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Preparation of modified diatomite filler *via* a starch-fatty acid complex coating method for improvement of paper strength properties

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In this work, diatomite particles were modified to improve the bondability of diatomite particles with pulp fibers *via* a starch-fatty acid complex coating method. The SEM results illustrated that the surface of the modified diatomite particles was covered by the complex coatings. The coating efficiency of the starch-fatty acid complex on diatomite surface was up to 98%. Modified diatomite had good shear resistance. Compared with the handsheet filled unmodified diatomite, the handsheet filled with modified diatomite had higher strength properties and smaller bulk. The higher zeta potential and larger particle size of modified diatomite were responsible for the higher retention of modified diatomite filler. This work provided a technical support for the application of diatomite as a novel papermaking filler.

Key words: Starch-fatty acid complex; Modified diatomite; Paper; Strength properties

INTRODUCTION

It has been a long history of using mineral fillers in paper industry. Many kinds of mineral fillers have been used, such as kaolin, calcium carbonate, talcum powder and titanium dioxide [1−5]. The application of fillers in paper industry is an active area of research and development [1−3]. Papermakers expect that higher filler content in the paper would improve the cost competitiveness of paper products. The increase of filler content in paper can reduce the energy demand and improve the optical and printing properties of paper [2−6]. Over the past few decades, all of the above improvements provide considerable benefits for paper industry [7−11].

Fillers are second only to pulp fibers as raw materials in paper industry. However, the use of fillers has a negative impact on the strength properties of the paper, especially at high filler addition levels [13−17]. One of the prominent problems in the use of fillers is that some strength properties of paper such as tensile, tear, folding, and stiffness usually decrease with the increase in filler addition level [2,18−25]. These adverse effects are due to the fact that fillers interfere with the hydrogen bonding of fibers, thereby reducing the physical properties of paper [2,30].

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Because of the above mentioned adverse effects, researchers have developed some techniques to overcome these shortcomings [7,19−22]. Many methods have been experimented, including filler preflocculation, [3,4,8] synthesis of fillers with various structures and functions [9−12], surface modification, lumen loading [10−18], and composite fillers. In recent years, filler modification has been an active area of research, because it has the potential to significantly increase the content of filler in the paper [23−26]. The surface modification of the filler for improving the hydrogen bonding between fibers has attracted more and more attention.

It has been reported that starch is suitable for surface modification of papermaking fillers because its chemical structure is similar to that of cellulose. Starch is often used as a dry additive to increase the bonding strength between fibers [19−21]. Starch can be attached to the filler surface in order to improve the bondability between fillers and fibers, and thereby to enhance paper strength. It has been widely used for the modification of clay and calcium carbonate fillers [22−30]. Yoon and Deng prepared a new clay−starch composite filler and claimed more than 100% increase in the tensile strength of the paper at a high addition level [22,23,29,33]. Zhao *et al*. prepared a starch-modified filler by spray drying and evaluated this technology at pilot or full scale [30,34].

Diatomite is a low-cost, environmentally friendly and natural micro/nanostructured material

derived from sedimentary silica, and has cylindrical and plate morphology with well-developed mesoporous and/or macroporous structure [31]. The use of diatomite as a novel papermaking filler is low, but it has become an increasingly important research area. Compared with traditional papermaking fillers, diatomite as a kind of novel papermaking filler has many advantages, such as light weight, high porosity, low wire wear and good adaptability. It is very interesting and important to study whether starch can be used to modify diatomite for improving the strength properties of paper.

In this work, diatomite particles were modified *via* a starch-fatty acid complex coating method. The basic characteristics of the modified diatomite particles including coating efficiency, particle size, ζ potential and shear resistance were evaluated. Meanwhile, the effect of modified diatomite filler on handsheet strength properties and filler retention was investigated.

EXPERIMENTAL

Materials

Analytical methods

Diatomite filler was provided by Hongyuan Co., China. Palmitic acid was purchased from Damao Co., China. Cationic polyacrylamide (Percol 182) was supplied by BASF (China) Co. Bleached hardwood kraft pulp board was supplied by Mudanjiang Hengfeng Paper Co., China. The pulp board was beaten to a beating degree of 45 °SR in a Valley beater. Raw corn starch was supplied by Ruixing Group Co., China.

