

Preparation of Chitosan Modified Talc and Its Application in High Filler Content Paper

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ABSTRACT: Chitosan (CS) with different viscosity was investigated as a modifier of talc which was used to improve the strength properties and filler retention in high filler content papers. The particle size and morphology of the resulting modified talc were studied to confirm the successful modification. The zeta potential and coating amount of the CS modified talc were also investigated. It was found that CS viscosity was a critical factor for the filler modification and final paper properties. When high viscosity CS was applied, the resulting tensile strength of filled paper was 64% higher than that of unmodified talc at the filler content of 37% as well as maintained favorable optical properties. Furthermore, with the filler loading of 70% (based on the solid fiber weight), compared with that of unmodified talc, filler retention of modified talc was increased by 39%, while the drainage was little influenced. The field emission scanning electron microscopy images showed a better bonding capacity between modified talc and fibers than that of untreated talc.
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KEYWORDS: high viscosity chitosan; talc; filler modification; high filler content paper; paper properties; filler retention

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INTRODUCTION

Fillers now have been widely used in the papermaking industry to lower production costs and meet the needs of functional papers.¹ The addition of filler can offer considerable benefits of significantly improving water removal for paper manufacture, resulting in energy saving, or enhanced paper machine speeds.² Many types of conventionally used inorganic fillers have been applied in the paper industry, including talc, calcium carbonate, kaolin clay, silica, and titanium dioxide.^{3,4} For example, talc is very commonly used in Asia, kaolin clay is usually used in North America, and calcium carbonate is generally used in Europe.⁵

High filler content paper has received a great deal of attention in the papermaking industry due to the lower cost and the improvement of paper properties.^{6,7} However, as filler content increased, especially at high mass fraction filler beyond conventional loading, the strength and filler retention are generally reduced. Various methods have been explored to improve or alleviate the aforementioned limitations and drawbacks without sacrificing paper properties, such as the incorporation of fillers into lumen or cell-wall,⁸ pulp fine-filler composite,^{9–11} and pre-flocculation of filler.^{6,12} However, poor compatibility between the inorganic filler and pulp fiber has a great influence on the pore structure of paper and the properties of high filler paper.^{5,13} To overcome such problems, filler modification via

surface treatment is one of the most promising methods for industrial applications. Several surface modifiers have been researched, such as inorganic compounds,¹⁴ synthetic polymers or resin,¹⁵ surfactants,¹³ latex, and coupling agent.¹⁶

A recently developed alternative strategy of filler surface modification method based upon surface coating or encapsulation using biodegradable and renewable carbohydrate polymers has been employed as a powerful way to achieve high filler level with good paper properties.^{17,18} It has been well known that the chemical structure of polysaccharides or their derivatives are very close to pulp fibers, thus many carbohydrate polymers [such as starch, cellulose, carboxymethylcellulose, chitin, and chitosan (CS)] were all chosen as modifiers by appropriate methods such as solvent, salting out, charge neutralization, or complexation and so on.^{4,5,19–27} Filler modified with carbohydrate polymers can improve the compatibility of the inorganic filler and organic polymer matrix and thus can potentially enhance the bond strength between fillers and fibers and lead to many other possible benefits.²⁸

Talc is finding numerous applications due to its specific properties such as thermal stabilities, hydrophobicity, organophilicity, and adsorption properties.²⁹ The talc is chemically inert, which leads to poor fiber-to-filler bonding, so our study aim at modifying the surface of talc in order to enhance its compatibility

and hence improve the paper properties. CS which is a derivative of nature polysaccharides is widely used in medicine, food, papermaking, printing, and dyeing since it can achieve excellent biocompatibility, biodegradability and flocculability.^{30,31} Earlier researches have indicated that it is possible to apply CS to modify inorganic particles.^{32,33}

In this work, a common carbohydrate polymer (CS) which is naturally compatible with pulp fibers was employed as a modifier for the surface treatment of talc. The effect of CS on talc modification and the use of the resulting modified filler in high filler content paper were investigated.

EXPERIMENTAL

Materials

CS of three different viscosity (30, 202, and 950 mPa s) with a degree of deacetylation of 90% was supplied by Shan Dong LaiZhou Highly Bio-Products Co., Ltd., China. Talc was provided by Gui Lin Lin gui Space Medical Talc, China. Cationic polyacrylamide (CPAM) ($M_w = 800,000$ g/mol) with a low-charge density of 3–5% as a retention aid was purchased from Guangxi Wuzhou Arakawa Chemical Industries, China. Bentonite was provided by Chang'an Renheng Chemical, China. Commercial bleached softwood and hardwood pulp were refined in a valley beater to beating degree of 32 and 35 °SR. Then, equivalent proportions of the two pulps were mixed as the base pulp furnish for the preparation of handsheets.

