

Diatomite Modified with an Alkyl Ketene Dimer for Hydrophobicity of Cellulosic Paper

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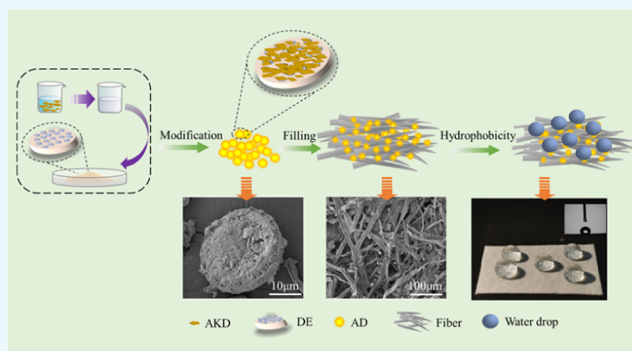
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ABSTRACT: Multifunctionalization of papermaking chemicals is one of the main developing strategies. Fillers and internal sizing agents are often mutually restricted in practice. Therefore, it is feasible to prepare a new papermaking chemical by combining the functions of both. A process of diatomite modified with an alkyl ketene dimer (AKD) was developed in this study. The modified diatomite (AD) can concurrently play the role of a mineral filler and sizing agent in the papermaking process. With the equal dosage of AKD, the AD showed 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 to be due to numerous hydrophobic sites and the microsurface structure of the paper sheet caused by the AD. Since ketones were not detected in Fourier-transform infrared spectra of the paper sheet filled by the AD, the chemical reaction may not be indispensable for its sizing performance. What is 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 nontraditional application fields of cellulosic paper.



1. INTRODUCTION

It is well known that vegetable fibers are the main component of cellulosic paper.¹ Compared with synthetic polymer materials, cellulosic paper is biodegradable, ecofriendly, and has a low cost.^{2–6} Cellulosic fibers are hydrophilic due to abundant hydroxyl groups in the molecule of cellulose. Therefore, cellulosic paper is inherently hydrophilic.⁷ However, the intrinsic hydrophilic nature 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 1807, and various sizing agents have been commercially promoted, such as rosin-based products, alkyl ketene dimer (AKD), alkenyl succinic anhydride (ASA) emulsions, and so forth.^{8–10} The 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.¹¹ AKD is one of the most popular internal sizing agents widely used after a decisive change from the acidic to neutral conditions of the papermaking process.^{12,13}

Mineral filler is the second-most important raw material in the papermaking industry after vegetable fibers.^{14,15} Furthermore, adding fillers in the papermaking process has been widely accepted and adopted to save cost and energy. In addition, adding fillers 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 fillers will also lead to some problems in 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 the AKD or ASA is used in the process of papermaking, the sizing agents are easily adsorbed into the microparticles with high specific areas in the stock, including fiber fines and fillers, and then are lost with the loss of these microparticles in the paper dehydration process. Therefore, the addition of fillers 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 fillers on the internal sizing agents and dispense them with the sizing agent emulsion preparation process, hydrophobic modification of mineral fillers is an alternative approach. Compared to the traditional addition process, that is, internal sizing agents and fillers are

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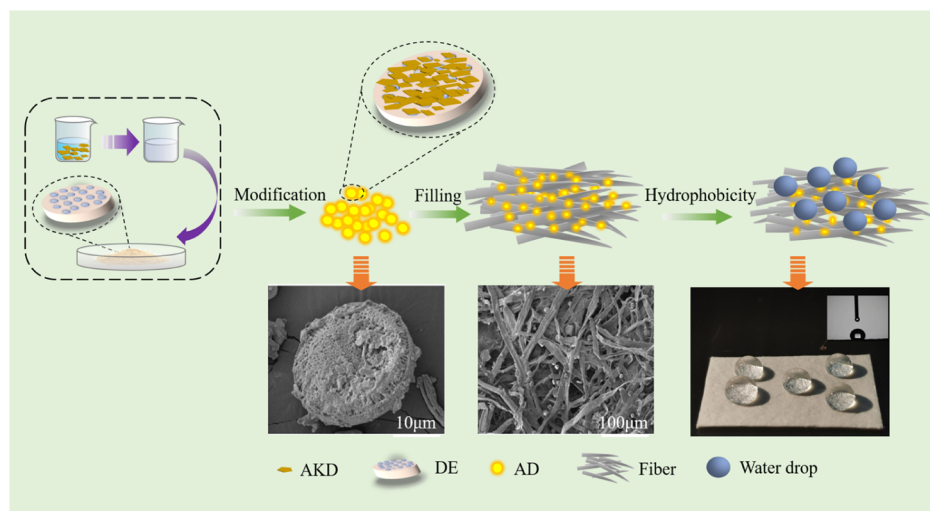


