Diatomite Modified With Alkyl Ketene Dimer For Hydrophobicity of Cellulosic Paper

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Abstract

Multi-functionalization of papermaking chemicals is one of its main developing strategies. Fillers and internal sizing agents are often mutually restricted in practice. Therefore, it is feasible to prepare a new papermaking chemical by combining its functions. A process of diatomite modified with Alkyl ketene dimer (AKD) was developed in this study. The modified diatomite (AD) can concurrently play the role of mineral filler and sizing agent in the papermaking process. With the equal dosage of AKD, the AD had better sizing and retention performance than the commercial AKD emulsion in the case of cationic polyacrylamide (CPAM) and the CPAM/ bentonite retention system. The sizing mechanism of the AD can be interpreted as numerous hydrophobic sites and micro-surface structure of the paper sheet caused by the AD. Since the ester linkages were not detected in FT-IR spectra of the paper sheet filled by the AD, the chemical reaction may not be indispensable for its sizing performance. What's more, an interesting “sticky” hydrophobicity phenomenon was observed when filling with AD. The approach in this study to prepare the “sticky” hydrophobic paper sheet can find its applications in some non-traditional application fields of cellulosic paper.

Introduction

It is well known that vegetable fibers are the main component of cellulosic paper (Xiao et al. 2015; Li et al. 2019). The cellulosic fibers are hydrophilic due to abundant hydroxyl groups in the molecule of cellulose. Therefore, the cellulosic paper is inherently hydrophilic (Wu et al. 2021). However, the intrinsic hydrophilic of cellulosic paper limits its application in some cases. It is necessary to grant hydrophobicity for paper sheets to meet some special applications such as writing, printing, and packaging. Hence, internal sizing technology has been well developed since the 1807s, and various sizing agents were commercially promoted, such as rosin-base products, alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA) emulsion, etc. (Huang et al. 2018; Ashish et al. 2019; Li and Neivandt 2019). AKD molecule has two long alkyl chains and one hetero four-membered ring that can react with hydroxyl groups of cellulose molecules by forming β-keto ester linkages (Yoshida et al. 2012). AKD is one of the most popular internal sizing agents, widely used after a decisive change from the acid to neutral conditions of the papermaking process (Jin et al. 2010; Wang et al. 2017).

Maybe mineral filler is the second most important raw material in the papermaking industry after vegetable fibers (Li et al. 2016; Lourenço et al. 2020). Furthermore, adding filler in the papermaking process has been widely accepted and adopted to save cost and energy. In addition, adding filler in the paper can improve the brightness, opacity, and other optical indicators of paper products, and to a certain extent, the uniformity of paper, printing, and writing performance. However, the use of filler will also bring some problems to the quality of paper products and the production process, such as the loss of paper strength and the reduction of the efficiency of the chemicals. As a synthesized sizing agent, when AKD or ASA is used in the process of papermaking, the sizing agents are easily absorbed to the micro-particles with high specific areas in the stock, including fiber fines and filler, and then lose with the loss of those
micro-particles in the paper dehydration process. Therefore, the addition of filler to a large extent will significantly reduce the efficiency of the internal sizing agents and increase the sizing expense.

To overcome the negative influence of filler on the internal sizing agents and dispense with the sizing agent emulsion preparation process, hydrophobic modification of mineral fillers is an alternative approach. Compared to the traditional adding process, i.e., internal sizing agents and fillers are added one by one in papermaking, the technology of hydrophobic modification of fillers could simplify the chemicals adding process of papermaking and improve their efficiency (Karademir et al. 2008; Chen et al. 2016). Mica, clay, and talc can be successfully modified by AKD and used to improve the hydrophobicity of cellulosic paper (Yang and Liu 2010). However, it has seldom been reported so far that the hydrophobic modification of diatomite and its application in papermaking as a mineral filler.

Diatomite (DE), also known as diatomaceous earth or bio-silica, is a naturally occurring lightweight sedimentary rock containing 87-91% silicon dioxide (Liang et al. 2015; Wang et al. 2016). Diatomite is abundant in reserves on earth. Owing to its high porosity, high chemical stability, small particle size, rigid structure, low density, low thermal conductivity as well as its unique micro-porous structure, the diatomite has been widely used as filter aids (Wang et al. 2016; Liang et al. 2015; Cacciotti et al. 2019), adsorbents (Zhang et al. 2020), and catalyst supports, etc. (Dehestaniathar et al. 2016; Jiang et al. 2016).