Preparation of CS Modified Filler

Talc slurry was created by adding 5 g of talc and 50 mL of deionized water into a 250 mL three-neck round-bottom flask. The mixture was stirred with high speed to ensure sufficient dispersing. Followed by adding 50 mL CS solution (5 wt % relative to talc, in 5 wt % acetic acid solution) into the dispersed mixture, 5 wt % NaOH was used to adjust the pH value to 10 and the resulting mixture was further stirred for 20 min.³³ The process of CS modified talc was shown in Figure 1. After the modification, two methods were used for the final treatment of the modified fillers. One was that filler aggregates was washed to pH neutral and redispersed again with an agitator of moderate stirring, the other was that the modified filler was vacuum dried at 50°C and ground to powder for field emission scanning electron microscopy (FESEM) measurement.

Characterization of CS Modified Talc

The coating amount of coated filler was measured according to the previously reported method.²² The pure talc and modified talc were both incinerated in a muffle oven at 575°C to determine the loss rate and to record the remaining weight, respectively. Coating amount (C) was evaluated using eq. (1).

$$C = \frac{m_1 - m_2/(1 - \alpha)}{m_2/(1 - \alpha)} \times 100\% \quad (1)$$

where m_1 is the original weight of modified talc, m_2 is the weight of modified talc after incinerating in the oven, and α is the mass loss rate of talc.

The particle size analysis was performed using a Malvern 2000 particle size analyzer to verify the successful modification. All

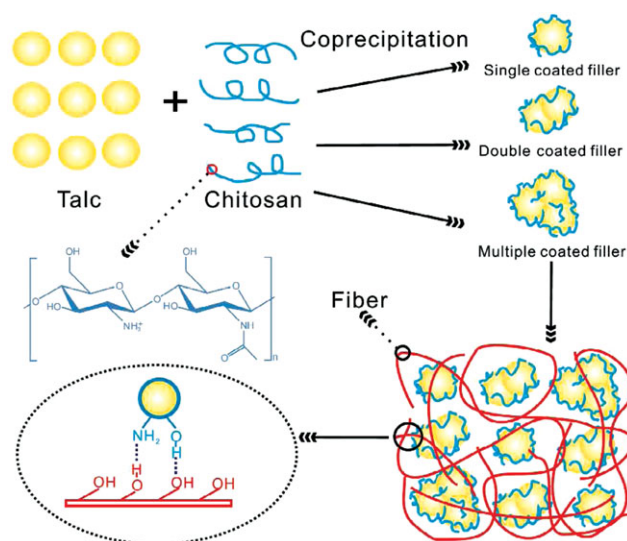


Figure 1. Schematic of CS modified talc process and the mechanism of fibers interact with modified fillers that contain three presumed structure, and schematic of interaction mechanism of fibers and modified fillers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

specimens were dispersed in water using ultrasonic wave prior to tests.

The zeta potential of pure talc and talc modified with various viscosity CS were measured using SZP-06 zeta potential tester (BTG, German).

Handsheet Preparation and Determination of Paper Properties

Handsheets were prepared with the same virgin pulp (a 1 : 1 mixture of 32 °SR of softwood and 35 °SR of hardwood) by adding various amounts of modified fillers during the papermaking processes. CPAM (0.2 wt % based on dry weight of fibers) and Bentonite (0.3 wt % based on dry weight of fibers) were added to retain the filler. Handsheets were formed using the standard sheet forming device (Shanxi University of Science & Technology), then the handsheets were dried at 105°C for 10 min under reduced pressure. Finally, the handsheets were conditioned under 23.0°C and 50.0% relative humidity in polyethylene bags prior to the properties tests.

For the tensile tests, paper specimens were cut into rectangular shapes that were 1.5 cm wide and 10 cm long. The strength properties (tensile index and burst index) of handsheets were measured using D-KZ (W) 300 tensile tester and DCP-NPY5600 burst tester (Sichuan Changjiang papermaking equipment, China). Tensile index and burst index were calculated by 10 replicates. The brightness and opacity of handsheets were determined using DC-NPY5600 brightness, opacity and light-scattering coefficient tester (Sichuan Changjiang papermaking equipment, China). The brightness and opacity were calculated by 10 replicates. The thickness values were measured using thickness tester (CH-1-ST, China), and the values of apparent density was then calculated based on thickness and grammage. The properties of handsheets were all determined according to

the Chinese National Standard (GB/T 3704-1999) for lab testing.