Figure 1. Schematic illustration of the preparation of AD and its application.

added one by one during papermaking, the technology of hydrophobic modification of fillers could simplify the chemicals addition process of papermaking and improve their efficiency.^{16,17} Mica, clay, and talcum can be successfully modified by AKD and used to improve the hydrophobicity of cellulosic paper.¹⁸ However, the hydrophobic modification of diatomite (DE) and its application in papermaking as a mineral filler has seldom been reported so far.

DE, also known as diatomaceous earth or biosilica, is a naturally occurring lightweight sedimentary rock containing 87–91% silicon dioxide.^{19,20} DE is abundant in reserves on the earth. Owing to its high porosity, high chemical stability, small particle size, rigid structure, low density, low thermal conductivity, and unique microporous structure, DE has been widely used in filter aids,^{19–21} adsorbents,²² catalyst supports, and so forth.^{23,24}

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

2. MATERIALS AND METHODS

2.1. Materials. DE 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 using a Valley Beater (JH-WLD, Xianyang Tongda Light Industry Equipment Co. Ltd, Xianyang, China) at a beating degree of 35° Schopper Riegel. 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.

2.2. Preparation of AD. In a typical preparation of AD, a certain amount of AKD wax was dissolved in 30 mL of alcohol under continuous stirring at room temperature, then heated to

80 °C in order to accelerate the dissolution rate of AKD wax, and kept at this temperature for 2–3 min until a clear solution was obtained. 2 g of DE (oven-dried) was soaked in a 5 mL solution of AKD 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 Figure 1.

2.3. 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 using 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 °C 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 the sizing degree and static contact angle (CA). The sizing degree was measured 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 the low bond axisymmetric drop shape analysis technique by fitting the best profile to the image of a 5 μL droplet of deionized water on the surface of the hand sheets.²⁵ The roughness of paper sheets was obtained from a roughness tester (S8–27, Beijing Huilong Environmental Instruments Co., Ltd, Beijing, China).

The tensile strength (TS) of the hand sheets was measured by a TS 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 formula 1. The filler retention in the paper sheet was obtained via ash content, as shown in formula 2.

$$X = \frac{m_1 - m_0}{m} \times 100\% \quad (1)$$

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-dried paper sheet sample, respectively.

$$R = X/A \quad (2)$$

where R and A are the actual retention of paper sheets (%) and the theoretical ash content of paper sheet sample (g/g), respectively.

Table 1. Modification Conditions of AD and Their Sizing Performance

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 ± 0.23 min

2.4. Characterization. The surface morphology of samples was observed using an XL-30 ESEM FEG SEM (FEI Company, Hillsboro, USA). The samples were treated with gold spraying before SEM observation. The microparticle size distribution of DE and AD was measured using a particle-size analyzer (Ambivalue, LFC101, NED, Guangzhou, China).

FTIR spectroscopy (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 and 500 cm^{-1} .

The thermal performance of samples was tested using TGA (Mettler Toledo TGA2, Mettler Company, Zurich, Switzerland) at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ in N_2 (40 mL min^{-1}), ranging from 30 to $800 \text{ }^\circ\text{C}$.

3. RESULTS AND DISCUSSION

3.1. 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-dried) was set as 0.20%. The paper sheets filled with AD-1~3 all exhibited excellent hydrophobicity. In comparison with AD-1 and AD-3, AD-2 showed better performance, which implied that the desired load amount of AKD wax on DE contributed to enhancement of the efficiency of AKD wax for hydrophobicity of the cellulosic paper. The subsequent work in this paper was also based on the sample AD-2 (denoted AD), considering its better performance as a sizing agent.