Preparation of starch-fatty acid complex modified diatomite

Diatomite particles were modified using a starch-fatty acid complex coating method. Raw corn starch suspension (3%) was cooked at 90 °C for 1 h, and then the pH of the cooked starch solution was adjusted to 11 using 0.3 mol/L sodium hydroxide solution. Subsequently, a certain amount of palmitic acid (on the basis of starch) was added to the cooked starch solution and further cooked at 90 °C for 30 min, to form a mixture of palmitic acid and starch. Dry diatomite particles were put into a 500 mL beaker, and then a certain amount of deionized water was added to the beaker, to form a diatomite slurry with a concentration of 150 g/L. The diatomite slurry was dispersed by mixing with a stirrer for 10 min, and then the mixture of palmitic acid and starch was added to the diatomite slurry and stirred for 10 min. The above mixture was poured into a twofold volume of hydrochloric acid solution with a pH of 2, and kept at room temperature for 3 h. The supernatant was collected to measure the total organic carbon (TOC), and the precipitate was washed with deionized water until neutral. Finally, the resultant precipitates were dried at 90 °C for about 3 h. Starch-fatty acid modified diatomite samples with different starch/diatomite ratios were obtained by the above preparation procedure.

Characterization of filler

The surface morphology of the filler was observed by a JSM6510A scanning electron microscope (SEM). The sample was coated with gold before observation.

The ζ potential of the diatomite filler was analyzed using Malvern Zetasizer 3000.

The coating efficiency (*CE*, %) of the starch-fatty acid complex on the diatomite surface was evaluated by the content of total organic carbon (TOC) in the supernatant determined by a TOC analyzer (Liqui TOC). *CE* was calculated by the following formula:

$$CE\ (\%) = [(W_i - W_d)/W_i] \times 100 \quad (1)$$

where, W_i and W_d (g) are the weights of the initial starch-fatty acid complex and the starch-fatty acid complex dissolved in the supernatant, respectively.

The particle size of the filler was analyzed by a particle size analyzer (OMEC LS-POP). After the filler suspension was well dispersed, the particle size was measured.

The shear resistance of the modified diatomite was evaluated by the following method. The modified diatomite suspension was mechanically stirred with an OA2500 stirrer at two stirring speeds (1000 rpm for 70 min and 2000 rpm after 70 min). One sample was taken every 10 min and the particle size was measured with the particle size analyzer.

Preparation of handsheets and determination of physical properties

Different dosages of unmodified or modified diatomite filler and 0.04 wt% (on the basis of filler) of Percol-182 used as retention aid were added to 1% bleached hardwood kraft pulp suspension. After adding retention aid and filler the slurry was stirred for 25 s, the handsheet with a target grammage of 150 g/m^2 was prepared with a ZQJ1-B handsheet former. All handsheets were dried at 105 °C for 15 min on a sheet dryer. The handsheets were then conditioned at 50±2% RH and 23±1 °C overnight.

Physical properties of the handsheets were determined according to TAPPI Test Methods.

Determination of filler retention in handsheets

The content of ash in handsheets was measured by ashing in a muffle furnace at 575±25 °C for 6 h. The filler retention (*FR*, %) was calculated by the following formula:

$$FR\ (\%) = [W_a/(A \times W_f)] \times 100 \quad (2)$$

where, W_a (g) is the weight of ash in the handsheets, and W_f (g) is the weight of the filler added. A is the weight fraction of diatomite in the filler. The value of A is equal to 1 for unmodified filler.

RESULTS AND DISCUSSION

When starch is gelatinized in the presence of fatty acid, the amylose from the starch granules forms a helical inclusion complex with the fatty acid [32]. The complex of starch-fatty acid can be dissolved in alkali aqueous solution. After adding the slurry of diatomite to the complex, diatomite particles are fully mixed with the complex. When the mixture is poured into hydrochloric acid solution with pH of 2, the starch-fatty acid complex precipitates. Thus, the precipitated starch-fatty acid complex is *in situ* coated individual diatomite particles or diatomite aggregates, and hence a modified diatomite filler is obtained.

The surface morphology of unmodified and modified diatomite filler particles was observed by SEM, and the images are shown in Figure 1. Unmodified diatomite had numerous micropores on the surface (Figure 1a), but the surface of modified diatomite was fully covered and no micropores were visible (Figure 1b), which illustrated that the surface of modified diatomite was coated by the starch-fatty acid complex.

