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Preparation and Oil-Resistant Mechanism of Chitosan/Cationic Starch Oil-Proof Paper

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Safe and environmentally friendly oil-resistant packaging paper is strongly desired in the food packaging industry. In the present work, chitosan (CTS) and chitosan/cationic starch (CTS/CS) coated papers were prepared and characterized. The results indicated that both the CTS and CTS/CS coated papers were highly oil resistant, and their oil resistance was increased with an increase in coating weight. The CTS/CS composite showed better thermal stability and water resistance than CTS. Paper coated with the CTS/CS composite containing 1:2 CTS to CS achieved an oil resistance level as required for food packaging. The mechanism of CTS/CS oil resistance, which has not been reported, was investigated by SEM, HPLC and particle size analyzer. The high oil resistance of the CTS/CS-coated paper was attributed to the formation of a film on the surface of the paper and the electrostatic binding between CTS and fatty acid to prevent oil from permeating and transferring.

INTRODUCTION

Paper packaging is in demand in the food packaging industry because of its environmentally friendly properties and other advantages. Ordinary paper materials have excellent physical and mechanical properties, but poor oil resistance and gas barrier capability. Therefore, special processes or additives are usually used to improve their oil resistance properties. Multi-layer composites of metal and plastic, such as vacuum aluminum and plastic coating on the surface of paper, have also been used to obtain dense oil-proof coatings (Crosby 1981). However, vacuum aluminum coating can greatly reduce gas permeability (Matsuo and Yamabe 1994), and the plastic component is extremely difficult to degrade and is not environmentally friendly. The most widely used method for improving paper oil resistance is to add a fluorine-containing oil-resistant agent to the paper material. The fluorine-based substance can reduce the surface tension of the paper, thus improving its oil resistance (Fukuda *et al*. 2013). Nevertheless, recent studies indicate that perfluoro-containing oil-resistant agents can migrate into foods and increase the risk of cancer (Lau *et al*. 2004; Cui *et al*. 2009). Therefore, paper wrapped with fluorine substances has been restricted in many countries. The development of new, non-toxic, and environmentally friendly oil-resistant agents has become a popular new research topic in the food industry.

Chitosan (CTS) is a partially de-acetylated derivative of chitin and is the only natural basic polysaccharide that exhibits excellent biocompatibility and biodegradability (Muzzarelli 1977; Roberts 1992; Myllytie *et al*. 2009; Imani *et al*. 2011). CTS coating on

food packaging paper provides an oxygen barrier (Kjellgren *et al*. 2006; Khwaldia *et al.* 2010; Liu and Chen 2011), a moisture barrier (Reis *et al*. 2011; Zhang *et al*. 2014), an antibacterial barrier (Dutta *et al*. 2009; Sun *et al*. 2010), and shows other special packaging performances. It can also significantly increase the mechanical strength of the paper sheet (Laleg and Pikulik 1991). Moreover, chitosan is a safe and edible additive. The positively charged amino group of CTS can attract the negative charges on the surface of cellulose fibers which are caused by hydroxyl and alduronic acid in the structure of cellulose in water, leading to strong adhesion to the paper surface after drying. The interaction between the amino group and negatively charged fats and lipids can improve its oil resistance (Jumaa and Müller 1999; Shu and Zhu 2002a,b,c). Muzzarelli *et al*. (2000) found that the reaction of CTS with micelles and lipid emulsion generated a soluble ionic structure that interfered with the absorption of lipids in lumen. Ham-Pichavant *et al*. (2005) investigated the reactions between CTS and fatty acids by calculating the amount of free fatty acids. In addition, cationic starch, a natural polysaccharide, is widely used in the coating process to improve the barrier and mechanical properties due to its excellent film-forming and biocompatibility (Ashori and Raverty 2007; Saraiva *et al.* 2010; Guazzotti *et al.* 2014), and the mixture of chitosan and cationic starch have been reported as sizing agent and dry strength agent of paper (Ashori *et al.* 2005, 2013). These studies indicate that CTS and CS can be used as a composite oil-resistant agent for food packing.

However, CTS is more expensive than the majority of other additives employed in the paper industry. In this experiment, relatively inexpensive cationic starch (CS) was used to partially replace CTS to form a CTS/CS composite oil-resistant agent, and the mechanism of oil-resistance was studied. Moreover, the structure, property, and performance of the CTS/CS oil-resistant agent were investigated.

EXPERIMENTAL

Materials and Equipment

Needle bleached kraft pulp (NBKP) with a beating degree of 80 °SR was used as a paper substrate. Cationic corn starch with substitution degree 2.8% and viscosity 12 mPa ∙ s (1 wt%, 25 °C) was obtained from the National Starch Industry Co., Ltd (Shanghai, China). CTS with a de-acetylation degree of 87% and molecular weight of 200,000, and other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

A thermogravimetric (TG) analyzer (TA Q600, Waters, USA), differential scanning calorimeter (DSC; Q200, Waters, USA), high performance liquid chromatography with evaporative light-scattering detector (HPLC-ELSD; 1100, Agilent, Germany), Fourier transform infrared spectrometer (FTIR; Is10, Nicolet, USA), scanning electron microscope (SEM; Su1510, Hitachi, Japan), drop shape analyzer (DSA100, Krüss, Germany), and nano particle size and zeta potential analyzer (Nano-ZS90, Malvern, UK) were used to characterize and investigate the properties and performances of the CTS/CS composite.

Methods

Preparation of oil-resistant agent

CTS was dissolved in 2% (mass fraction, all are the same below) acetic acid with a final concentration of 1.5% to produce a CTS oil-resistant agent (Peng and Long 2013).

The CTS oil-resistant agent solution was mixed with 10% gelatinized cationic starch with a CTS/CS mass ratio of 1:2 at room temperature to produce a CTS/CS composite oil-resistant agent.