The SEM images of AKD and DE before and after modification of AKD are shown in Figure 2. Figure 2b,c shows that DE has a clean surface with micropores.²⁶ It is distinctly observed that AKD was loaded on the surface of DE, as shown in Figure 2d–f. The mean particle diameter of DE and AD is approximately 45 and $56 \mu\text{m}$, respectively, as shown in Figure 2g,h. We probably inferred that AKD was successfully loaded on the surface of DE and therefore increased its mean particle diameter.

The FT-IR spectrum (Figure 3) showed that the prominent characteristic peak of 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 the Si–O–Al symmetrical stretching and bending vibration.²⁷ Compared with DE, AD displayed a new characteristic peak at 2910 cm^{-1} .²⁸ The unique characteristic peak belonged to the symmetric and antisymmetric stretching vibrations of $-\text{CH}_2-$ in the AKD alkyl chain, demonstrating that AKD had been successfully loaded on DE.

3.2. Application of AD as a Filler in Papermaking. The addition ratio of AD to cellulosic fibers and the corresponding 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

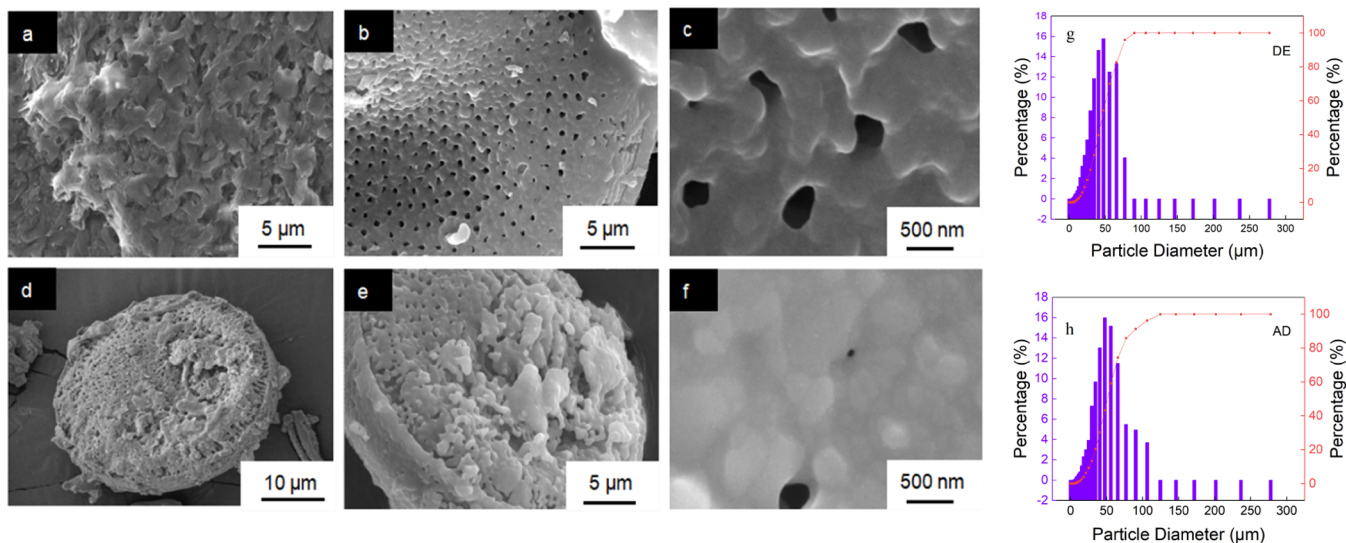


Figure 2. Surface morphologies of AKD (a), DE (b,c), modified DE particles with AKD (d–f), and the corresponding microparticle size and its distributions (g,h).

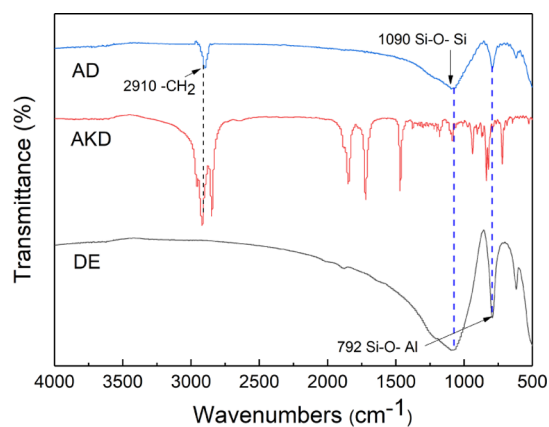


Figure 3. FTIR spectra of DE, AKD wax, and AD.