The retention and flocculation of the diatomite filler in pulp fiber networks are affected by the ζ potential of the diatomite particles. In this work, the ζ potentials of unmodified and starch-fatty acid complex modified diatomite fillers with different dosages of fatty acid were measured, and the results are shown in Table 1. The ζ potential of unmodified diatomite is −63.12 mV. However, the ζ potential increased after the diatomite was modified with the starch-fatty acid complex. Furthermore, the ζ potential increased with the increase in fatty acid dosage.

For instance, the ζ potential of modified diatomite was −45.26 mV at a fatty acid dosage of 5%, and the ζ potential increased to −10.13 mV

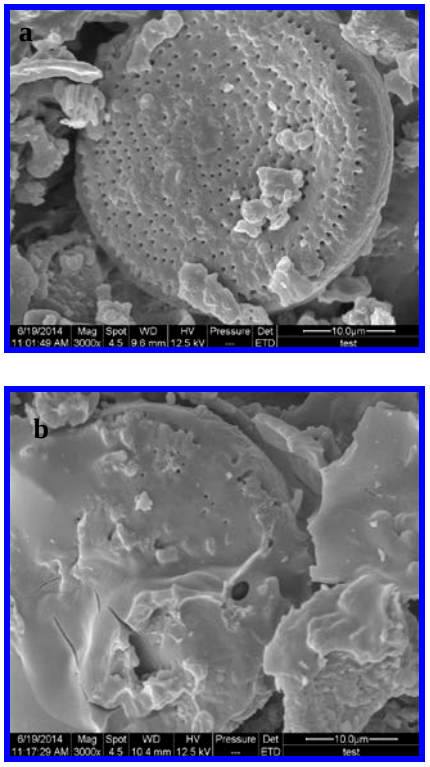

Fig. 1. SEM images of unmodified (a) modified (b) diatomite filler.

Table 1. ζ Potential of starch-fatty acid complex modified diatomite filler

Sample no.	Condition	ζ Potential (mV)
1	Unmodified diatomite	−63.12
2	Starch: diatomite, 1:4; fatty acid, 5%	−45.26
3	Starch: diatomite, 1:4; fatty acid, 10%	−22.28
4	Starch: diatomite, 1:4; fatty acid, 20%	−10.13
5	Starch: diatomite, 1:8; fatty acid, 10%	−24.36
6	Starch-fatty acid complex (fatty acid, 10%)	−7.52

when fatty acid dosage was 20%. It is primarily because the high ζ potential (−7.52 mV) of the starch-fatty acid complex can significantly contribute to the increase of the ζ potential of the modified diatomite. Because the ζ potential of the starch-fatty acid complex was far higher than that of diatomite, the ζ potential increased when diatomite was coated with starch-fatty acid complex.

For modified diatomite, it is very important to effectively utilize the starch-fatty acid complex. If the utilization efficiency of the starch-fatty acid complex is low, no good coating could be formed on the surface of diatomite. In this research, the *CE*

of the starch-fatty acid complex on the surface of diatomite was measured, and the results are shown in Table 2. It was found that about 98% of the starch-fatty acid complex was coated on the surface of diatomite. Fatty acid dosage had almost no effect on *CE*, which revealed that 5% fatty acid was enough to effectively utilize the starch-fatty acid complex. Filler particle size is very important because it affects filler retention and paper physical properties. The particle size of unmodified diatomite was about 5.5 μm, but the size increased to 10−20 μm after modification. The shear resistance of the filler directly affects the particle size of the filler.

Table 2. *CE* of starch-fatty acid complex on the surface of diatomite

Sample no.	Condition		TOC (ppm)	*CE* (%)
	Starch: Diatomite	Fatty acid (%)		
1	1:4	5	61.25	98.02
2	1:4	10	59.42	97.97
3	1:4	15	58.35	97.89
4	1:4	20	57.15	97.80
5	1:8	10	57.52	98.03

The shear resistance of modified diatomite is very important for its application, because the filler must pass through a high-shear zone in papermaking system. Therefore, it is necessary to study the shear resistance of modified diatomite. The change of the size of modified diatomite with stirring time is shown in Figure 2. The particle size of modified diatomite was kept unchanged for 70 min at a stirring speed of 1000 rpm. For the filler of modified diatomite with a low starch/diatomite ratio (less than 1:4), the particle size was only slightly decreased with prolonging stirring time after 70 min at a stirring speed of 2000 rpm. The results indicated that the starch-fatty acid complex modified diatomite filler had a high shear resistance.