Preparation of oil-resistant paper

A paper substrate with a basis weight of 70 ± 0.5 g/m^2 was coated by wire bar coater (coating film thickness of 30 μm) with the CTS and CTS/CS oil-resistant agents in the speed of coating 150 mm/s. The coating weight was 2.5 g/m^2. The coated paper was dried at 70 °C for 180 s and kept in the constant temperature and humidity chamber under 47% RH for 24 h to balance the moisture.

Test method for thermal stability

A small amount of CTS and CTS/CS composite was poured into two paper cups, respectively, and dried at 80 °C to form a thin film (Bourtoom and Chinnan 2008). A small piece of well-dispersed transparent film was analyzed on a TG-DSC analyzer. For the thermogravimetric (TG) analysis, the sample was heated from 0.00 to 350.00 °C, at a heating rate of 10.00 °/min. For the DSC test, the sample was equilibrated at 25 °C, and heated to 400 °C at a heating rate of 10.00 °/min.

The thermal stability of CTS and CTS/CS coated papers were directly tested by TG analysis, and the sample was heated from 35 °C to 800 °C with the heating rate of 10.00 °/min.

Oil kit test

The oil kit test (TAPPI T 559 cm-12) is the international standard testing method currently used in the greaseproof paper and paperboard industry. It measures the oil-resistant properties of paper with 12 liquids with various surface tensions, as shown in Table 1.

A drop of oil from glass dropper was dropped onto the paper from a height of 2.54 cm (1 inch) and allowed to be absorbed for 15 s (Brown 2004). The droplet on the paper was then gently wiped with a clean sponge. If the color of the contact area between the oil droplet and the paper remained unchanged, it indicated the paper met the grease resistance standard. In contrast, a dark contact area indicated that the oil penetrated the paper and the paper failed the test. Five independent experiments were conducted with an error of less than 0.5.

Contact angle measurement (ASTM D 5725-99)

CTS, and CTS/CS coatings, with a size of 20 mm × 15 mm were prepared on separate papers. The contact angle of water on the paper substrate and coated papers was measured after the water droplet reached its equilibrium. The measurement range of the contact angle was between 0 and 180°±0.1. Related software was used to calculate contact angle.

SEM and FTIR of CTS and CTS/CS coated papers

The surface structures of the papers coated with 2.5 g/m^2 CTS and CTS/CS were examined with FTIR and SEM. The contents of CTS and CS in the composite were 0.4% and 1.0%, respectively. FTIR spectra were recorded using an attenuated total refraction (ATR) method on an IR spectrometer (Is10, Nicolet, USA).

Table 1. Components of Kit and Surface Tension

Grease resistance value	Castor oil (g)	Methylbenzene (mL)	Heptanes (mL)	Surface tension (N·m^{-1})
1	969.0	0	0	0.0345
2	872.1	5	5	0.0327
3	775.2	10	10	0.0293
4	678.3	15	15	0.0254
5	581.4	20	20	0.0250
6	484.5	25	25	0.0241
7	387.6	30	30	0.0232
8	290.7	35	35	0.0228
9	193.8	40	40	0.0225
10	96.9	45	45	0.0225
11	0	50	50	0.0224
12	0	45	55	0.0220

Sorption test of CTS and fatty acid (Ham-Pichavant et al. 2005)

The CTS-oleic acid solution was mixed by 0.5% (w/v) CTS solution in 1% acetic acid and 0.5% (w/v) oleic acid aqueous solution and magnetically stirred at 500 rpm with different reaction time or different pH value under room temperature. The residual-free oleic acid in solution was extracted by hexane five times at room temperature, and hexane was evaporated by rotary evaporator. The residual of the solution was diluted with acetonitrile to 100 mL, and the concentration of free oleic acid was investigated by HPLC-ELSD (Orellana *et al.* 2005; Bravi *et al.* 2006). The ELSD was operated at 87 °C with acetonitrile as mobile phase. The 0.5% (w/v) gelatinized CS was added in CTS-oleic acid solution to prepare the CTS/CS-oleic acid solution. The experimental and test methods of CTS/CS-oleic acid were the same as above.

The well-distributed liliquoid (pH 5) of CTS and oleic acid with the reaction time of 2 h was observed by micrography and by evaluating the particle size distribution.

RESULTS AND DISCUSSION

Thermal Stability of CTS and CTS/CS Oil-Resistant Agents

Figure 1 shows the differential scanning calorimetry results for CTS and CTS/CS films. The endothermic peak at 85 °C for CTS can be attributed to the moisture in the film, and the exothermic peak at 280 °C can be assigned to the thermal decomposition of the glycosidic bond and the formation of a low-relative molecular mass volatile compound. CTS/CS composite films showed a broad endothermic peak at 80 °C because of the moisture and residues in the polysaccharide structure. The exothermic peak at 180 °C was caused by crystallization of CTS and CS. The blend of CTS/CS reached to melting state, leading to a new absorption peak at 225 °C. The broad exothermic peak at 280 °C can be assigned to thermal degradation. The higher exothermic temperature of CTS/CS films indicated that they have a higher thermal stability than CTS films.

