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Preparation of a modified diatomite filler via polyethyleneimine impregnation and its application in papermaking

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ABSTRACT: In this study, we sequentially modified diatomite (DM) particles with sodium dodecyl sulfate and polyethyleneimine with an impregnation method. Modified DM was used as both a filler and an anionic trash catcher in the papermaking process. The surface morphology, ζ potential, particle size, and Fourier transform infrared spectrum of the modified DM were investigated, and the application performance of the modified DM was evaluated through filler retention, ζ potential, drainability, and cationic demand of the papermaking furnish and the paper strength properties. The results show that the modified DM could be used as a good, novel filler in papermaking. The ζ potential of the surface of the modified DM particles was changed from electronegative to electropositive, and the particle size of the modified DM particles was increased. The retention of the modified DM filler was 16% higher than that of the unmodified DM when the filler dosage was 40%. The higher ζ potential was responsible for the higher retention of the modified DM filler. The drainability of the papermaking furnish was improved efficiently. The anionic trash in the papermaking system was anchored efficiently, and the cationic demand of the papermaking furnish decreased over 85% when the dosage of modified DM was 35%. Compared with the handsheets filled with unmodified DM, the handsheets filled with modified DM had higher strength properties. © 2018 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2018**, *135*, 46275

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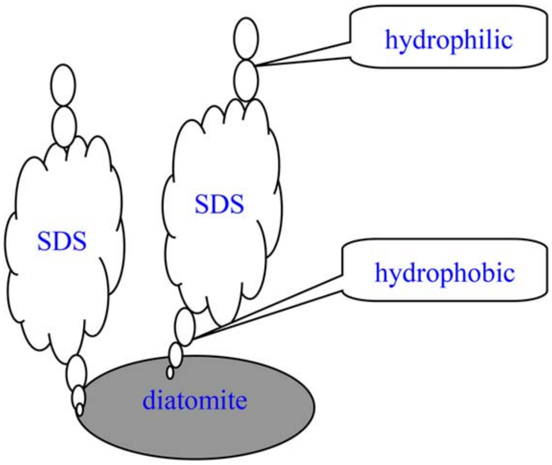
INTRODUCTION

Diatomite (DM) is a low-cost, environmentally friendly, and natural microstructured/nanostructured material derived from sedimentary silica. It has cylindrical and plate morphologies with well-developed mesoporous and/or macroporous structures.[1–6] The highly developed pore structure, low density, and high surface area of DM results in it having a number of industrial applications, including as filtration media for various inorganic and organic chemicals and absorbents.[2–7]

Although DM is not frequently used as a novel papermaking filler, its use has become an increasingly important research area.[4–10] Compared with traditional papermaking fillers, DM as a kind of novel papermaking filler has many advantages; these include its light weight, high porosity, low wire wear, and good adaptability. In the modern papermaking process, great changes in fibrous raw materials have taken place, and deinked pulp and high yield pulp are used extensively. As the closure degree of white water increases, the accumulation of anionic trash in paper furnish causes a lot of problems to wire operation and sheet properties.[11–19]

Anionic trash is one of the popular names used to describe a wide range of dissolved anionic polymeric and colloidal materials. Another common name for this is DCSs, which stands for dissolved and colloidal substances. At present, the main methods of eliminating anionic trash are chemical and biological methods.[5–9,20–26] The chemical fixation method uses anionic trash catchers (ATCs), such as polyethyleneimine (PEI) and poly(aluminum chloride), to remove anionic trash and neutralize the electronegativity of DCSs. ATCs have some beneficial effects on the elimination of anionic trash, but they may also cause new problems. They may have a negative impact on the effectiveness of cationic additives and may be unable to firmly anchor anionic trash onto pulp fibers. Nowadays, there have been plenty of studies on the application of ATCs in anionic trash elimination.[2–9,20–31] However, the use of ATCs to modify the DM surface and the application of the modified product to the papermaking process have not been reported.