Determination of Filler Content in the Handsheet

The filled handsheets with varied filler added dosage were incinerated in a muffle oven at 575°C for 4 h. Then the filler content were determined by the ash of filled handsheets.

Retention and Drainage Measurements

The retention and drainage experiments were performed using a DFR-04 device (BTG, German). In the beginning, 1 kg of pulp suspension (5 g/L) containing different filler loading that is relative to dry weight of fibers was transferred to the stirring chamber and the additives were added during the stirring process (the stirring speed and time were 600 r/min for 10 s and 800 r/min for another 15 s) of the selected profile. As for retention, measurements will be terminated when the preset weight defined in the profile is reached. At the same time, the system will additionally measure the total consistency and the fines/filler consistency using the RET-20 lab sensor.

The drainage tests that were tested in normal pressure were performed using a 60 mesh screen, through which 1 kg of pulp suspension (5 g/L) was filtered. The filtrate time was then recorded when the filtrate weight (800 g) defined in the profile was attained. The retention and drainage tests were calculated by three times.

Field Emission Scanning Electron Microscope (FESEM)

Observations

FESEM analysis for fillers and papers was performed with ULTRA-55 electron microscope (Carl Zeiss SMT Pte, Germany). Before analysis, all samples were mounted on aluminum stubs using carbon adhesive tape and sputter-coated a layer of gold (20–40 nm).

RESULTS AND DISCUSSION

Forming and Characterization of the Modified Filler Aggregates

The particle sizes of unmodified and modified talc are both presented in Table I. It was able to be seen that the unmodified talc mainly distributed in the size of about 10 μm . Compared with the unmodified talc, the particle size range of modified talc (40–45 μm) was significantly increased after the modification. The coating mechanism of modified talc can be explained in Figure 1. Besides the encapsulation of one single filler particle, the CS modified talc can be the physical encapsulation of several particles to bind them together simultaneously.^{4,18,19,21,23,24}

The zeta potential of filler particles was measured to determine the change of talc particles charge and observe the influence on retention and flocculation on fibers.⁵ Table I shows the effect of CS viscosity on the zeta potential of talc particles. After the modification with CS, the zeta potential of filler particles increased. The high viscosity CS modified talc particles were more positively charged than that of the other CS. Consequently, the introduction of CS onto the talc surface is benefit for increasing the zeta potential.

The coating amounts of modified talc are listed in Table I. When compared the coating amounts of CS-coated talc with different viscosity (low, medium, or high viscosity), the coating amounts were all nearly 5%. It indicated that CS could be effectively coated on the surface of talc under the experimental conditions.

The FESEM and optical microscope images of virgin talc and modified talc are shown in Figure 2. Obviously, the surface morphology of unmodified talc showed a marked change after the modification, which also confirmed that filler particles were successfully coated with CS. It is shown in Figure 2(A,B) that the image of original talc is corresponding to flattened tabular crystals with a hexagonal cross section.²⁹ In Figure 2(C,D), the modified talc aggregates were seen to be larger than that of pure talc. Meanwhile, the optical microscope images in Figure 2(A,C) showed that the talc particles became dark or dim after modification due to the light opaqueness of the absorbed CS molecule.

Effects of the CS Modified Filler on Paper Strength and Optical Properties

The strength and optical properties of handsheets prepared with different viscosity CS modified talc at different filler content were measured and compared with the virgin talc filled handsheet in Figures 3 and 4.

In Figure 3(A), it can be seen that the tensile index of the pure talc filled paper decreased with the increase of filler content. This indicated that increased filler content can result in a marked reduction in paper strength because the filler particles in the handsheet decrease fiber-filler bonding.^{4,5,19,25} Although the strength properties of paper with different viscosity CS modified fillers also decreased with the increase of filler content, for a given filler contents, the strengths were still much higher than those of paper with unmodified filler. Especially for high viscosity CS as modifier, with the filler content increased from 20 to 37%, the tensile strength of filled sheets increased by 15 and 64% compared to that of pure talc filled paper. In this case, the filler-fiber bonding can be improved by coating CS on the filler surface and forming H-bonding with wood fibers, resulting

Table I. Particle Size, Zeta Potential, and Coating Amount of Modified Talc with Varying Chitosan Viscosity