The thermal stability of films and coated papers was further investigated using TG analysis. As shown in Fig. 2 (a), the initial weight loss in the temperature range between 40 and 120 °C can be attributed to the removal of moisture from the films. The weight loss of CTS films in the temperature range of 140 to 240 °C was 14.26% and was caused by thermal degradation. The 33.37% weight loss in the temperature range of 240 to 350 °C

can be attributed to rapid thermal degradation and the formation of a large amount of volatile substances. CTS/CS composite films were very stable between 120 and 220 °C, and only an exothermic peak at 180 °C was observed. This peak resulted from the increased crystallization of CTS and CS, instead of the degradation of the CTS/CS composite (Fig. 2). The 42.79% weight loss of the CTS/CS composite films in the temperature range of 220 to 330 °C can be assigned to rapid thermal degradation.
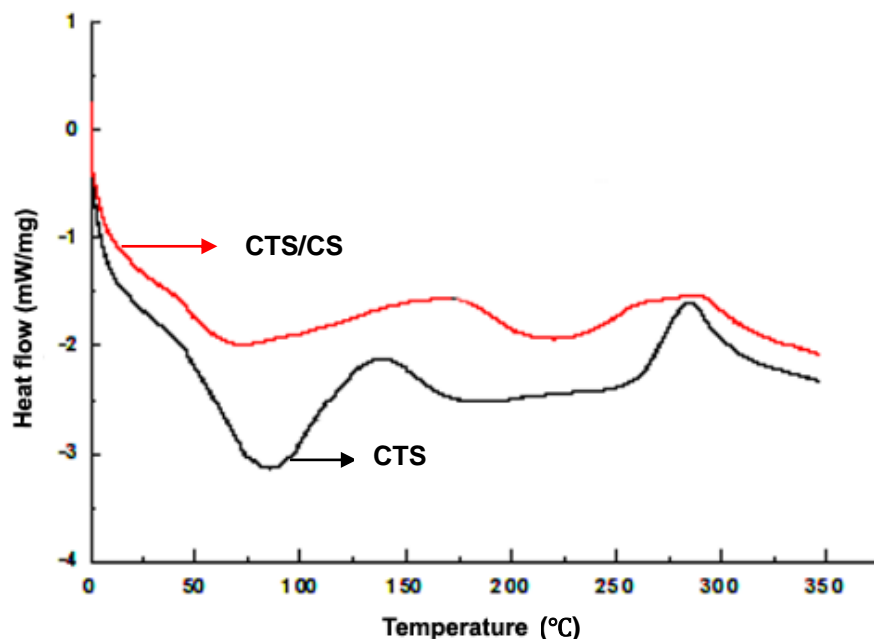
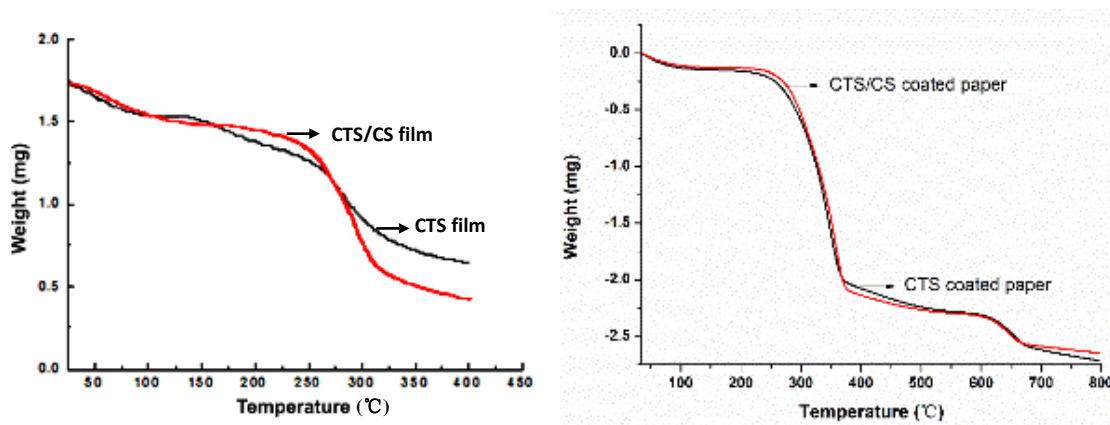**Fig. 1.** Differential scanning calorimetries of CTS and CTS/CS films

Fig. 2. TGA of films (a) and coated papers (b)

The weight losses for both CTS and CTS/CS films at temperatures over 400 °C can be attributed to carbonization. Compared with CTS films, CTS/CS films showed a higher decomposition temperature and lower weight loss. Therefore, the introduction of CS increased the thermal stability of CTS. Moreover, the thermal stability of CTS and CTS/CS coated paper were investigated in Fig. 2 (b). There was no significant change of the thermal

stability between CTS and CTS/CS coated paper, the 80% weight loss of coated paper in temperature range of 270 °C to 370 °C was attributed to cellulose pyrolysis. The degradation of CTS and CS, the weight loss at 630 °C was due to the decomposition of filler. Because of the large proportion of cellulose in coated paper, CTS and CS had less effect on the thermal stability of coated papers.

Oil and Water Resistances of CTS/CS Coated Papers

Oil-resistant properties

Figure 3 shows the increased oil resistance of the CTS and CTS/CS coated paper with increasing coating weight. For CTS coated paper, the oil resistance with a coating weight of 1.5 g/m^2 reached level 6 more than 5, which is in the safe oil-resistance range required for regular food packaging paper. The oil resistance of CTS/CS coated paper was lower than CTS coated paper. This indicates that the oil resistance of CTS is suitable for the preparation of oil-resistant paper.
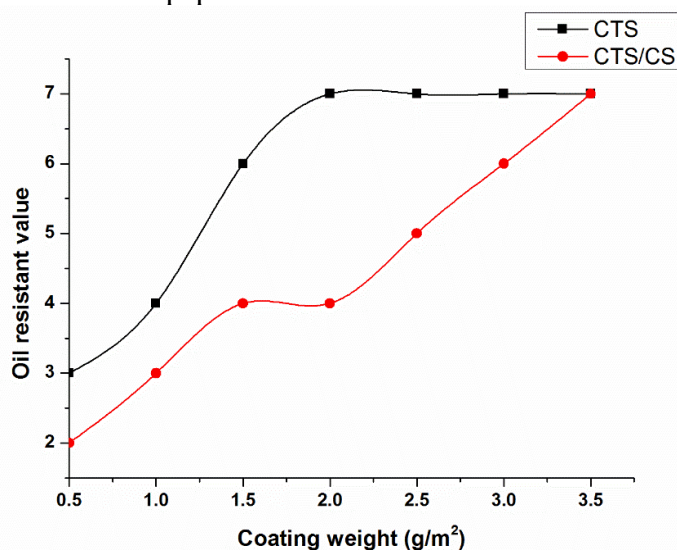