Scheme 1. Diagrammatic representation of the interactions between SDS and DM. [Color figure can be viewed at wileyonlinelibrary.com]

PEI is a water-soluble polyamine; there are a large quantity of nitrogen atoms of amino groups on its macromolecular chains. Commercial PEI often has branch chains (branched PEI), and these contain primary, secondary, and ternary amino groups in a ratio of approximately 1:2:1. The majority of amino groups on the molecular chains of PEI are in the protonated state in aqueous solutions with pHs of less than 10, so PEI is a kind of cationic polyelectrolyte. These characteristics of PEI have attracted wide attention from scholars, and PEI has been used in many fields, including separation and purification.[20,21,26–29] This is an effective approach for preparing functional materials with PEI molecules to modify the surface of porous particles.[19–21,25–32]

The use of fillers in paper products can provide cost and energy savings. However, there are many problems associated with the use of fillers; these include negative effects of the filler loading on the paper strength, sizing, and retention. To solve these problems and make better use of fillers, many methods have been proposed, among which filler modification has been a hot topic. Filler modification can improve the retention and optical properties of the fillers and enhance the fiber–filler bonding.[7,32–35] It is very interesting and important to study whether PEI can be used to modify DM to anchor anionic trash and whether modified DM as a kind of novel papermaking filler can improve the retention of the filler and the strength properties of the paper.

In this study, we sequentially modified DM particles with sodium dodecyl sulfate (SDS) and PEI with an impregnation method, and the modified DM was used in the papermaking process. SDS, a hydrophilic anionic surfactant, increased the electronegativity of the DM particle surface. The function of SDS was to promote the adsorption of PEI with a high cationic charge density on the DM particle surface. The hydrophobic part of SDS resulted in interactions with DM, as shown in Scheme 1. We expected that the modified DM would be able to not only anchor anionic trash but also improve the filler retention (FR). The surface morphology, ζ potential, particle size, and Fourier transform infrared (FTIR) spectroscopy characteristics of the modified DM were investigated, and the application performances of the modified DM were evaluated through the FR, paper properties, ζ potential, drainability, and cationic demand of the papermaking furnish.

EXPERIMENTAL

Materials

DM was provided by Hongyuan Co., Ltd. (China). PEI (molecular weight = 20,000–30,000 Da) was purchased from Wengjiang Co., Ltd. (China). SDS was supplied by Tianjin Guangfu Co., Ltd. (China). Cationic polyacrylamide (Percol 182) was supplied by BASF (China) Co., Ltd. Alkaline Peroxide Mechanical Pulp (APMP) pulp board was supplied by Hengxing Paper Co., Ltd. (China) and was beaten to a beating degree of 45° Schopper–Riegel (SR) in a Valley beater for use.

Measurement of the Adsorption Capacity of DM for PEI

First, the characteristic absorptions of PEI aqueous solutions with different concentrations at 200 nm were determined on a Labomed UV-2602 UV–visible spectrometer, and the standard absorption curve of PEI was plotted. Second, experiments of the absorption capacity of DM for PEI were carried out. An amount of 0.4 g of DM was added to 400 mL of different PEI solutions with different concentrations. The mixture was stirred for 3 h at 20 °C and left standing for 48 h. Then, the supernatant was taken out and centrifuged at a rate of 2500 rpm for 30 min. The clear solution was decanted and diluted with deionized water, and the UV absorbance was measured at 200 nm. The amount of adsorbed PEI on DM (M; mg/g) was calculated on the basis of the following equation:

$$M = (n_0 - n_1)V/m \qquad (1)$$

where n_0 and n_1 are the initial and equilibrium concentration of PEI (mg/mL), respectively; V is the volume of the solution (400 mL); and m is the mass of the DM absorbent (0.4 g). Finally, the curve of M against n_1 was plotted.