Sample	Particle size (mm)	Zeta potential (mV)	Coating amount (%)
Unmodified talc	10.11 \pm 2.05	-42.4 \pm 0.4	—
Modified talc (5% low viscosity chitosan)	40.02 \pm 3.27	-21.2 \pm 0.3	4.74 \pm 0.05
Modified talc (5% medium viscosity chitosan)	41.20 \pm 3.51	-20.8 \pm 0.3	4.82 \pm 0.08
Modified talc (5% high viscosity chitosan)	45.05 \pm 2.90	-18.5 \pm 0.2	4.93 \pm 0.08

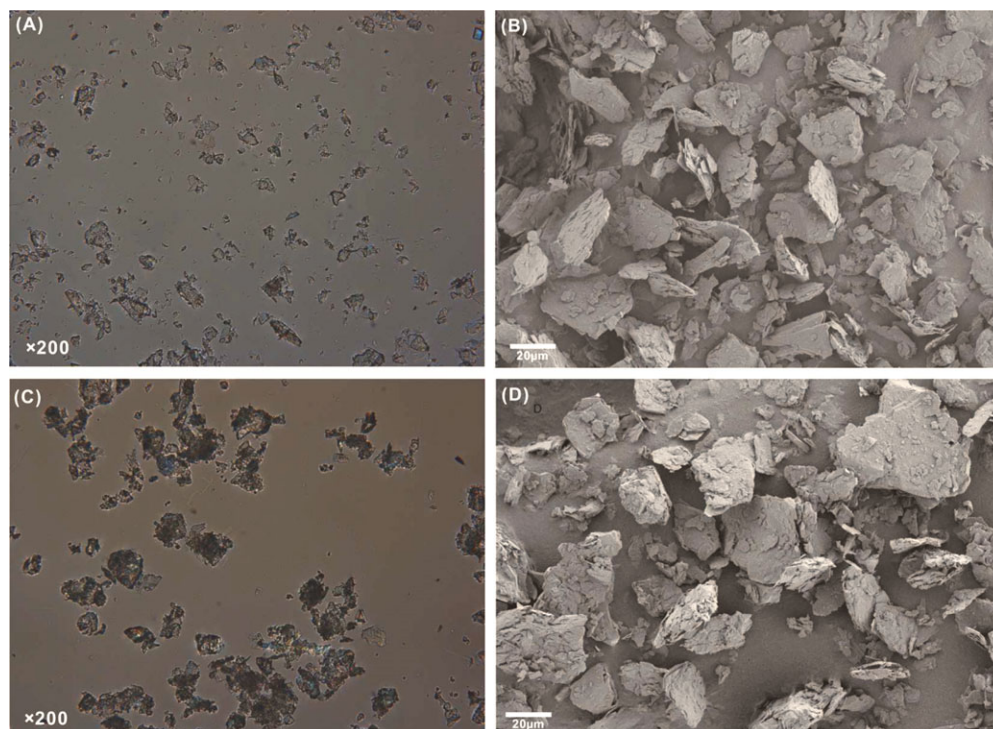


Figure 2. FESEM and optical microscope images of virgin talc and modified talc: optical microscope image of virgin talc ($\times 200$) (A), FESEM image of virgin talc (B), optical microscope image of modified talc ($\times 200$) (C), FESEM image of modified talc (D). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

in a great increase in the tensile strength of papers prepared with modified talc compared with that of pure talc filled paper.^{5,25} A schematic illustration of the forming of H-bonding between fibers and modified talc particles is also shown in Figure 1. This resulting interaction is believed source of high paper strength. The tensile strength of handsheets prepared from modified talc using high viscosity CS is evidently higher than that of the other two kinds of lower viscosity CS modified talc at the same filler content. It indicated that more H-bonding between filler and pulp fiber can be effectively formed due to the longer molecular chain of high viscosity CS. As shown in Figure 3(B), the burst strength was also investigated, which was similar to the results of tensile strength. When choosing high viscosity CS as the modifier, the burst strength was the best compared with the other two CS of viscosity degree.

Figure 4 showed the brightness and opacity of handsheets made with CS modified talc and that of handsheets made with pure talc. Clearly, the brightness and opacity can be improved with the increase of filler content. It can be seen in Figure 4(A), at the same talc content, with high viscosity CS as modifier the brightness of filled handsheets was the best than that of the other CS grades. However, the brightness of the papers containing modified talc was just a slightly lower than that of unmodified talc, most likely due to the smaller particle size of the untreated filler.⁴ Similar results can be seen of the opacity of filled paper in Figure 4(B) except that the opacity of papers made with modified talc was increased compared with that of

unmodified talc filled paper. Additionally, the tendency of opacity of the papers containing modified talc is just contrary to that of apparent density (Figure 5). This indicates that it is just the lower of apparent density containing modified talc than that of unmodified talc resulting to the higher of opacity containing modified talc than that of unmodified talc.