Fig. 3. Relationship between coating weight and oil resistance of coated paper
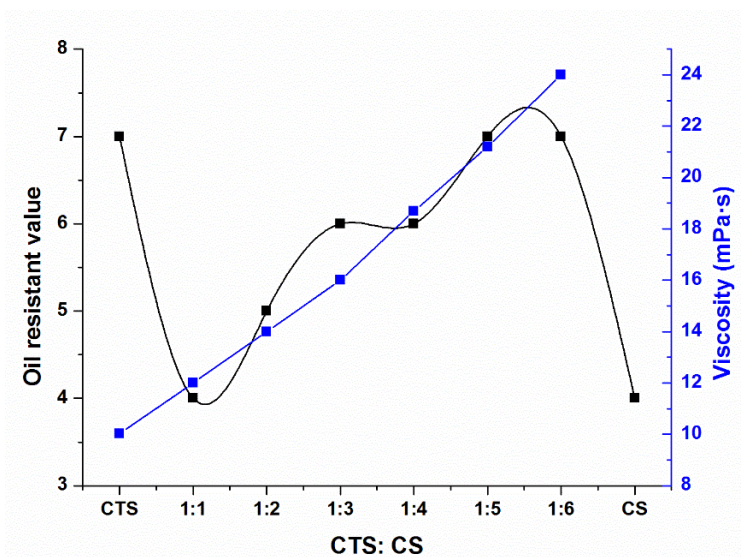

Fig. 4. Effects of mass ratio of CTS to CS on the viscosity (750 rpm, 25 ℃) and oil resistance of CTS/CS coated paper

The effects of the mass ratio of CTS to CS on the viscosity and oil resistance of CTS/CS coated paper with a total coating weight of 1.5 g/m^2 are shown in Fig. 4. The viscosity of the CTS/CS composite linearly increased, the oil resistant value of coated paper with CTS can reach the level 7, but paper coated with CS was only 4, and the oil resistance gradually increased from 1: 1 to 1: 6 with increasing CS fraction.

This may be explained by the fact that CS can form a film on the paper surface during drying, inhibiting the oil permeation instead of reacting with oil. However, CTS played a main role in oil resistance comparing with CS. The oil resistance of CTS/CS coated paper with a 1:2 mass ratio of CTS to CS reached level 5, the standard for oil-resistant paper in food packaging. Higher content of gelatinized CS in composite, especially more than 1:6 (CTS: CS), cannot tested by rotational viscometer due to higher viscosity, leading to a low uniform coating layer. Therefore, the experiment was only investigated the mass ratio of CTS to CS from 1:1 to 1:6, and finally optimized at 1:2.

Water-resistant properties

According to definition, the contact angle of a water drop on a hydrophilic surface is less than 90°, and it is greater than 90° on a hydrophobic surface. As shown in Fig. 5, the contact angles of water droplets on paper, CTS coated paper, and CTS/CS coated paper were 46.25°, 79.34°, and 79.63°, respectively. This indicates that the water resistance of the paper was improved with CTS and CTS/CS coatings.
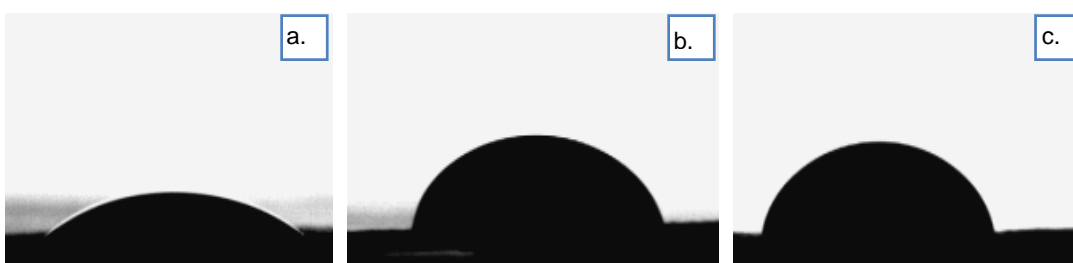

Fig. 5. Contact angle of water on (a) paper substrate, (b) CTS coated paper, and (c) CTS/CS coated paper

The absorption property of a substrate can be estimated by knowing the contact angle change and the increase in contact time (Table 2).

Table 2. Contact Angle Change on Paper Substrate, CTS Coated Paper, and CTS/CS Coated Paper in 0.5 s

Contact time (s)	Paper substrate		CTS coated paper		CTS/CS coated paper	
	Contact angle (°)	Decline (°)	Contact angle (°)	Decline (°)	Contact angle (°)	Decline (°)
0.1	46.25	0	79.34	0	79.63	0
0.2	44.05	2.20	77.17	2.17	79.55	0.08
0.3	41.93	2.12	75.12	2.05	79.47	0.08
0.4	38.65	3.28	72.40	2.72	79.39	0.05
0.5	36.59	2.06	70.38	2.02	79.32	0.07
Total decline (°)	9.66		8.96		0.31	

A faster contact angle change indicates better droplet absorption properties and a lack of water resistance. The water contact angle changes on paper, CTS coated paper, and CTS/CS coated papers, with their increases in contact time, as shown in Table 2. The contact angle, which is caused by water penetration and diffusion, declined by only 0.31° for CTS/CS coated paper. This contrasts with a 9.66° change on paper substrate and an 8.96° change on CTS coated paper in 0.5 s, indicating excellent water resistance for CTS/CS coated paper. Therefore, the CTS/CS coated paper is suitable for food packaging materials.