Preparation of the PEI-Modified DM

An amount of 20 g of DM was added to a 500 mL beaker, and then, 200 mL of deionized water was added to the beaker. After full stirring, 0.381 g of the anionic surfactant, SDS, was added, and then, the pH of the previous mixture was adjusted to 1.0 with a 0.15 mol/L hydrochloric acid solution. The previous mixture was shaken on a laboratory shaker at room temperature for 3 h. Subsequently, the mixture was centrifuged for 25 min, and the supernatant was removed. Then, deionized water was added to the precipitate, the mixture was centrifuged for another 25 min, and the supernatant was removed. The precipitate was washed eight times with deionized water. Finally, the precipitate was dried at 55 °C and passed through a 200 mesh sieve; thus, the complex of DM and SDS, sodium dodecyl sulfate–pretreated diatomite (SDS–DM), was obtained. Subsequently, a certain amount of SDS–DM was added to the PEI solution with a concentration of 0.24 g/L. The mixture of SDS–DM and PEI was dispersed via mixing with a stirrer for 24 h and left to stand at room temperature for 48 h. Then, the mixture was centrifuged for 25 min, and the supernatant was removed. Subsequently, deionized water was added to the precipitate, the mixture was centrifuged for another 25 min, and

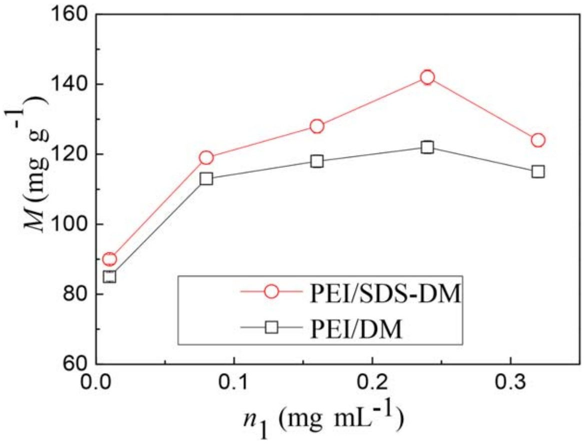


Figure 1. Adsorption of PEI onto SDS–DM and DM. [Color figure can be viewed at wileyonlinelibrary.com]

the supernatant was removed. The precipitate was washed eight times with deionized water, dried at 55 °C, and passed through a 200 mesh sieve; thus, the PEI-modified DM was obtained.

Filler Characterization

The surface morphology of the DM filler was observed with a JSM6510A scanning electron microscope. The sample was coated with gold before observation. The ζ potential of the DM filler was measured with Malvern Zetasizer-3000. The particle size of the DM filler was detected by a particle size analyzer (OMEC LS-POP). The FTIR spectrum of the DM filler was tested with an IRAffinity-1 FTIR spectrophotometer.

Measurement of the ζ Potential and Cationic Demand of the Papermaking Furnish

A volume of 500 mL of the pulp suspension (0.5%) sample was put into a 1000 mL beaker, and then, a certain amount of DM filler was added to the beaker to form the mixture of pulp and DM. The mixture was fully stirred, and the ζ potential was measured with a Malvern Zetasizer 3000. The same mixture was prepared by the same method as mentioned previously. The mixture was filtered through a 200 mesh sieve, and then, the filtrate was centrifuged for 25 min to obtain the supernatant. Finally, the cationic demand of the supernatant was analyzed with a Mütek PCD-03 particle charge detector (Herrsching, Germany).

Measurement of the Drainability

A volume of 1000 mL of the pulp suspension (0.2%) sample was prepared. Then, a certain amount of DM filler was added to the pulp suspension sample, and the sample was stirred for 15 s to form the mixture. Sequentially, 0.05 wt % cationic polyacrylamide (Percol-182) was added to the previous mixture, which was stirred for 20 s. The drainability of the mixture was tested with a Canadian standard freeness tester.