In this work, AKD was used to modify diatomite, and the modified diatomite (AD) simultaneously played the role of mineral filler and sizing agent in the papermaking process. The AD was characterized by scanning electron microscope (SEM), Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA). We also investigated the sizing performance and mechanism of AD. This research provides an alternative strategy for adding papermaking chemicals.

**Materials And Methods**

**Materials**

Diatomite was obtained from Tianjin Damao Chemical Reagent Factory (Tianjin, China). AKD wax was provided by Taian Yikui Chemical Co. Ltd (Taian, China), and industrial AKD emulsion was purchased from Tangshan Aodong Chemical Co. Ltd (Tangshan, China). Softwood bleached kraft pulp (SBKP) was obtained from Dalian Yangrun Trading Co. Ltd (Dalian, China) and processed with a Valley Beater (JH-WLD, Xianyang Tongda Light Industry Equipment Co. Ltd, Xianyang, China) to a beating degree of 35° Schopper Riegel (SR). Cationic Polyacrylamide (CPAM) was obtained from Tianjin Zhiyuan Chemical Reagent Co. Ltd (Tianjin, China). Bentonite was obtained from Wuhan Fengtai Weiyuan Technology Co. Ltd (Wuhan, China). All materials were used as received.

**Preparation of AD**

In a typical preparation of AD, a certain amount of AKD wax was dissolved in alcohol of 30 mL under continuous stirring at room temperature, then heated to 80°C and kept at this temperature for 2-3 min
until formed a clear solution. The diatomite of 2 g (oven dry) was soaked in the solution of AKD with 5 mL for 1 min and then thoroughly mixed by ultrasonic treatment. Finally, AD was obtained after the alcohol in the mixture was evaporated and condensed. The schematic illustration of the preparation of AD and its application is shown in Fig. 1.

Preparation and evaluation of paper sheets

A certain amount of SBKP with 1% consistency and AD/AKD emulsion in an aqueous medium were sufficiently mixed under stirring. Then the mixture was further diluted to 0.2% with deionized water. A certain amount of CPAM aqueous solution with a concentration of 0.01% was added into the mixture under mild stirring for 60 s, and a certain amount of bentonite aqueous dispersed mixture with a concentration of 0.1% was subsequently added under vigorous stirring for 30 s. Finally, the hand sheets of paper were made from the above stock by a standard paper sample maker (TD10-200A, Xianyang Tongda Light Industry Equipment Co. Ltd, Xianyang, China) with a base-weight of 70 g/m². The prepared hand sheets were air-dried at room temperature. Some were heated in an oven at 105℃ for 0.5 h before sizing examination. The control paper sheet samples were marked as CP. The paper sheet samples filled with AD and sized with AKD emulsion were denoted as ADP and ASP, respectively.

The hydrophobicity of the paper sheets was evaluated with sizing degree and static contact angle (CA). The sizing degree was tested according to the national standard method of PRC (GB/T 5405-2002). The CA of the paper sheets was evaluated by a static sessile drop method at room temperature using a CA measurement instrument (SZ-CAMA1, Shanghai Xuanxun Instrument Co., Ltd, Shanghai, China) with a high-resolution Proscope camera capable of recording 15 fps at a 640×3480 resolution. The CA was determined by Low Bond Axisymmetric Drop Shape Analysis (LB-ADSA) technique by fitting the best profile to the image of a 5 µL droplet of deionized water on the surface of the hand sheets (Sedai et al. 2016). The roughness of paper sheets was obtained from a roughness tester (58-27, Beijing Huilong Environmental Instruments Co., Ltd, Beijing, China).

The tensile strength (TS) of the hand sheets was measured by a Tensile strength tester (VLD-300, Changchun Yueming testing machine Co., Ltd, Changchun, China) and reported as the average value of nine samples. The ash content of the paper sheet was calculated as shown in the formula (1). The filler retention in the paper sheet was obtained via ash content, as shown in the formula (2).

\[
X = \frac{m_1 - m_0}{m} \times 100\%
\]

Where \(X\), \(m_1\), \(m_0\), and \(m\) are the ash content (%), the mass of crucible with ash residue (g), the mass of crucible (g), and the mass of the oven-dry paper sheet sample, respectively.

\[
R = \frac{X}{A}
\]
Where R and A are the actual retention of paper sheets (%), and the theoretical ash content of paper sheet sample (g/g), respectively.