Table 2. 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

roughness of the topside/backside increased from 8.78 to 9.27 and 9.53 to 10.52 μm , respectively (the paper sheet samples filled with AD are denoted as ADP). 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 lost in the backside during the dehydration process of the stock. According to the results in Figure 4a, the roughness of both the top and back sides increased when adding more AD to 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 to 0.2%, as shown in Figure 4b, which seemed to suggest that 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

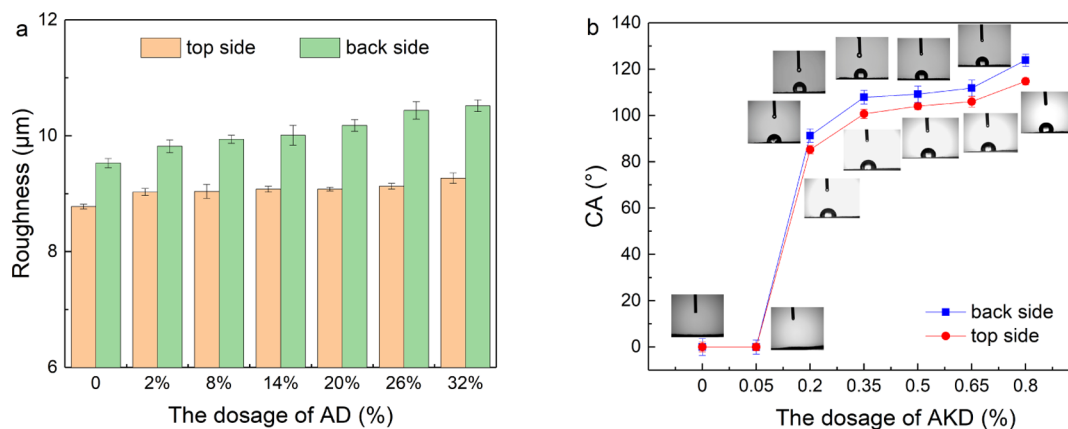


Figure 4. Effect of AD on the surface properties of ADP. (a) Effect of AD on the roughness of ADP; (b) effect of AKD on the CA of ADP.

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 this; that is, the two necessary conditions for the super-hydrophobic surfaces are low surface free energy and microscopic rough surface.²⁹ 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 exhibit better hydrophobicity.

Figure 5 shows the retention of AD and corresponding TS of ADP (ADP-2) in the case of various dosages of CPAM. The

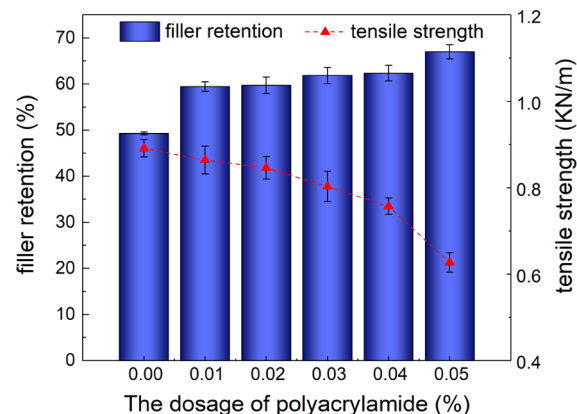


Figure 5. Effect of polyacrylamide (CPAM) on the filler retention and TS properties of ADP.

filler retention of AD in paper sheets gradually increased from 49.29 to 67.00% as the dosage of CPAM increased. However, the TS 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.^{30,31} Like other commonly used paper fillers, the increase in the amount of AD will also lead to a significant decrease in the TS of cellulosic paper.