Preparation of the Handsheets and Determination of the Physical Properties

Different dosages of DM filler and 0.05 wt % (on the basis of the sum of pulp and filler) of Percol-182 (cationic polyacrylamide) used as retention aid were added to the 1% APMP pulp suspension, respectively, and then, the slurry was stirred for 25 s. The handsheets, with a target grammage of 60 g/m^2, were prepared with a ZQJ1-B handsheet former. All of the handsheets were dried at 105 °C for 10 min on a sheet dryer. The handsheets were then conditioned at 50 ± 2% RH and 23 ± 1 °C overnight. The physical properties of the handsheets were determined according to TAPPI test methods.

Determination of FR in the Handsheets

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

$$\text{FR }(\%) = [W_a/(A \times W_f)] \times 100 \qquad (2)$$

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

RESULTS AND DISCUSSION

Adsorption of PEI onto DM

The adsorption of PEI on DM and SDS–DM is shown in Figure 1. The amount of adsorbed PEI on both DM and SDS–DM increased with increasing n_1. The maximum adsorption amount of PEI approached when n_1 was 0.24 g/L. When n_1 continued to increase, the electrostatic repulsion between the PEI on the DM surface and the PEI in the solution caused the PEI to fall off the surface of DM; thereby, the adsorption amount of PEI decreased. Meanwhile, the adsorption amount of SDS–DM for PEI was higher than that of DM. This was mainly because PEI had plenty of protonated amino groups when it was in the aqueous solution. Therefore, the PEI molecular chain had a positive electricity and could firmly adhere to the surface of the negatively charged SDS–DM by electrostatic adsorption. The adsorption of SDS–DM for PEI was easier; this was mainly because the surface of the SDS–DM particles had more electrostatic adsorption sites.

Characterization of the Modified DM

The ζ potential and particle size of the modified DM are shown in Figure 2. The ζ potential of the unmodified DM was −36 mV. The surface charge of the modified DM particles changed from negative to positive. This mainly resulted from the adsorption of cationic polyelectrolyte PEI on the surface of DM. PEI

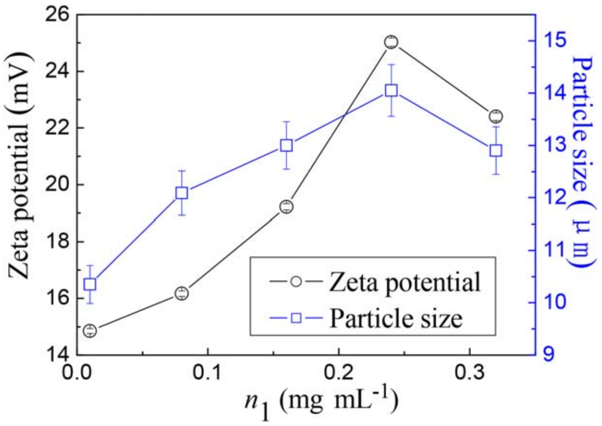


Figure 2. ζ potential and particle size of the modified DM. [Color figure can be viewed at wileyonlinelibrary.com]

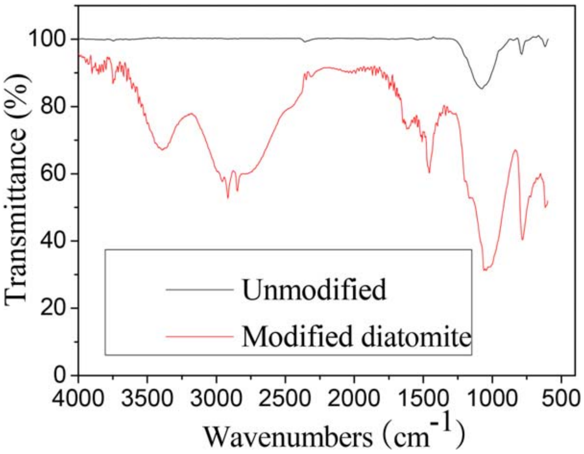


Figure 3. FTIR spectra of the unmodified and modified DM fillers. [Color figure can be viewed at wileyonlinelibrary.com]

