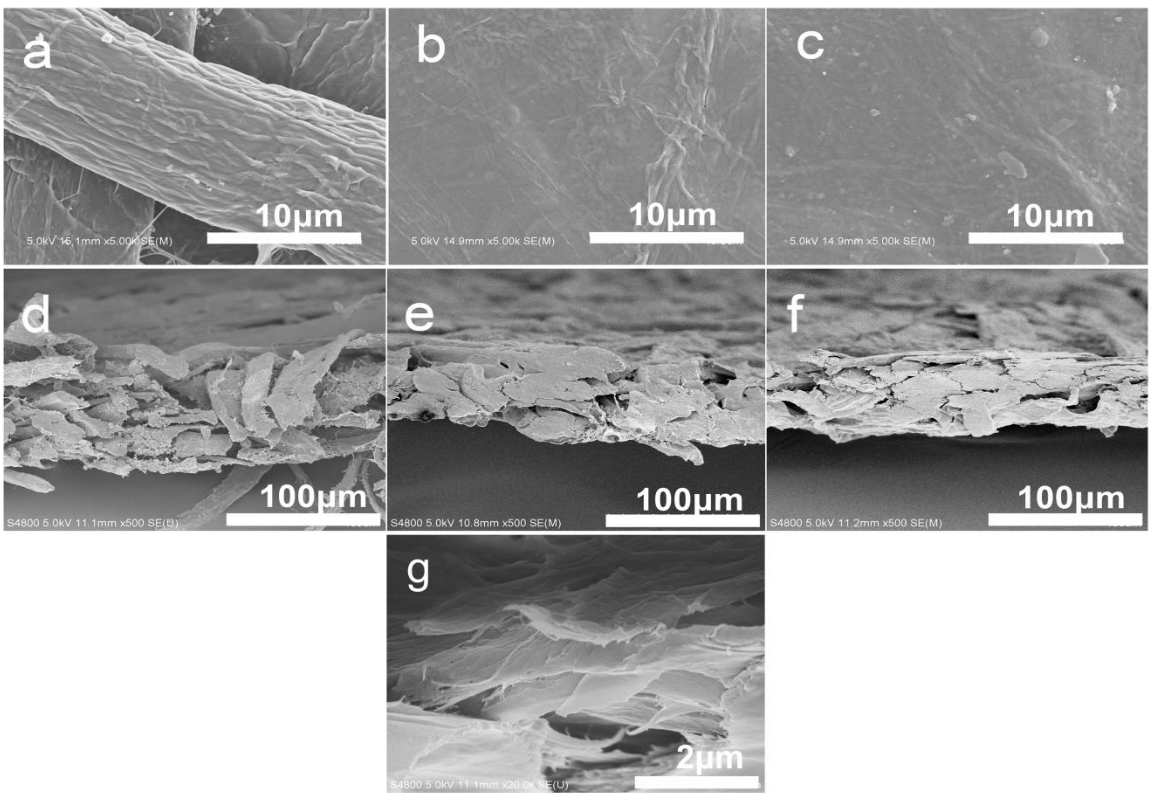

Fig. 2. The surface morphology of Xuan paper before and after coating (a) X-0, (b) X-CS-10, (c) X-CS-20, and cross section (d) X-0, (e) X-CS-10, (f) X-CS-20, (g) X-CS-20with high magnification

Flame Retardancy of Xuan Paper

The LOI values and vertical burning test of Xuan papers before and after coating are shown in Table 1. The photographs of Xuan papers after vertical burning test are shown in Fig. 3. The flame retardancy of Xuan papers after LbL assembly CS/SA coating was improved. The LOI value of uncoated Xuan paper was only 18.0%, while it increased with the CS/SA BLs. The add-on of CS/SA coating also increased with the BLs. The LOI value of X-CS-5 was 23.7% when Xuan paper was coated with 5 BLs CS/SA to obtain the add-on of 19.3%. The LOI value reached 30.6% of X-CS-10 when it was coated by 10 BLs CS/SA coating with the add-on of 38.0%. The add-on of Xuan paper reached to 110.5% when it was coated by 20 BLs CS/SA, and its LOI value reached to 33.3%.

In the vertical burning test, the results also revealed that the flame retardancies of coated Xuan papers were enhanced. The uncoated Xuan paper was burned out, and its after flame time and after-glow time were 7.6 s and 24.5 s, respectively. When the Xuan paper was coated by 5 BLs CS/SA, both the after-flame time and after-glow time were reduced to 0 s, though the Xuan paper was burned out. The char length of X-CS-10 was greatly reduced to 11.2 cm, and its after-flame time and after-glow time were 0 s. The char length of X-CS-15 and X-CS-20 decreased further to 9.5 cm and 8.8 cm, respectively. The photographs of Xuan papers after vertical burning test are shown in Fig. 3. These results showed the char length of Xuan papers decreased with the increasing CS/SA BLs. Therefore, the flame retardancy of Xuan paper was improved after LbL assembly CS/SA coating.