Thus, under our experimental conditions, the results suggest that the modification process did not have an evident effect on paper optical properties. The enhancement of modified filler paper strength may relate to enhanced fiber-filler bonding.

Effects of the CS Modified Filler on Filler Retention and Drainage Properties

It is shown in Table II that the high viscosity CS modified filler has a higher filler retention rate compared with the unmodified filler. At a filler loading of 30% (based on dry weight of fibers), the modified filler retention was higher than 90% while the retention of unmodified filler was less than 80%. However, the total retention of modified talc was a little decrease than that of unmodified filler, which maybe probably lie to charge interaction effect between modified talc and retention aid,¹² which may cause the less adsorption of fiber with CPAM resulting to improve the filler retention and lower the total retention. With the filler loading increase to 70% (based on dry weight of fibers), the modified filler retention (86.5%) can achieve 39% higher without sacrificing the total retention compared with that of unmodified talc. In this case, the talc modification can give a positive effect on filler retention. This is mainly because

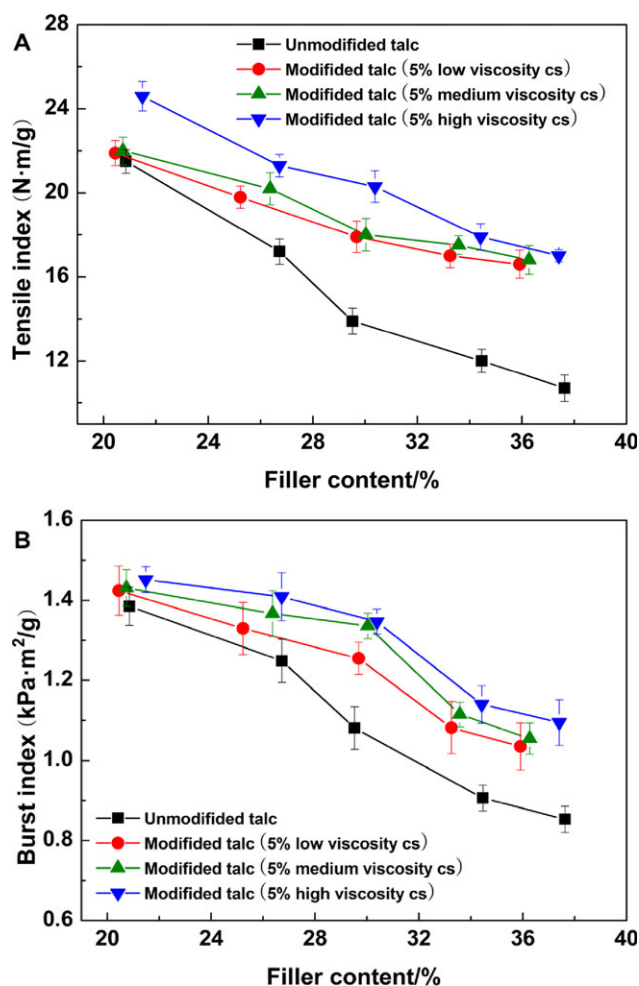


Figure 3. Tensile index (A) and burst index (B) as a function of filler content in paper with different CS viscosity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the CS coated fillers are small aggregates with a size of about 45 μm (Table I) rather than individual particles. Other than the size effects, this enhanced filler retention may presumably link to the increased zeta potential due to the coated CS,^{34,35} which could reduce the negative charge of filler surface and be easier for talc to retain in paper by adding the appropriate retention aid.^{5,36}

As shown in Table II, the dynamic drainage properties of the filler-containing furnish showed a slight decrease with the increase of the filler loading. In comparison with that of unmodified talc, the dynamic drainage of furnishes containing modified talc was little decrease. Therefore, it can be concluded that the filler modification process will not significantly affect the dynamic drainage property.