The physical properties of filled handsheets are shown in Figures 3−5. All strength properties of handsheets decreased with increasing filler dosage, which is in agreement with the general knowledge about the influence of filler addition on handsheet strength properties. However, the strength properties of handsheets with modified diatomite filler were far higher than those of handsheets filled with unmodified diatomite at any filler addition level.

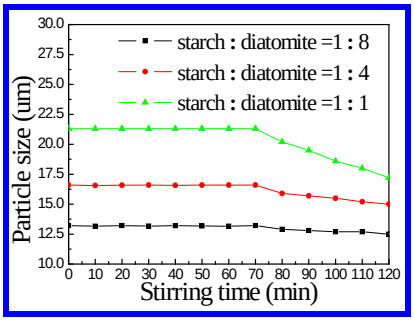

Fig. 2. Change in particle size of modified diatomite with stirring time. Note: the stirring speed is 1000 rpm for 70 min and it is 2000 rpm after 70 min. Fatty acid dosage is 10%.

Furthermore, the handsheets filled with modified diatomite with a higher starch/diatomite ratio had higher strength properties, especially for tensile and tearing strengths. This was because diatomite modified at a higher starch/diatomite ratio was coated with a larger amount of starch-fatty acid complex.

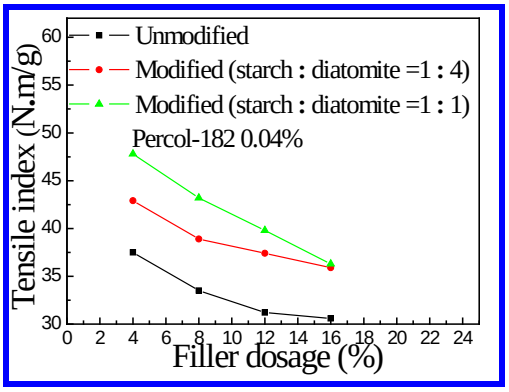

Fig. 3. Effect of filler dosage on the tensile index of filled handsheets.

The effect of filler addition level on the bulk of the handsheet is shown in Figure 6. The bulk of the handsheet increased with the increase of filler addition level. Meanwhile, the bulk of modified diatomite filled handsheet was lower than that of unmodified diatomite filled handsheet.

It indicated that the starch-fatty acid complex coatings on the surface of diatomite could improve the bondability of diatomite particles with pulp fibers. Generally, the smaller the bulk, the higher is the strength. Therefore, the bulk data were well in agreement with the strength data. All the above results indicated that starch-fatty acid complex modified diatomite can improve the strength properties of filled handsheets.

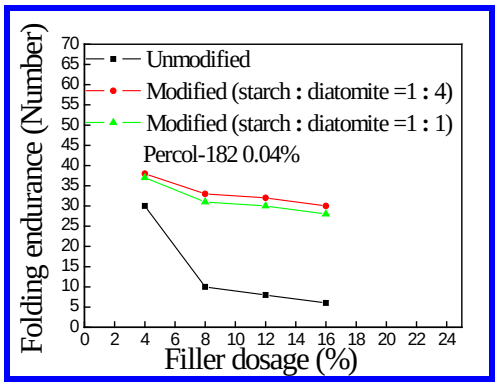

Fig. 4. Effect of filler dosage on the folding endurance of filled handsheets.

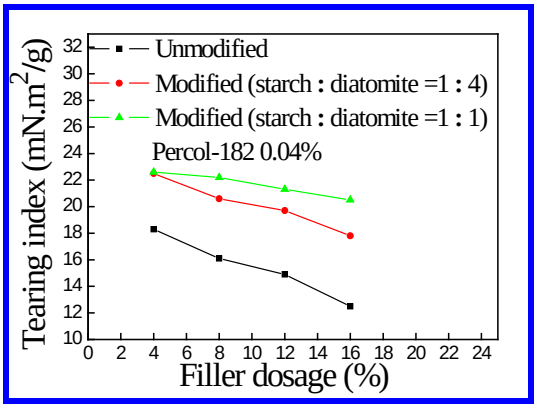

Fig. 5. Effect of filler dosage on the tearing index of filled handsheets.