The LbL assembly method is a simple method, but it is also time consuming, and this restricts its industrialization. However, the optimization of the Xuan paper making process by adding chitosan and sodium alginate in the process of manual or mechanical paper making will promote its further industrial application.

Table 1. Flame Retardancy of Uncoated and Coated Xuan Papers

Sample	Add-on (%)	LOI (%)	Vertical Burning Test		
			Char length (cm)	After-flame time (s)	After-glow time (s)
X-0	-	18.0	Burn out	7.6	24.5
X-CS-1	2.6	20.3	Burn out	0	2.4
X-CS-5	19.3	23.7	Burn out	0	0
X-CS-10	38.0	30.6	11.2	0	0
X-CS-15	82.2	31.4	9.5	0	0
X-CS-20	110.5	33.3	8.8	0	0

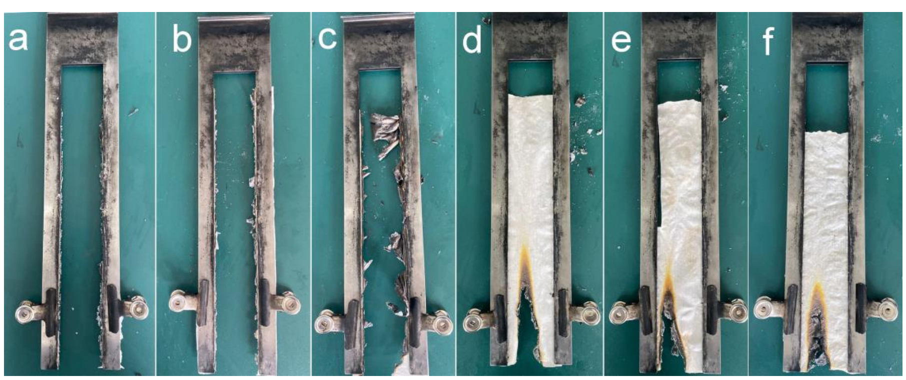

Fig. 3. The photographs of the uncoated and coated Xuan paper after vertical burning testing (a) X-0, (b) X-CS-1, (c) X-CS-5, (d) X-CS-10, (e) X-CS-15 and (f) X-CS-20

Thermal Stability of Xuan Paper

The TG and DTG curves of Xuan papers before and after coating are shown in Fig. 4, and the TGA data are given in Table 2. As shown in Fig.4, there existed obvious mass loss around 100 °C no matter under nitrogen or air atmosphere belonging to the loss of the absorbed moisture water. The results showed that the CS/SA coating possessed a strong ability of absorbing moisture due to the ionic groups in both alginate and chitosan. As shown in Fig. 4a, the uncoated Xuan paper showed only one mass loss stage under nitrogen atmosphere, while the coated Xuan papers showed two mass loss stages. The onset degradation temperature of coated Xuan papers decreased with the CS/SA BLs. The T-10% was reduced to 190 °C of X-CS-10 and 180 °C of X-CS-20 compared with 315 °C of the uncoated one. The lower degradation temperature of CS and SA resulted in the lower initial degradation temperature of Xuan paper (Liu and Xiao 2018). The mass loss rate at the T_{max} of coated Xuan papers decreased with CS/SA BL number. These results showed that CS/SA coating could slow down the thermal degradation of Xuan paper. The char residues of X-CS-10BL and X-CS-20BL at 700 °C were 5.92% and 12.82%, respectively, compared with 3.22% of uncoated paper, thus revealing that the CS/SA coating on Xuan paper fiber formed stable char under nitrogen atmosphere.