Figure 6a,c shows that the sizing degree and CA of ADP and ASP increased when more CPAM was added. Moreover, AD exhibited better sizing performance than the AKD emulsion. At the same time, the CA of ADP was also higher than that of ASP in the case of the same side, that is, topside versus topside

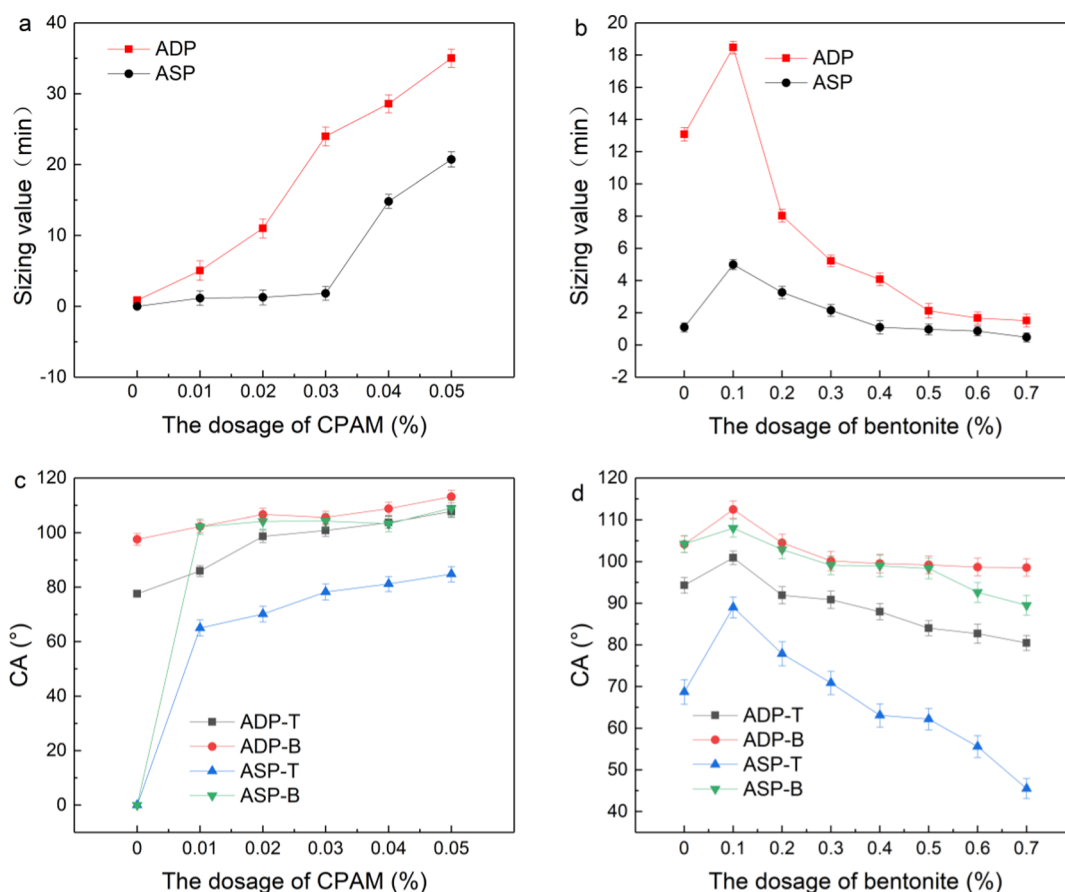


Figure 6. (a,b) Effect of the CPAM and CPAM/bentonite retention system on the sizing degree of ADP and ASP. (c,d) Effect of the CPAM and CPAM/bentonite retention system on the CA of ADP and ASP (the dosage of AD is 8%; i.e., the dosage of AKD in AD is 0.2% in ADP; the dosage of AKD in AKD emulsion is 0.2% in ASP; the paper sheet samples sized with the AKD emulsion were denoted as ASP; top side and back side were denoted as T and B, respectively; the dosage of the CPAM was 0.02% in Figure 6b,d).

and backside versus backside. Figure 6b,d shows that with the bentonite dosage increasing from 0.0 to 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 the AKD emulsion under CPAM retention aid and CPAM/bentonite retention aid system.