The effect of filler dosage on filler retention is shown in Figure 7. The filler retention (*FR*) decreased with increasing filler dosage, which is in agreement with the general knowledge about the influence of filler addition level on *FR*. However, the *FR* of the modified diatomite filler was higher than that of the unmodified diatomite filler.

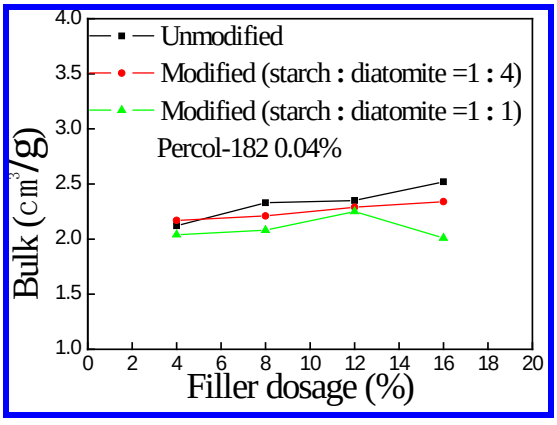

Fig. 6. Effect of filler dosage on the bulk of filled handsheets.

In addition, the *FR* of the modified diatomite filled handsheet was less affected by the filler addition level compared with the unmodified diatomite filled handsheet. It is primarily because that the particle size of starch-fatty acid complex modified diatomite was much larger than that of unmodified diatomite. Furthermore, as mentioned earlier, the modified diatomite has a higher ζ potential compared with the unmodified diatomite, which was also responsible for the high retention of modified diatomite.

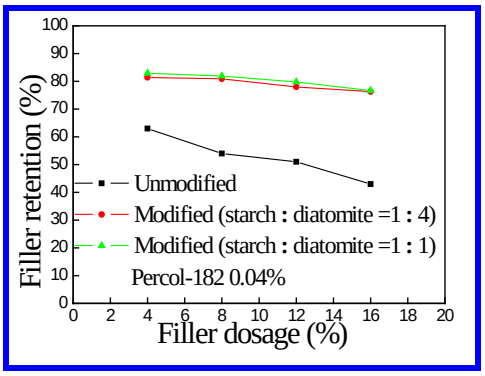

Fig. 7. Effect of filler dosage on filler retention.

CONCLUSION

Diatomite filler was successfully modified *via* a starch-fatty acid complex coating method. The SEM images showed that the surface of modified diatomite particles was covered by the complex of starch-fatty acid coatings. The coating efficiency (*CE*) was as high as 98%. The modified diatomite had larger particle size and higher ζ potential compared with the unmodified diatomite. The modified diatomite had good shear resistance. Compared with the handsheet filled with unmodified diatomite, the handsheet filled with modified diatomite displayed higher strength properties and smaller bulk. The retention of modified diatomite filler was higher than that of unmodified diatomite due to its larger particle size and higher ζ potential.

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REFERENCES

1. Y. Deng, P. Jones, L. McLain, J. A. Ragauskas, *Tappi J.*, **9,** 31 (2010).
2. K. Koivunen, H. Alatalo, P. Silenius, *J. Mater., Sci*, **45,** 3184 (2010).