Characterization of CTS and CTS/CS Coated Papers

FTIR analysis

The IR spectra of the paper substrate, CTS coated paper, and CTS/CS coated paper are shown in Fig. 6. The broad band at 3409 cm^{-1} can be assigned to O-H stretching, and the strong absorption peak at 3443 cm^{-1} is attributed to N-H stretching. The bands at 1657 and 1600 cm^{-1} in the CTS and CTS/CS coated paper spectra are attributed to the stretching of C=O and NH_2 of the coating, respectively. These two peaks are absent in the IR spectrum of the paper substrate. The CTS/CS coated paper exhibited the characteristic absorptions of CS at 1409 cm^{-1} for C-N stretching and at 1954 and 1657 cm^{-1} for CTS (Xu *et al.* 2005). The intensity of the peak at 3414 cm^{-1} for both CTS and CTS/CS coated papers was lower than that of the paper substrate, probably resulting from the partially consumed carbonyl groups caused by the crosslinking between CTS and CS.
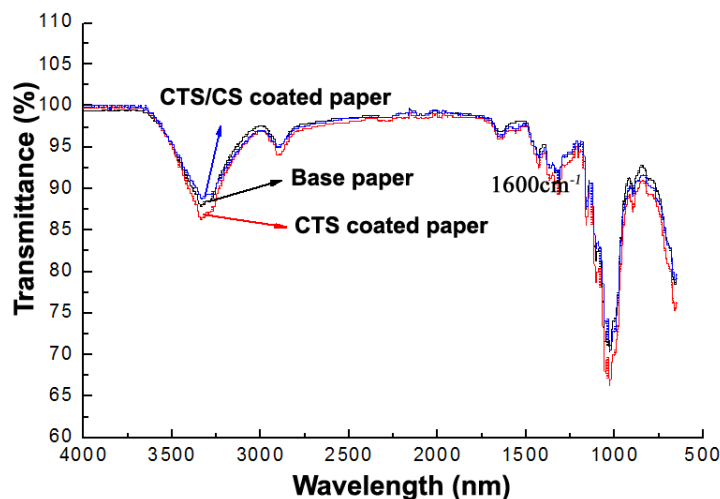

Fig. 6. The FTIR spectra of the paper substrate, CTS coated paper, and CTS/CS coated paper

SEM analysis

Scanning electron micrographs for the paper substrate and CTS/CS coated paper are shown in Fig. 7. A porous structure with fibrillation and brooming was found in the paper substrate (Fig. 7a and c). Oil and grease can diffuse into the paper through the pores by capillary action and gradually penetrate the paper substrate. In contrast, the CTS/CS composite can fill the gaps between the fibers, resulting in a tighter fiber alignment and a smooth and uniform film on the paper (Fig. 7b and d). The tight structure and smooth surface can reduce the surface energy and prevent the paper from oil wetting, resulting in the desired oil resistance.
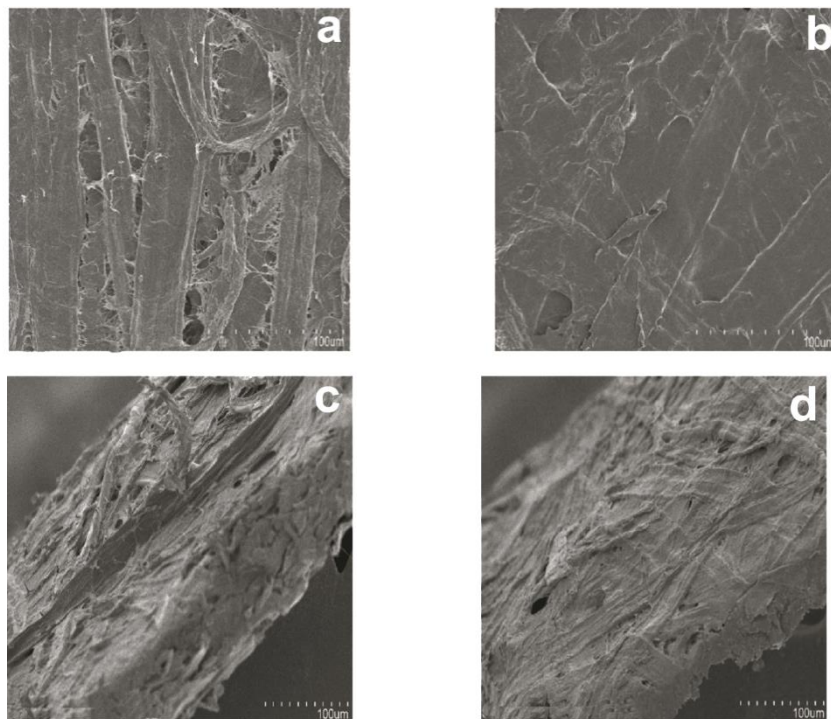
Fig. 7. SEM micrographs of paper substrate and CTS/CS coated paper, (a) surface of paper substrate, (b) surface of CTS/CS coated paper, (c) cross-section of paper substrate, (d) cross-section of CTS/CS coated paper

Reaction of CTS/CS with Fatty Acid

Because of the unclear oil-resistance mechanism of CTS and CS in the composite, as discussed above, the reaction between CTS/CS and grease was investigated. Oleic acid is a common fatty acid in food and was selected as an example. Neutral hydroxypropyl methyl cellulose was used as a blank to examine the influence of CTS/CS on the reaction. A white liliquoid was gradually formed with the increase of reaction time. No white matter was observed in the blank and CS solution. Because the white matter cannot be exacted by hexane, the effect of contact time and pH value on the reaction of CTS/CS with fatty acid were analysed by detecting the amount of residual free oleic acid (FOA) in Fig. 8.