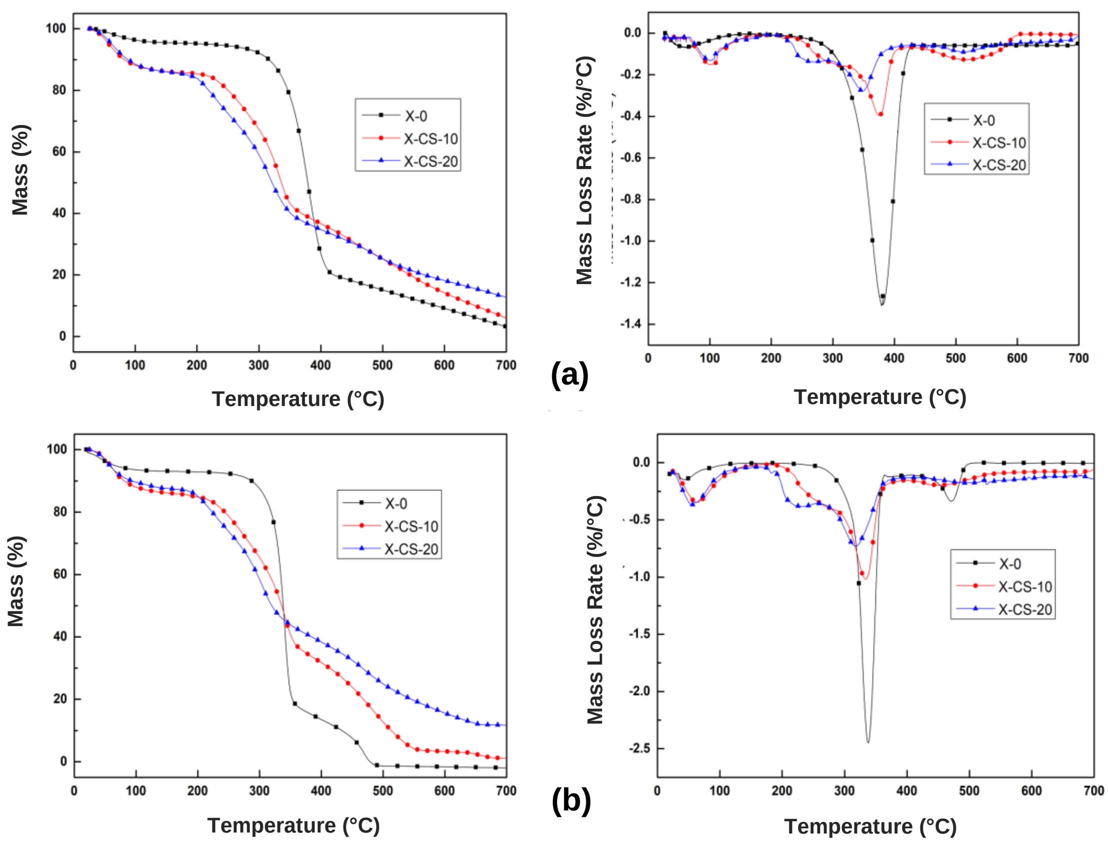

Fig. 4. TG and DTG curves of uncoated and coated Xuan papers (a) under nitrogen (b) air atmosphere

Both the uncoated and coated Xuan papers showed two mass loss stages under air atmosphere, as shown in Fig. 4b and Table 2. The onset degradation temperature of coated Xuan paper was lower than the uncoated one, which may be the same reason with that under nitrogen atmosphere. The mass loss rate at the T_{max} of the two stages also decreased with the CS/SA BLs under air atmosphere. The char residues of X-CS-10BL and X-CS-20BL at 700 °C were 2.08% and 11.71%, while there was no char residue of uncoated paper. These results also demonstrated that the CS/SA coating could form the stable char layer under air atmosphere.

Table 2. TGA Data of Uncoated and LbL Assembly Coated Xuan Paper under Nitrogen and Air Atmosphere

Atmosphere	Samples	$T_{-10\%}$ (°C)	Stage 1		Stage 2		Residue at 700 °C (wt%)
			T_{max} (°C)	The mass loss rate at T_{max} (%/°C)	T_{max} (°C)	The mass loss rate at T_{max} (%/°C)	
N_2	X-0	315	382	1.30			3.22
	X-CS-10	190	372	0.40	526	0.13	5.92
	X-CS-20	180	350	0.28	520	0.09	12.82
Air	X-0	287	340	2.45	470	0.33	0
	X-CS-10	185	333	1.02	465	0.20	2.08
	X-CS-20	170	317	0.73	480	0.17	11.71

$T_{-10\%}$ is the onset degradation temperature defining as the temperature of 10 wt% mass loss; T_{max} is the temperature of maximum mass loss rate.

Therefore, LbL assembly coated Xuan paper with CS/SA could slow down the thermal degradation process of Xuan paper and form stable char layer both under nitrogen and air atmosphere. The self-flame retardant sodium alginate improved the thermal stability of Xuan paper (Liu *et al.* 2022). The CS/SA coating formed a stable char layer covering on the Xuan paper surface, thus inhibiting the heat transfer and diffusion of combustible gases showing obvious condensed phase flame retardant action.

Morphology of the Char Residues

The CS/SA coating formed a stable char layer on Xuan paper, which was confirmed by the SEM images of char residues of Xuan papers after vertical burning test, as shown in Fig. 5.