FESEM Images of Filled Papers

FESEM images of pure talc and modified talc filled papers are shown in Figure 6. In Figure 6(A), the unmodified filler particles were retained and dispersed on the fiber surface or between fibers by mechanical entrapment. On the

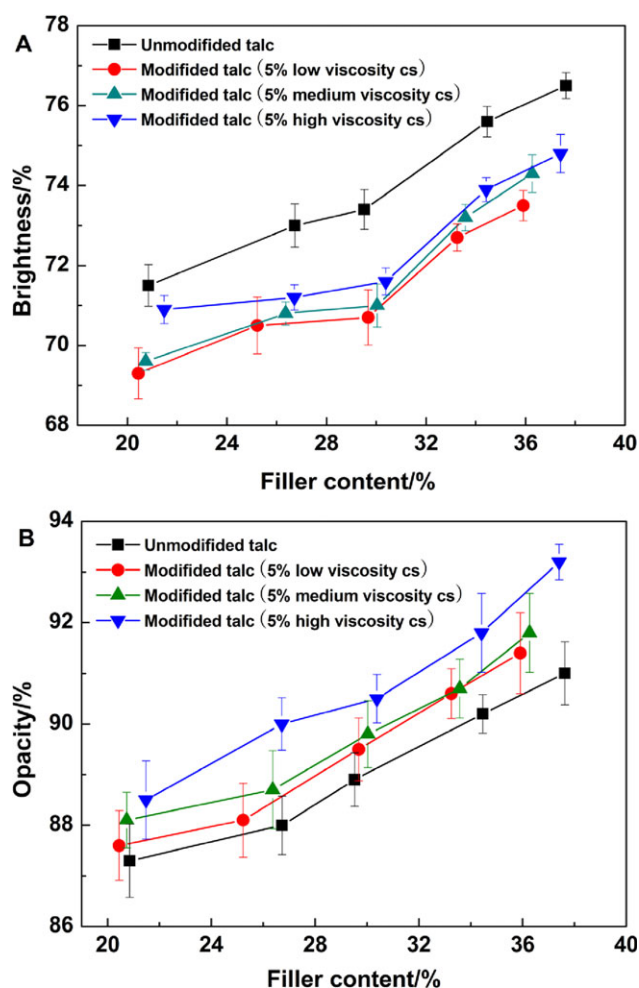


Figure 4. Brightness (A) and opacity (B) as a function of filler content in paper with different CS viscosity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

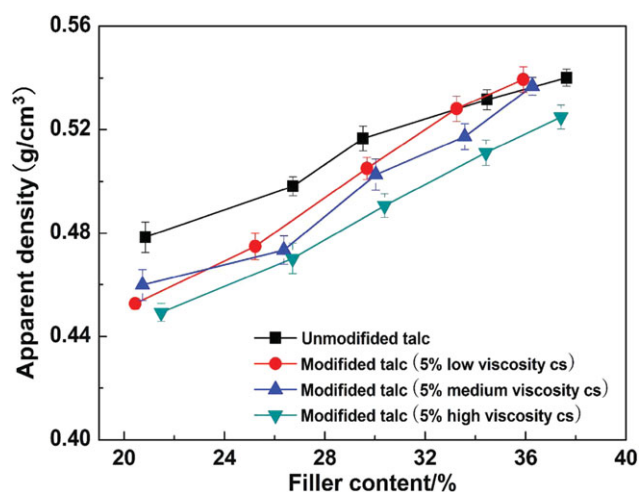


Figure 5. Apparent density as a function of filler content in paper with different CS viscosity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