Characterization

The surface morphology of samples was observed with an XL-30 ESEM FEG scanning electron microscope (SEM) (FEI Company, Hillsboro, USA). The samples were treated with gold spraying before SEM observation. The micro-particle size distribution of the DE and AD was measured by a Particle-size analyzer (Ambivalence, LFC101, NED, Guangzhou, China).

Fourier-transform infrared spectroscopy (FTIR) (VERTEX 70, Bruker Company, Karlsruhe, Germany) was used to evaluate the chemical functional groups of paper sheets. The KBr and ATR method was applied with a resolution of 4 cm\(^{-1}\), 16 scans for each spectrum, and all spectra were recorded between 4000 cm\(^{-1}\) and 500 cm\(^{-1}\).

The thermal performance of samples was tested using thermogravimetric analysis (TGA) (Mettler Toledo TGA2, Mettler Company, Zurich, Switzerland) with a heating rate of 10°C min\(^{-1}\) in N\(_2\) (40 ml min\(^{-1}\)), ranging from 30°C to 800°C.

Results And Discussion

Modification of DE with AKD

The modification conditions of AD and their sizing performance are listed in Table 1, where the weight ratio of AKD wax in AD and cellulosic fibers (oven dry) was set as 0.20%. The paper sheet filled with AD-1~3 all exhibited excellent hydrophobicity. In comparison with AD-1 and AD-3, AD-2 had better performance, which implied that the desired load amount of AKD wax on diatomite contributed to enhancing the efficiency of AKD wax for hydrophobicity of the cellulosic paper. The subsequent work in this paper was also based on the sample of AD-2 (denoted as AD), considering its better performance as a sizing agent.

| Sample | AKD Conc. (g/mL) | AKD volume (mL) | DE mass (g) | AKD/DE (%) | Sizing degree (min) |
|--------|-----------------|-----------------|-------------|-------------|---------------------|
| AD-0   | 0.000           | 5               | 2           | 0.0         | 0                   |
| AD-1   | 0.003           | 5               | 2           | 0.8         | 4 ±0.25 min         |
| AD-2   | 0.010           | 5               | 2           | 2.5         | 10 ±0.18 min        |
| AD-3   | 0.017           | 5               | 2           | 4.3         | 6±0.23min           |
Thermo Gravimetric Analysis of DE, AKD wax, and AD are shown in Fig. 2. It can be seen that the weight of DE roughly became stable with the increasing of the temperature due to its excellent thermal stability, and few impurities existed in it (Zhao et al. 2021). The AKD wax underwent two obvious weight loss steps when heated from 30 to 800°C (Ryu et al. 2020). The weight loss of 5% occurred below 242°C may be attributed to the loss of physically absorbed water on the surface of AKD and the decomposition of AKD with low molecular weight. The weight loss of 95% occurred in the temperate range of 242-500°C owing to the decomposition of AKD with high molecular weight. In contrast, the weight loss of AD was 27% in the temperate range of 30-450°C, which was attributed to the decomposition of AKD. When the temperature was higher than 450°C, the sample tended to be stable, and no further mass loss was observed in the TG curve, which can be attributed to the complete decomposition of AKD.

SEM images of AKD, the diatomite before and after modification of AKD are shown in Fig. 3. Fig. 3b-3c show that DE has a clean surface with micro-pores (Li et al. 2021). It is distinctly observed that AKD was loaded on the surface of DE, as shown in Fig. 3d-3f. The mean particle diameter of DE and AD is approximately 45 µm and 56 µm, respectively, as shown in Fig. 3g-3h. We probably inferred that AKD was successfully loaded on the surface of DE and therefore increased its mean particle diameter.