From the curves of CTS in Fig. 8, the concentration of FOA decreased from 76% to 15% during 2 h, and finally it was maintained almost a constant over 2 h. The results indicated that there probably was a reaction between CTS and oleic acid and that the reaction terminated in 2 h. Moreover, if the occurrence of reaction between CTS/CS and oleic acid caused by electrostatic bonding, the emulsion should be pH-sensitive. The amount of extracted FOA was rapidly reduced with relatively low pH within the range of 1 to 6. In particular, only 7% was obtained at pH 6, whereas 71% was obtained at pH 7. The electrostatic absorption which largely influenced by pH value occurred between CTS and oleic acid because of the protonation of the amino group in acid condition. This could finally lead to the lower concentration of residual FOA at pH 6 (CTS pK_a=6.5). But the concentration of residual FOA was significantly increased due to the lack solubility of CTS at pH 7. Compared to CTS, the similar results were obtained with the CTS/CS composite emulsion. This indicated that there was almost no interaction between CS and oleic acid. Furthermore, adding CS in CTS-oleic solution had little impact on the reaction of CTS and oleic acid. However, FOA cannot be completely analysed by HPLC-ELSD because the

concentration was only 76% at 0 h. Therefore, this method can only be used as comparative analysis instead of quantitative analysis.

In order to further investigate the mechanism of the reaction between CTS and fatty acid, photomicrograph and particle size distribution of emulsions were detected (2 h, pH 5). Figure 9 showed a white emulsion formed with 0.5% CTS and 0.5% oleic acid. The whiter matter may be formed by the reaction between the positive amino group of CTS and negative carboxyl group of oleic acid. As shown in Fig. 10, the initial particle size in the mixture was mostly distributed at approximately 900 nm. The particle size increased to approximately 5000 nm after a 2 h reaction (Fig. 11), this is consistent with the above analysis.
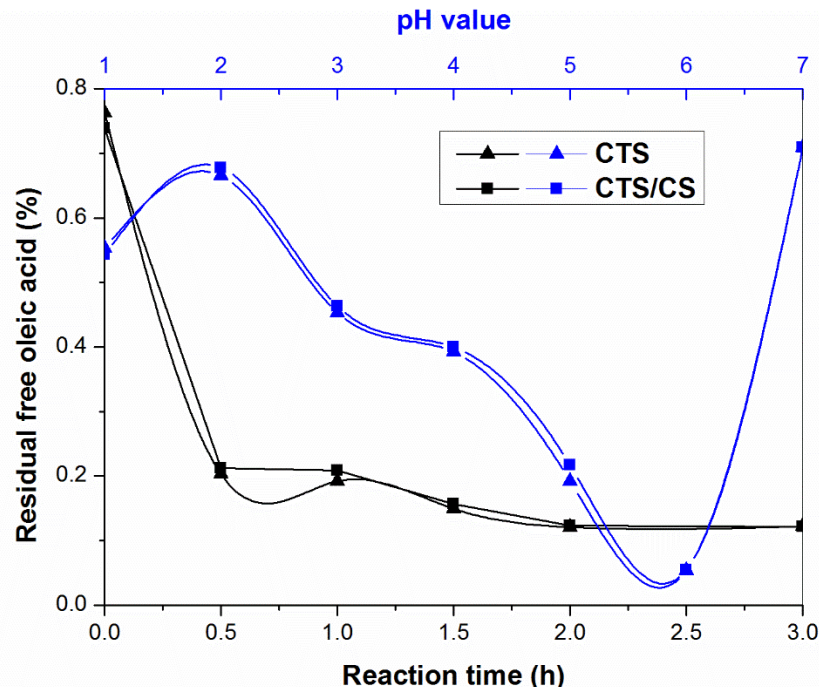

Fig. 8. Influence of contact time and pH value on residual free oleic acid
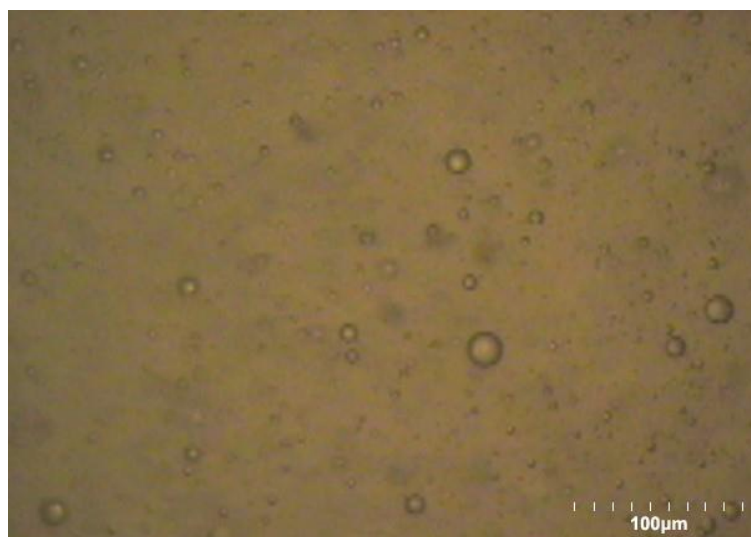