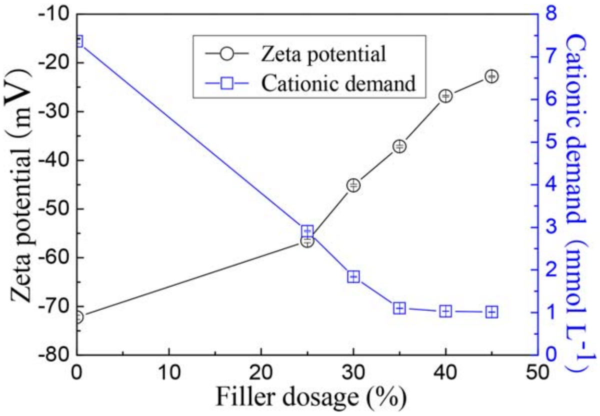


Figure 5. Effect of the modified DM filler dosage on the ζ potential and cationic demand of the papermaking furnish. [Color figure can be viewed at wileyonlinelibrary.com]

was firmly attached to the surface of the DM particles; hence, the modified DM showed positive electricity. The particle size of the unmodified DM was 4.81 μm. The particle size of modified DM increased over that of the unmodified DM particles. This was probably because PEI led to the aggregation of two or more DM particles by the bridge effect. The increases in the ζ potential and particle size of DM laid a solid foundation for its application. The ζ potential and particle size of the modified DM approached the maximum at an n_1 of 0.24 g/L. When n_1 continued to increase, the particle size and ζ potential of the modified DM decreased, probably because the adsorption amount of PEI decreased (Figure 1).

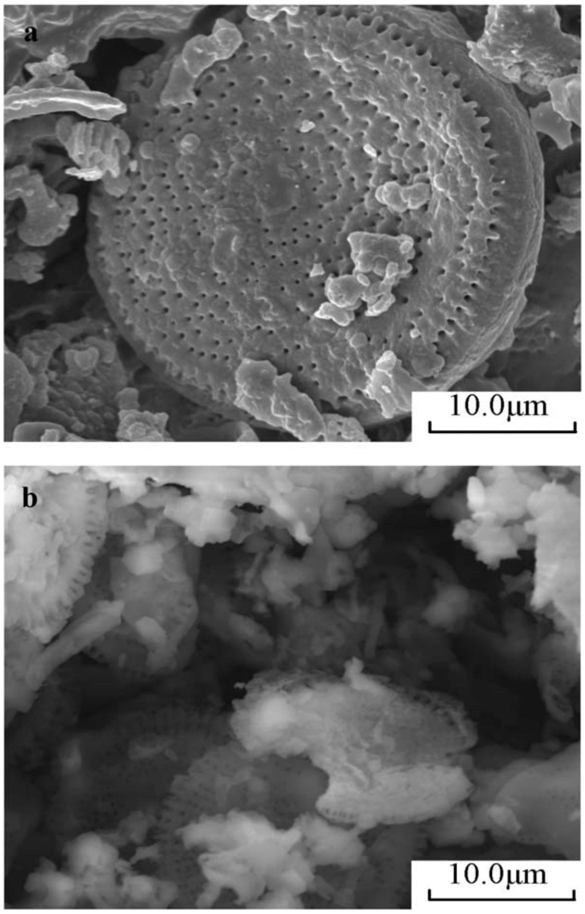


Figure 4. Scanning electron microscopy images of the (a) unmodified and (b) modified DM fillers.