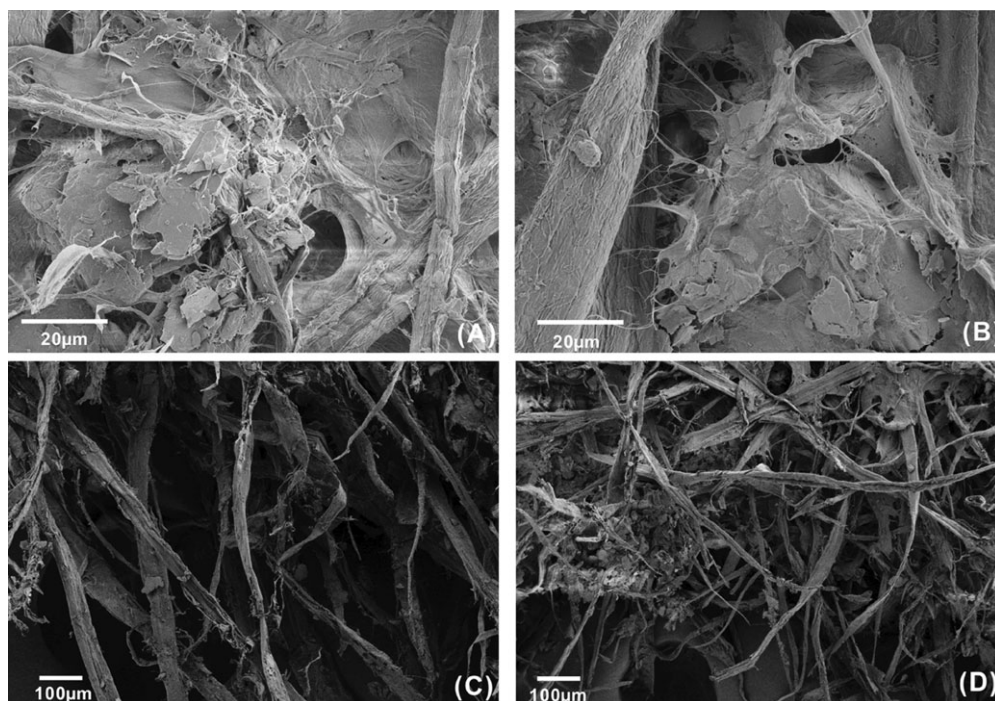


Figure 6. FESEM images of different talc filled papers: paper filled with unmodified talc (A), paper filled with modified talc (B), edge of unmodified talc filled paper after tensile strength measurements (C), edge of modified talc filled paper after tensile strength measurements (D).

contrary, the modified talc particles were effectively bonded to the fiber surface as shown in Figure 6(B). This structure suggests that the surface modification of talc particles was favorable to enhance the compatibility and affinity of filler-to-fiber.

As can be seen in Figure 6(C), the fibers of unmodified talc filled paper after tensile strength measurements were pull-out directly. However, in Figure 6(D), it can be confirmed using FESEM that many fibers were cut or broken rather than pull-out directly. This may probably due to the strong bonding between fiber and modified filler than that of unmodified filler. This phenomenon indicates that the bond strength between fibers and modified fillers is high enough to be compatible with the fiber strength due to the formation of H-bonding between the fiber and filler.

CONCLUSIONS

In this study, CS was proved to be an effective modifier in the modification of talc, and a high coating amount was achieved. The particle size analysis and FESEM observations confirmed the formation of coated filler or aggregates. With respect to filled sheets, the modification of talc and the CS viscosity can both influence the resulting paper strength. As to high viscosity modified talc filled paper, at the filler content of 37%, the tensile strength is 64% higher than that of pure filler paper. At the same time, optical properties of the filled paper with modified talc can maintain nearly the same as the filled paper with pure talc. The filler retention rate of high viscosity CS modified filler was found higher than that of unmodified filler. However, the drainage properties were a little influenced by the modification of filler and the filler loading level. FESEM images of filled

Table II. Retention and Drainage of High Viscosity Chitosan Modified Talc with Varied Filler Loading

Filler loading (%) ^a	Total retention (%)		Filler retention (%)		Drainage (s)	
	Talc	Modified talc	Talc	Modified talc	Talc	Modified talc
30	87.3 ± 1.1	82.5 ± 0.9	77.6 ± 1.4	90.9 ± 1.2	11.3 ± 0.2	14.8 ± 0.2
40	86.8 ± 0.8	81.5 ± 1.3	75.6 ± 1.0	87.1 ± 0.9	12.4 ± 0.3	15.0 ± 0.2
50	85.9 ± 0.9	86.5 ± 1.2	72.8 ± 0.9	87.0 ± 1.3	12.8 ± 0.1	15.2 ± 0.4
60	84.8 ± 1.3	85.2 ± 1.5	70.8 ± 0.9	86.8 ± 0.8	15.3 ± 0.3	17.0 ± 0.3
70	84.1 ± 0.8	84.8 ± 1.0	62.3 ± 0.7	86.5 ± 1.1	15.5 ± 0.4	17.5 ± 0.1

^aFiller loading was based on dry weight of fibers.

papers showed better bonding between modified talc and fibers than that of untreated talc.