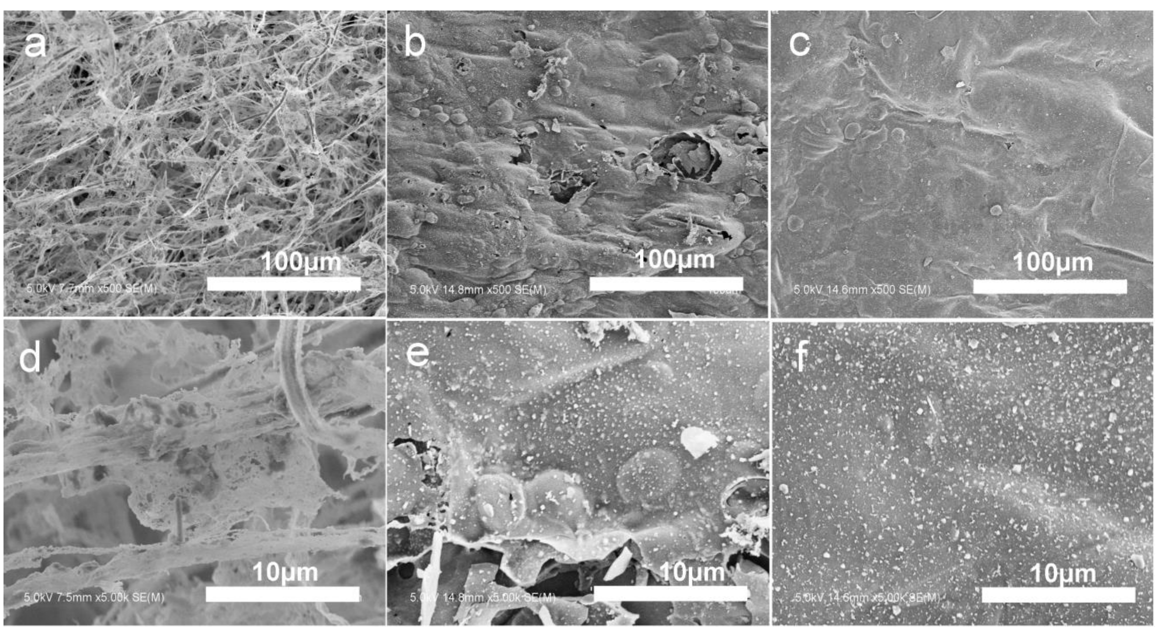

Fig. 5. Morphology of char residuals of uncoated and coated Xuan papers with low magnification (×500) (a) X-0, (b) X-CS-10, (c) X-CS-20, and high magnification (×5000) (d) X-0, (e) X-CS-10, (f) X-CS-20.

The uncoated Xuan paper after burning formed unstable ash, but not char. The CS/SA coated Xuan paper formed a stable char layer. The covering char layer became thicker and more intact with the increasing of the CS/SA BLs. These results confirmed that the CS/SA coated Xuan paper formed a stable covering layer on Xuan paper. These stable covering char layers inhibit the combustible gas diffusion and blocking heat transmission (Li *et al.* 2022a). The SEM images also showed bubbles on the char layer surface. These bubbles have been attributed to the nitrogen element in chitosan, which could form non-flammable nitrogen-containing gases (Li *et al.* 2022b). These results showed that the CS/SA coating formed non-flammable gases to enhance the flame retardant properties of Xuan paper.

CONCLUSIONS

1. Fully bio-based chitosan/sodium alginate (CS/SA) coating was assembled layer-by-layer (LbL) on Xuan paper to improve its flame retardancy. The scanning electron microscopy (SEM) results of coated Xuan paper confirmed the presence of the CS/SA coating.
2. The lower oxygen index (LOI) value of Xuan paper increased with the number of CS/SA bilayers (BLs), which reached 33.3% after being coated by 20 BLs CS/SA. The vertical burning properties of coated Xuan papers were also improved. The char length of X-CS-10 was greatly reduced to 11.2 cm even when it was coated by 10 BLs CS/SA, and its after-flame time and after-glow time were 0 s. The char length of X-CS-20 that was coated by 20 BLs CS/SA continued to decrease to 8.8 cm. Therefore, these results demonstrated that the flame retardancy of Xuan paper could be greatly improved by LbL assembly CS/SA coating.
3. Thermogravimetric analysis (TGA) results revealed that LbL assembly CS/SA coating could slow down the thermal degradation process of Xuan paper and form stable char under nitrogen and air atmosphere. The stable char layer formation by CS/SA coating covered on the Xuan paper was able to inhibit the heat transfer and diffusion of combustible gases, showing obvious condensed phase flame retardant action. SEM images of Xuan paper char residues further confirmed that the coated Xuan paper by CS/SA coating on paper fiber promoted the char formation to form the stable covering layer. They also confirmed that CS/SA coating could form non-flammable gases to further enhance the flame retardant property of Xuan paper showing a certain gas phase flame retardant action. This research would provide a new approach for the fire-resistant Xuan paper by using fully bio-based compounds.

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