As Figure 3 shows, the main characteristic peak of the unmodified DM appearing at 1082 cm^{-1} was due to Si—O stretching vibrations. The peak at 751 cm^{-1} was attributed to Si—O—Si stretching vibrations, and the adsorption band at around 510 cm^{-1} was attributed to the antisymmetric stretching vibrations of Si—O—Si. Compared with the unmodified DM, the modified DM showed new characteristic peaks. New characteristic peaks appeared at 2852 and 2919 cm^{-1}; these belonged to the symmetric and antisymmetric stretching vibrations of $—\text{CH}_2$ in the SDS alkyl chain. This indicated that SDS was incorporated into DM.[36] The peaks at 3500 and 1650 cm^{-1} were $—\text{NH}_2$ vibration peaks, and the peaks at 1564 and 1465 cm^{-1} were C—N vibration peaks.[36–38] These characteristic peaks proved that PEI had adhered to the surfaces of the DM particles.

The surface morphologies of the unmodified and modified DM particles were observed by scanning electron microscopy, and the images are shown in Figure 4. The unmodified DM had numerous micropores on the surface [Figure 4(a)]. However, the surface and pore wall of the modified DM was covered by some floccules [Figure 4(b)]; this showed that DM was modified by PEI.

Impact of the Modified DM on the ζ Potential and Cationic Demand of the Papermaking Furnish

We expected that anionic trash in the papermaking furnish system would be neutralized and the retention of DM filler would be high. The retention and flocculation of the DM filler in the pulp fibers networks were affected by the ζ potential of the DM particles. In this study, the ζ potentials of papermaking furnish with different dosages of unmodified and modified DM fillers were measured, and the results are shown in Figure 5. The ζ potential of the papermaking furnish increased with increasing

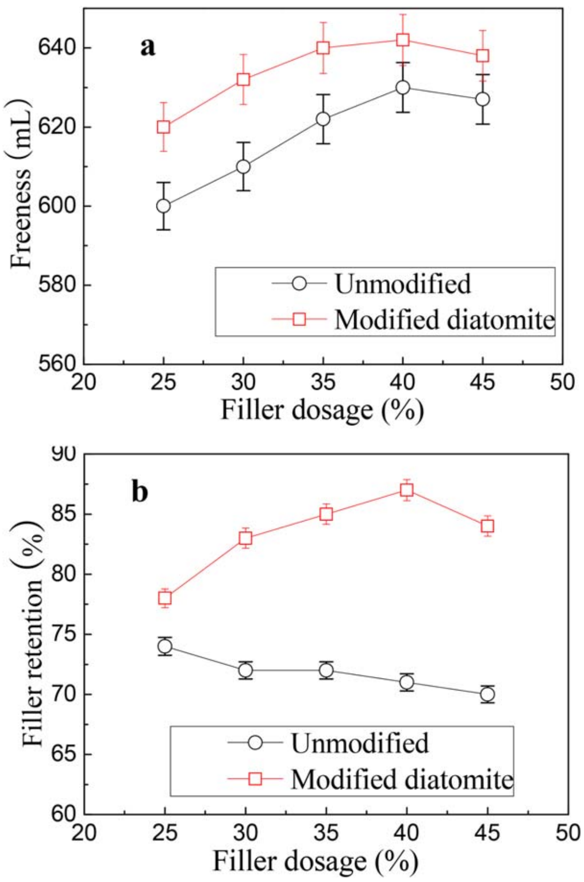


Figure 6. Effect of the filler dosage on the (a) freeness of the papermaking furnish and (b) FR. [Color figure can be viewed at wileyonlinelibrary.com]

modified DM filler dosage. The APMP pulp fibers contained a number of carboxyl groups; this led to the APMP pulp fibers showing electronegativity. The positive charge on the surface of the modified DM not only neutralized the anionic trash but also compounded with the APMP pulp fibers by electrostatic adsorption.