The FT-IR spectrogram (Fig. 4) showed that the prominent characteristic peak of the DE appearing at 1090 cm\(^{-1}\) is due to Si-O-Si antisymmetric stretching vibrations. The peak at 792 cm\(^{-1}\) could be ascribed to Si-O-Al symmetrical stretching and bending vibration (Yuan et al. 2013). Compared with DE, the AD displayed a new characteristic peak of 2910 cm\(^{-1}\) (Shang et al. 2018). The unique characteristic peak belonged to the symmetric and antisymmetric stretching vibrations of -CH\(_2\) in the AKD alkyl chain, demonstrating that AKD had been successfully loaded on the DE.

Application of AD as a filler in papermaking

The adding ratio of AD to cellulosic fibers and the correspondent ratio of AKD to cellulosic fibers in hand sheets are listed in Table 2. When the AD in ADP increased from 0 to 32%, the roughness of the topside/backside increased from 8.78 to 9.27µm and 9.53 to 10.52µm, respectively. It is well known that the roughness of the backside of the hand sheets paper is generally higher than that of the topside because of more filler and fiber fines loss in the backside during the dehydration process of the stock. According to the results in Fig. 5a, the roughness of both the top and back sides increased when adding more AD in hand sheets. Meanwhile, the difference in the roughness between the back and top sides also became more significant. The CA of the hand sheets remarkably increased from 0° to more than 80° when the dosage of AKD in AD increased from 0.05-0.2%, as shown in Fig. 5b, which seemed to suggest there is a minimum amount of AKD to grant hydrophobic properties for cellulosic paper. While the dosage of AKD was more than 0.2%, the CA was further enhanced. It is worth noting that the backside of the hand sheets had a higher CA than the topside regardless of the dosage of AKD, which seemed paradoxical because AD lost more on the backside of the hand sheets. The super-hydrophobic theory may explain it, i.e., the two necessary conditions for the super-hydrophobic surfaces are low surface free energy and microscopic rough surface (Kwon et al. 2009). In this study, under the combined effect of
roughness and AD retention of both sides of the hand sheets, the backside had a larger CA than the topside; therefore, the backside was expected to perform better hydrophobicity.

### Table 2

The sizing conditions of paper sheets

| Sample | AD/dry fiber (%) | AKD wax/dry fiber (%) |
|--------|------------------|-----------------------|
| ADP-0  | 0                | 0.00                  |
| ADP-1  | 2                | 0.05                  |
| ADP-2  | 8                | 0.20                  |
| ADP-3  | 14               | 0.35                  |
| ADP-4  | 20               | 0.50                  |
| ADP-5  | 26               | 0.65                  |
| ADP-6  | 32               | 0.80                  |

Figure 6 shows the retention of AD and corresponding tensile strength of ADP (ADP-2) in the case of various dosages of CPAM. The filler retention of AD in paper sheets gradually increased from 49.29–67.00% as the dosage of CPAM increased. However, the tensile strength of the paper sheet decreased when more AD was retained in the hand sheets because the AD particles occupied the space among the pulp fibers and weakened the hydrogen bonding between the cellulosic fibers (Huang et al. 2013; Kinoshita et al. 2000). Like other commonly used paper fillers, the increase in the amount of AD will also lead to a significant decrease in the tensile strength of cellulosic paper.

Figure 7a and 7c show that the sizing degree and CA of ADP and ASP increased when more CPAM was added. Moreover, AD had better sizing performance than AKD emulsion. At the same time, the CA of ADP was also higher than that of ASP in the case of the same side, *i.e.*, topside versus topside and back side versus back side. Fig. 7b and 7d show that with bentonite dosage increasing from 0.0–0.1%, the CA and sizing degree of both ADP and ASP increased. The CA and sizing degree decreased when its dosage was further supplemented by more than 0.1%. Compared with the mean particle size of AKD in the emulsion, AD had a larger mean particle size, which could facilitate AD to perform better than AKD emulsion under CPAM retention aid and CPAM/ bentonite retention aid system.