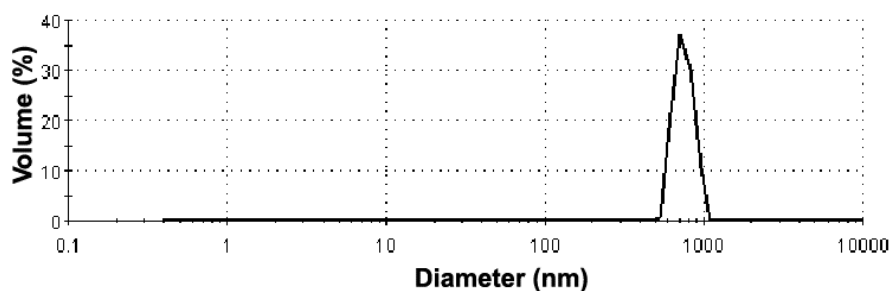**Fig. 9.** Photomicrograph of emulsions with 0.5% chitosan and 0.5% oleic acid

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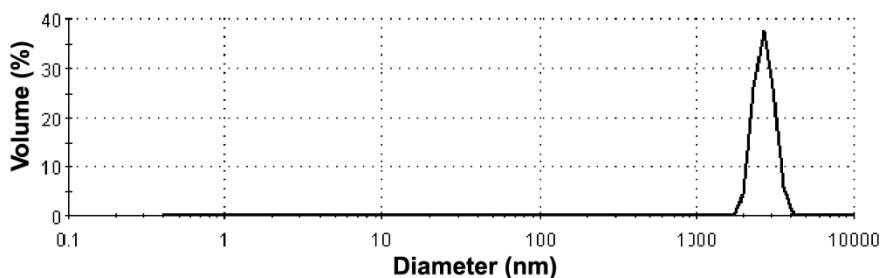**Fig. 10.** Size distribution of chitosan-oleic acid at 0 h

Fig. 11. Size distribution of chitosan-oleic acid at 2 h

CONCLUSIONS

1. The chitosan/cationic starch (CTS/CS) oil-resistant agent showed better thermal stability and oil resistance than the corresponding chitosan (CTS) agent. Paper coated with a 1:2 mass ratio of CTS to CS and coating weight of 1.5 g/m^2 can achieve the oil resistance required for food packaging.

2. The effect of CS in the blend of CTS/CS on paper was to improve the oil resistance by film-forming, and the mechanism was different from CTS by means of electrostatic adsorption with fatty acid to prevent oil spreading. Therefore, CTS and CS acted together, and CTS played the main role on oil resistant property of paper.

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REFERENCES CITED

Ashori, A., and Raverty W. D. (2007). "Printability of sized kenaf (*Hibiscus cannabinus*) papers," *Polymer-Plastics Technology and Engineering* 46(7), 683-687. DOI: 10.1080/03602550701429250

Ashori, A., Raverty, W. D., and Harun, J. (2005). "Effect of chitosan addition on the surface properties of kenaf (*Hibiscus cannabinus*) paper," *Fibers and Polymers* 6(2), 174-179. DOI: 10.1007/BF02875611

Ashori, A., Cordeiro, N., Faria, M., and Hamzeh, Y. (2013). "Effect of chitosan and cationic starch on the surface chemistry properties of bagasse paper," *Int. J. Biol. Macromol.* 58, 343-348. DOI: 10.1016/j.ijbiomac.2013.04.056

ASTM D5725-99 (2008). "Standard test method for surface wettability and absorbency of sheeted materials using an automated contact angle tester," ASTM International, West Conshohocken, PA.

Bourtoom, T., and Chinnan M. S. (2008). "Preparation and properties of rice starch–chitosan blend biodegradable film," *LWT - Food Science and Technology* 41(9), 1633-1641. DOI:10.1016/j.lwt.2007.10.014

Bravi, E., Perretti, G., and Montanari, L. (2006). "Fatty acids by high-performance liquid chromatography and evaporative light-scattering detector," *J Chromatogr A* 1134(1-2), 210-214. DOI:10.1016/j.chroma.2006.09.007

Brown, R. W. (2004). *Development of a Novel Grease Resistant Functional Coating for Paper-Based Packaging and Assessment of Application by Flexographic Press*, University of North Texas, Denton, TX.

Crosby, N. T. (1981). "Plastic packaging materials," in: *Food Packaging Materials*, Applied Science Publisher, England, pp. 19-22.

Cui, L., Zhou, Q. F., Liao, C. Y., Fu, J. J., and Jiang, G. B. (2009). "Studies on the toxicological effects of PFOA and PFOS on rats using histological observation and chemical analysis," *Archives of Environment Contamination and Toxicology* 56(2), 338-349. DOI: 10.1007/s00244-008-9194-6

Dutta, P. K., Tripathi, S., Mehrotra, G. K., and Dutta, J. (2009). "Perspectives for chitosan based antimicrobial films in food applications," *Food Chemistry* 114(4), 1173-1182. DOI: 10.1016/j.foodchem.2008.11.047

Fukuda, S., Chaussy, D., Belgacem, M. N., Bruas, N. R., and Thielemans, W. (2013). "Characterization of oil-proof papers containing new-type of fluorochemicals. Part 1: Surface properties and printability," *Applied Surface Science* 277(15), 57-66. DOI: 10.1016/j.apsusc.2013.03.174

Guazzotti, V., Marti, A., and Piergiovanni, L. (2014). "Bio-based coatings as potential barriers to chemical contaminants from recycled paper and board for food packaging," *Food Addit Contam Part A Chem Anal Control Expo Risk Assess* 31(3), 402-413. DOI: 10.1080/19440049.2013.869360

Ham-Pichavant, F., Sèbe, G., Pardon, P., and Coma, V. (2005). "Fat resistance properties of chitosan-based paper packaging for food applications," *Carbohydrate Polymers* 61(3), 259-265. DOI: 10.1016/j.carbpol.2005.01.020