A high degree of system closure led to high levels of DCSs in the process liquors. The effect of the modified DM filler dosage on the cationic demand of papermaking furnish was evaluated, and the result is shown in Figure 5. When the dosage of modified DM filler was below 35%, the cationic demand of the papermaking furnish decreased significantly with increasing modified DM filler dosage. The cationic demand was changed from 7.36 to 1.10 mmol/L (decreased by 85%) with increasing modified DM filler dosage from 0 to 35%. However, the cationic demand was almost unchanged, although the ζ potential continued to increase when the modified DM dosage was greater than 35%.

From the results, the modified DM was more effective in capturing anionic trash than in attaching to fibers. At a filler content below 35%, the modified DM mainly captured anionic trash. At filler contents over 35%, there was not sufficient anionic trash, and the modified DM started to fix more fibers as the ζ potential increased.

The previous interpretation led to the conclusion that the following two mechanisms contributed to the strength: (1) the cleaning effect by the capture of detrimental substances, which reduced fiber–fiber interactions (the dusting effect observed by cationic demand) and (2) the creation of hydrogen bounding between the fibers and filler (fiber saturation observed from the ζ potential). The optimal strength was observed at a 35% filler loading (Figure 7, shown later). This probably indicated that the fiber–fiber bonds within the pulp were stronger than the ones created by the modified DM filler and the fibers.

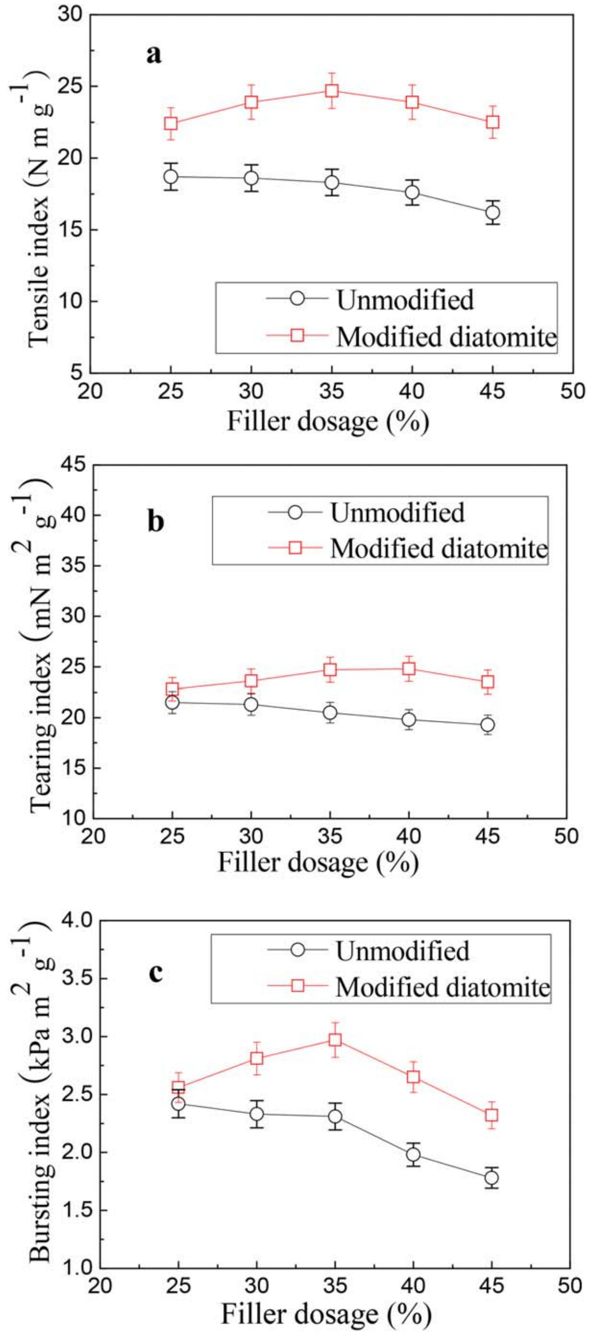


Figure 7. Effect of the filler dosage on the strength properties of the filled handsheets. [Color figure can be viewed at wileyonlinelibrary.com]