REFERENCES

1. Shen, J.; Song, Z.; Qian, X.; Ni, Y. *Ind. Eng. Chem. Res.* **2011**, *50*, 661.
2. Dong, C.; Song, D.; Patterson, T.; Ragauskas, A.; Deng, Y. *Ind. Eng. Chem. Res.* **2008**, *47*, 8430.
3. Shen, J.; Qian, X. *Bioresources* **2012**, *7*, 1385.
4. Zhao, Y.; Kim, D.; White, D.; Deng, Y.; Patterson, T.; Jones, P.; Turner, E.; Ragauskas, A. *J. Tappi J.* **2008**, *7*, 3.
5. Cao, S.; Song, D.; Deng, Y.; Ragauskas, A. *Ind. Eng. Chem. Res.* **2011**, *50*, 5628.
6. Cheng, W.; Li, J.; Zhao, Y.; Rao, O. L. U.S. Patent 12/323,976, **2008**.
7. Wagberg, L. E. R.; Lindstrom, T. S. C. U.S. Patent 4,824,523, April 25, **1989**.
8. Kumar, P.; Negi, Y. S.; Singh, S. P. *Bioresources* **2011**, *6*, 3526.
9. Lei, Y.; Yan, Q. X.; Liu, S. P.; Yuan, J. Z. *J. Sci. Ind. Res. India* **2010**, *69*, 215.
10. Silenius, P. EP Patent 0,930,345, **2003**.
11. Subramanian, R.; Maloney, T.; Paulapuro, H. *Tappi J.* **2005**, *4*, 23.
12. Sang, Y.; McQuaid, M.; Englezos, P. *Bioresources* **2012**, *7*, 354.
13. Ibrahim, M. A.; Mobarak, F.; El-Din, E. I. S.; Ebaid, A.; Youssef, M. A. *Tappi J.* **2009**, *4*, 15.
14. Gamelas, J.; Lourenco, A. F.; Ferreira, P. J. *J. Sol-Gel Sci. Technol.* **2011**, *59*, 25.
15. Gill, R. A. U.S. Patent 5,147,507, September 15, **1992**.
16. Laleg, M. U.S. Patent 7,074, B2, July 11, **2006**.
17. Chauhan Vipul, S.; Bhardwaj Nishi, K.; Chakrabarti Swapan, K. *J. Ippta.* **2011**, *23*, 93.
18. Song, D.; Dong, C.; Ragauskas, A.; Deng, Y. *J. Biobased Mater. Bioenergy* **2009**, *3*, 321.
19. Deng, Y.; Yoon, S. Y.; Ragauskas, A.; White, D. U.S. Patent 7,964,063 B2, June 21, **2011**.
20. Fairchild, G. H.; EP Patent 0,731,826, **2008**.
21. Nelson, K.; Deng, Y. *J. Appl. Polym. Sci.* **2008**, *107*, 2830.
22. Shen, J.; Song, Z.; Qian, X. *Appita J.* **2009**, *62*, 360.
23. Shen, J.; Song, Z. Q.; Qian, X. R.; Yang, F. *Carbohydr. Polym.* **2010**, *81*, 545.
24. Yan, Z.; Liu, Q.; Deng, Y.; Ragauskas, A. *J. Appl. Polym. Sci.* **2005**, *97*, 44.
25. Yoon, S.; Deng, Y. *Tappi. J.* **2006**, *5*, 3.
26. Yoon, S. Y.; Deng, Y. *Ind. Eng. Chem. Res.* **2007**, *46*, 4883.
27. Myllymäki, V.; Aksela, P.; Sundquist, A.; Karvinen, S. M. WO Patent 22006, **2006**.
28. Yoon, S. Y. Bonding material coated clay for improving paper properties. Ph. D. Thesis, Georgia Institute of Technology, May **2007**.
29. Ibrahim, M. M.; Mobarak, F.; El-Din, E.; Ebaid, A.; Youssef, M. A. *Carbohydr. Polym.* **2009**, *75*, 130.
30. Bratskaya, S. Y.; Avramenko, V. A.; Sukhoverkhov, S. V.; Schwarz, S. *Colloid J.* **2002**, *64*, 681.
31. Chi, H.; Li, H.; Liu, W.; Zhan, H. *Colloids Surf. A* **2007**, *297*, 147.
32. Sabesan, S.; Bolt, J. D. U.S. Patent 2007/0181038 A1, August 9, **2007**.
33. Soane, D. S.; Berg, M. C.; Mowers, W. A. U.S. Patent 2008/0271865 A1, November 6, **2007**.
34. Shen, J.; Song, Z. Q.; Qian, X. R.; Song, C. J. *China Pulp Paper* **2008**, *27*, 21.
35. Li, H.; Du, Y.; Xu, Y.; Zhan, H.; Kennedy, J. F. *Carbohydr. Polym.* **2004**, *58*, 205.
36. Li, H.; Du, Y.; Wu, X.; Zhan, H. *Colloids Surf. A* **2004**, *242*, 1.