**Sizing mechanism of AD in the paper sheet**

SEM images of CP and ADP are shown in Fig. 8. AD was evenly distributed inside the paper sheet and on its surface, as shown in Fig. 8d-f. Furthermore, some particles with irregular shapes were also observed, which could be some broken diatomite enveloped with AKD. It is evident that the amount of AD used in this study is not capable of thoroughly changing the hydrophilic property of the cellulosic fibers. However, AD can provide numerous hydrophobic sites, which are enough to endow the paper sheets with hydrophobic properties (Hao et al. 2015).
The sticky super-hydrophobicity of rose petals is a typically super-hydrophobic phenomenon found in the natural world (Yu et al. 2017); the water droplets easily adhere to the microstructured surfaces of rose petals (Su et al. 2016; Rahman et al. 2020). An interesting sticky hydrophobicity phenomenon was also observed in this study. Water droplets did not slide or roll even when we turned upside the paper sheet, as shown in Fig. 8g. ADP possessed adhesion with water droplets, attributing to the surface microstructure of the hydrophobic paper sheet. We inferred that the wetting behavior of water droplets on the paper sheet conformed to the Wenzel model (Shirtcliffe et al. 2010), and the droplets were trapped in the grooves, as shown in Fig. 8g. It was challenging to overcome the barrier when the droplets slipped off, and the droplets did not roll. This study provides a facile method to prepare the sticky hydrophobic paper sheet and can further find its application in some non-traditional application fields such as no loss micro-droplet transportation and chemical microreactors (Li et al. 2014; Cheng et al. 2013; Mata-Cruz et al. 2017).

The peak at 1090 cm\(^{-1}\) illustrated the existence of diatomite (Fig. 9). The peak at 2890 cm\(^{-1}\) was related to the symmetric stretching vibration of -CH\(_2\), which revealed the presence of cellulose (Li et al. 2018). The absorption peak at 3340 cm\(^{-1}\) was associated with the stretching vibration of -OH. Yan et al. reported that AKD might react with free hydroxyl groups of cellulose to form \(\beta\)-keto ester linkages, endowing paper sheets with hydrophobicity (Yan et al. 2016). However, the formed \(\beta\)-keto ester linkages were not observed in the ADP spectrum, which could be due to the low amount of AKD in the paper sheet. It also implied that the chemical reaction of forming ester linkage during AD sizing might not be indispensable.

**Conclusions**

Diatomite modified with AKD was successfully prepared, and AKD was evenly distributed on the diatomite. The AD was used as filler and sizing agent in the hand sheet paper. Compared with the commercial AKD emulsion, under the equal dosage of AKD, the AD had better sizing and retention performance using the CPAM or CPAM/bentonite retention system. The chemical reaction of forming ester linkage during AD sizing may not be indispensable. The sizing mechanism of the AD mainly depended on numerous hydrophobic sites and the micro-surface structure of the paper sheet caused by the AD. Meanwhile, we observed an interesting “sticky” hydrophobicity phenomenon in the paper sheet filled by the AD. This study also provides a facile method to prepare the “sticky” hydrophobic paper sheet and enlarges its application in some non-traditional application fields.

**Declarations**

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**Figures**

**Figure 1**

Schematic illustration of the preparation of AD and its application
Figure 2

TGA curves of DE AKD wax and AD [1]

Figure 3

Surface morphologies of AKD, DE (a-c), the modified DE particles with AKD (d-f) and the corresponding micro-particle size and its distributions (g-h) [2]
Figure 4

FTIR spectra of the DE, AKD wax, and AD \[3\]

Figure 5

Effect of AD on the surface properties of ADP

(a) Effect of AD on the roughness of ADP; (b) Effect of AKD on CA of ADP \[4\]
Effect of the polyacrylamide (CPAM) on the filler retention and tensile strength properties of the ADP\textsuperscript{[5]}
Figure 7

Effect of the retention and drainage system on sizing degree and CA of ADP and ASP (The dosage of AD is 8%, i.e., the dosage of AKD in AD is 0.2% in ADP; the dosage of AKD in AKD emulsion is 0.2% in ASP; Top side and back side were noted as T and B, respectively; the dosage of the CPAM was 0.02% in Fig.7 b and d) [6]
Figure 8

SEM images of the CP (a-b) and ADP (d-e) and corresponding cross-sectional SEM images (c and f); (g) Schematic of “sticky” hydrophobic paper sheet

(The dosage of AD is 8%, i.e., the dosage of AKD in pulp fibers is 0.2%)
Figure 9

FTIR spectra of the CP and ADP at different temperatures of 20°C and 105°C.

(The dosage of AD is 8%, i.e., the dosage of AKD in pulp fibers is 0.2%) [7]