Impact of the Modified DM on the Drainability of the Papermaking Furnish and FR

The drainability of the papermaking furnish is of significant importance to paper production. The drainability of papermaking furnish with different dosages of the unmodified and modified DM fillers were measured, and the results are shown in Figure 6(a). DM is a siliceous rock, and its main chemical component is silicon oxide. In this study, we used the cationic polyacrylamide Percol-182 as a retention aid to improve the drainability of the papermaking furnish. In addition, the interactions between the pulp fibers were reduced with increasing unmodified DM dosage, the interspace between pulp fibers was increased, and the drainability was improved. However, too many DM particles decreased the interspaces between pulp fibers and, thereby, reduced the drainability of the papermaking furnish.

The freeness of the papermaking furnish with the modified DM filler was higher than that of the papermaking furnish with the unmodified DM. This demonstrated that filling modified DM improved the drainability of the papermaking furnish. This was mainly because the modified DM could neutralize the anionic trash of the papermaking furnish and provide favorable conditions for the drainage of APMP. Moreover, the modified DM surface was electropositive, and it could anchor some fines with a barrier effect. The freeness of the papermaking furnish increased with increasing filler dosage, and it reached a maximum when the filler dosage was 40%. The freeness decreased slightly as the filler dosage continued to increase. This indicated that too many DM particles decreased the voidage among the pulp fibers and, thereby, reduced the drainability of the papermaking furnish.

The effect of the filler dosage on FR is shown in Figure 6(b). FR of the modified-DM-filled handsheets was higher than that of the unmodified-DM-filled handsheets. FR decreased with increasing unmodified DM filler dosage; this was in agreement with general knowledge about the influence of the filler addition level on FR. FR of the modified-DM-filled handsheets increased with increasing filler dosage and reached a maximum value of about 87% when the filler dosage was 40%. This was mainly because the surface of the modified DM particles was positively charged; this could promote the retention of modified DM particles on the surface of the negatively charged pulp fibers by electrostatic adsorption.

Strength Properties of the Modified-DM-Filled Handsheets

The physical properties of the filled handsheets are shown in Figure 7. All of the strength properties of the handsheets filled with modified DM were higher than those of the handsheets filled unmodified DM at any filler addition level. This was mainly because the modified-DM-filled handsheets had stronger hydrogen bonding between the fibers and fillers. The contact between the modified DM fillers and pulp fibers was a soft contact; hence, it was beneficial to the improvement of the handsheet strengths.

Furthermore, all of the strength properties of the handsheets filled with unmodified DM decreased with increasing filler dosage. However, the strength properties of the handsheets filled with modified DM first increased and then decreased with increasing filler dosage. When the modified DM filler dosage was greater than 35%, the fiber–fiber bonding ability decreased because of the interference effect of more filler particles; thereby, a decreasing strength trend was observed.

Many methods have been widely used for the modification of papermaking fillers such as clay and calcium carbonate. These methods include the milling of the filler, the preflocculation of the filler, the surface modification of the filler, and the use of composite fillers.[7,39–41] Clay and calcium carbonate modification showed a positive role in the improvement of the filler loading level. In this study, the DM particles were sequentially modified with SDS and PEI with an impregnation method. Compared with traditional papermaking fillers, the modified DM effectively improved the drainability of papermaking furnish, FR, and strength properties of filled handsheets.

CONCLUSIONS

DM particles were sequentially modified with SDS and PEI with an impregnation method. Compared with the unmodified DM, the ζ potential of the modified DM was changed from electronegative to electropositive, and the particle size grew larger. The modified DM effectively improved the retention of the DM filler. The physical properties of the paper and the drainability of the papermaking furnish were significantly improved. Moreover, anionic trash was effectively anchored by the modified DM. The efficiency of retention and drainage aid (cationic polyacrylamide) was improved. The modified DM could be used as a good, novel filler in papermaking.

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