3. S. Li，S. Wang, *Journal Of Northeast Dianli University*, **03**, 69 (2016).
4. V. S. Chauhan, N. K. Bhardwaj, *Tappi J.*, **13,** 17 (2014).
5. S. W. Mabee, R. Harvey, *Proceedings of TAPPI Papermakers Conference, Vancouver, BC, Canada, April*, 2000.
6. J. Shen, Z. Song, X. Qian, *BioResources*, **4,** 1190 (2009).
7. L. Liu, Y. Huang, K. Lu, *Journal Of Northeast Dianli University*, **06**, 95 (2015).
8. S. W. Mabee, *Proceedings of TAPPI Papermakers Conference, Cincinnati, OH, USA, March* (2001).
9. H. Yang, L. Qiu, X. Qian, J. Shen, *BioResources*, **8,** 5449 (2013).
10. S. Song, M. Zhang, Z. He, J. Z. Li, Y. Ni, *Ind. Eng. Chem. Res.*, **51,** 16377 (2012).
11. S. C. Vipul, K. B. Nishi, *Ind. Eng. Chem. Res.*, **53,** 11622 (2014).
12. Y. Zhang, J. Li, W. Li, *RSC Adv.*, **5,** 85673 (2015).
13. R. Juuso, D. M. Katarina, K. Jonna, C. M. Thad, *Cellulose*, **22,** 4003 (2015).
14. J. Fan, Y. Cao, T. Li, J. Li, X. Qian, J.Shen, *ACS Sustain Chem Eng*., **3,** 1866 (2015).
15. Y. Deng, S. Y. Yoon, J. A. Ragauskas, *US Patent No. US2008/087396 A1*, (2008).
16. X. Huang, X. Qian,; J. Li, S. Lou, J. Shen, *Carbohydrate Polymers*, **117,** 78 (2015).
17. X. Huang, J. Shen, X. Qian, *Carbohydrate Polymers*, **98,** 931 (2013).
18. Y. Zhang, L. Lv, C. Shi, *Journal Of Northeast Dianli University*, **05**, 17 (2015).
19. S. Bratskaya, S. Schwarz, G. Petzold, T. Liebert, T. Heinze, *Ind. Eng. Chem. Res.*, **45,** 7374 (2006).
20. C. Gaiolas, P. Mendes, M. S. Silva, A. P. Costa, M. N. Belgacem, *Appita J.*, **58,** 282 (2005).
21. T. Lv，L. Dong，Y. Shi, et al., *Journal Of Northeast Dianli University*, **02**, 51 (2016).
22. S. Y. Yoon, Y. Deng, *Ind. Eng. Chem. Res*., **46,** 4883 (2007).
23. S. Y. Yoon, Y. Deng, *Tappi J.*, **5,** 3 (2006).
24. J. Shen, Z. Q. Song, X. R. Qian, *Appita J.*, **62,** 360 (2009).
25. Cao, S.; Song, D.; Deng, Y.; Ragauskas, A. J. *Ind. Eng. Chem. Res.*, **50,** 5628 (2011).
26. H. Fan, S. Wang, J. Liu, *BioResources*, **9,** 5883 (2014).
27. Y. Sang, M. McQuaid, P. Englezos, *BioResources*, **7,** 354 (2012).
28. H. Fan, D. Wang, W. Bai, J. Liu, *BioResources*, **7,** 3317 (2012).
29. S. Y. Yoon, Y. Deng, *J. Appl. Polym. Sci.*, **100,** 1032 (2006).
30. Y. Zhao, Z. Hu, A. J. Ragauskas, Y. Deng, *Tappi J.* **4,** 3 (2005).
31. X. Ye, S.Kang, H. Wang, H. Li, Y. Zhang, G. Wang, H. Zhao, *J. Hazard. Mater.*, **289,** 210 (2015).
32. S. Meng, Y. Ma, J. Cui, D. W. Sun, *Starch-Stärke*, **66,** 809 (2014).
33. Y. Zhang, Y. Sun，H. Zhang, *Journal of Northeast Dianli University*, **06**, 67 (2014).
34. W. Shang, X. Meng, Y. Tan, *Journal of Northeast Dianli University*, **03**, 55 (2015).

ПОЛУЧАВАНЕ НА МОДИФИЦИРАН ДИАТОМИТЕН ПЪЛНИТЕЛ ЧРЕЗ НАНАСЯНЕ НА КОМПЛЕКС ОТ НИШЕСТЕ И МАСТНА КИСЕЛИНА ЗА ПОДОБРЯВАНЕ НА ЗДРАВИНАТА НА ХАРТИЯ

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(Резюме)

Диатомитовите частици са модифицирани за подобряване на свързващите им свойства с влакната на хартиения пулп чрез нанасяне на комплекс от нишесте и мастна киселина. Резултатите от SEM анализа показват, че повърхността на модифицираните диатомитови частици е покрита с комплексния слой. Ефективността на покриване с комплекса от нишесте и мастна киселина е до 98%. Модифицираният диатомит проявява високо съпротивление на срязване. В сравнение с хартиени листове, пълни с немодифициран диатомит, тези пълни с модифициран диатомит имат по-голяма здравина и по-малък обем. По-високият зета потенциал и по-големият размер на частиците на модифицирания диатомит са причина за по-доброто задържане на модифицирания диатомитов пълнител. Настоящото изследване предлага техническо потвърждение на приложението на диатомит като нов пълнител в хартиеното производство.