Imani, R., Talaiepour, M., Dutta, J., Ghobadinezhad, M. R., Hemmasi, A. H., and Nazhad, M. M. (2011). "Production of antibacterial filter paper from wood cellulose," *BioResources* 6(1), 891-900. DOI: 10.15376/biores.6.1.891-900

Jumaa, M., and Müller, B. W. (1999). "Physicochemical properties of chitosan-lipid emulsions and their stability during the autoclaving process," *International Journal of Pharmaceutics* 183(2), 175-184. DOI: 10.1016/S0378-5173(99)00086-1

Khwaldia, K., Tehrany, E. A., and Desobry, S. (2010). "Biopolymer coatings on paper packaging materials," *Comprehensive Reviews in Food Science and Safety* 9(1), 82-91. DOI: 10.1111/j.1541-4337.2009.00095.x

Kjellgren, H., Gällstedt, M., Engström, G., and Järnström, L. (2006). "Barrier and surface properties of chitosan-coated greaseproof paper," *Carbohydrate Polymers* 65(4), 453-460. DOI: 10.1016/j.carbpol.2006.02.005

Laleg, M., and Pikulik, I. I. (1991). "Wet-web strength increase by chitosan," *Nordic Pulp and Paper Research Journal* 6(3), 99-103. DOI: 10.3183/NPPRJ-1991-06-03-p099-103

Lau, C., Butenhoff, J. L., and Rogers, J. M. (2004). "The developmental toxicity of perfluoroalkyl acids and their derivatives," *Toxicology and Applied Pharmacology* 198(2), 231-241. DOI:10.1016/j.taap.2003.11.031

Liu, Y. S., and Chen, G. (2011). "Study on the application of chitosan in paper barrier coating," *China Pulp & Paper* 30(11), 1-6. DOI: 10.3969/j.issn.0254-508X.2011.11.001

Matsuo, M., and Yamabe, M. (1994). *Development of Fluoro Functional Materials*, CMC Publishing Co., Japan.

Muzzarelli, R. A. A. (1977). *Chitin*, Pergamon Press, Oxford, UK.

Muzzarelli, R. A. A., Frega, N., Miliani, M., Muzzarelli, C., and Cartolari, T. M. (2000). "Interactions of chitin, chitosan, N-lauryl chitosan and N-dimethylaminopropyl chitosan with olive oil," *Carbohydrate Polymers* 43(3), 263-268. DOI: 10.1016/S0144-8617(00)00170-3

Myllytie, P., Salmi, J., and Laine, J. (2009). "The influence of pH on the adsorption and interaction of chitosan with cellulose," *BioResources* 4(4), 1647-1662. DOI: 10.15376/biores.4.4.1647-1662

Orellana-Coca, C., Adlercreutz, D., Andersson, M. M., Mattiasson, B., and Hatti-Kaul, R. (2005). "Analysis of fatty acid epoxidation by high performance liquid chromatography coupled with evaporative light scattering detection and mass spectrometry," *Chem Phys Lipids* 135(2), 189-199. DOI:10.1016/j.chemphyslip.2005.02.014

Peng, H and Long, Z. (2013). "Preparation and application of chitosan type paper oil-proof agent," *Packaging Engineering* 34(1), 12-17.

Reis, A. B., Yoshida, C. M. P., Reis, A. P. C., and Franco, T. T. (2011). "Application of chitosan emulsion as a coating on kraft paper," *Polymer International* 60(6), 963-969. DOI: 10.1002/pi.3023

Roberts, G. A. E. (1992). *Chitin Chemistry*, Macmillan Press, London, UK.

Saraiva, M. S., Gamelas, J. A. F., Mendes de Sousa, A. P., Reis, B. M., Amaral, J. L., and Ferreira, P. J. (2010). "A new approach for the modification of paper surface properties using polyoxometalates," *Materials* 3(1), 201-215. DOI:10.3390/ma3010201

Shu, X. Z., and Zhu, K. J. (2002a). "The influence of multivalent phosphate structure on the properties of ionically cross-linked chitosan films for controlled drug release," *European Journal of Pharmaceutics and Biopharmaceutics* 54(2), 235-243. DOI: 10.1016/S0939-6411(02)00052-8

Shu, X. Z., and Zhu, K. J. (2002b). "The release behavior of brilliant blue from calcium-alginate gel beads coated by chitosan: The preparation method effect," *European Journal of Pharmaceutics and Biopharmaceutics* 53(2), 193-201. DOI: 10.1016/S0939-6411(01)00247-8

Shu, X. Z., and Zhu, K. J. (2002c). "Controlled drug release properties of ionically cross-linked chitosan beads: The influence of anion structure," *International Journal of Pharmaceutics* 233(1-2), 217-225. DOI: 10.1016/S0378-5173(01)00943-7

Sun, S. L., An, Q. Z., Li, X., Qian, L. Y., He, B. H., and Xiao, H. N. (2010). "Synergistic effects of chitosan–guanidine complexes on enhancing antimicrobial activity and wet-strength of paper," *Bioresource Technology* 101(14), 5693-5700. DOI: 10.1016/j.biortech.2010.02.046

TAPPI T559 cm-12 (2012). "Grease resistance test for paper and paperboard," TAPPI Press, Atlanta, GA.

Xu, Y. X., Kim, K. M., Hanna, M. A., and Nag, D. (2005). "Chitosan–starch composite film: Preparation and characterization," *Industrial Crops and Products* 21(2), 185-192. DOI:10.1016/j.indcrop.2004.03.002

Zhang, W., Xiao, H., and Qian, L. (2014). "Beeswax–chitosan emulsion coated paper with enhanced water vapor barrier efficiency," *Applied Surface Science* 300, 80-85. DOI: 10.1016/j.apsusc.2014.02.005