3.3. Sizing Mechanism of AD in the Paper Sheet. The SEM images of CP and ADP are shown in Figure 7. AD was evenly distributed inside the paper sheet and on its surface, as shown in Figure 7d–f. Furthermore, some particles with irregular shapes were also observed, which could be some broken DE 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.³²

The sticky super-hydrophobicity of rose petals is a typical super-hydrophobic phenomenon found in the natural world; the water droplets easily adhere to the microstructured surfaces of rose petals.^{33–35} An interesting sticky hydrophobicity phenomenon was also observed in this study. Water droplets did not slide or roll even when we turned the paper sheet upside, as shown in Figure 7g. ADP showed adhesion with water droplets, attributed 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,³⁶ and the droplets were trapped in the grooves, as shown in Figure 7g. 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 sticky hydrophobic paper sheets and can further find its application in some nontraditional application fields such as no-loss microdroplet transportation and chemical microreactors.^{37–39}

The peak at 1090 cm^{-1} illustrated the existence of DE (Figure 8). The peak at 2890 cm^{-1} was related to the symmetric stretching vibration of $-\text{CH}_2$, which revealed the presence of cellulose.⁴⁰ The absorption peak at 3340 cm^{-1} was associated with the stretching vibration of $-\text{OH}$. Isogai reported that most AKD components were present in paper sheets as ketones, without forming β -ketoesters, endowing paper sheets with hydrophobicity.⁴¹ However, the ketones were not observed in the ADP spectrum, which could be due to the low temperature of the heat treatment of AKD in the paper sheet. It also implied that the chemical reaction forming ester linkage during AD sizing might not be indispensable.

4. CONCLUSIONS

DE modified with AKD was successfully prepared, and AKD was evenly distributed on DE. AD was used as a filler and sizing agent in the hand sheet paper. Compared with the commercial AKD emulsion, with the equal dosage of AKD, AD

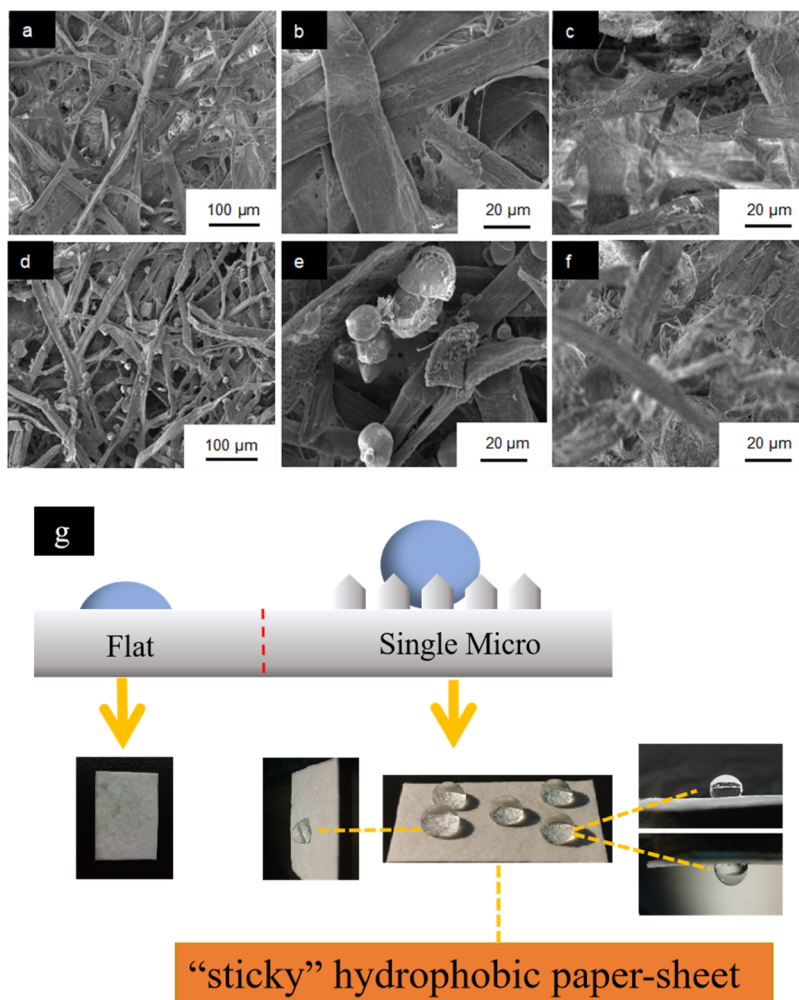


Figure 7. SEM images of CP (a,b) and ADP (d,e) and corresponding cross-sectional SEM images (c,f). (g) Schematic of the “sticky” hydrophobic paper sheet (the dosage of AD is 8%; i.e., the dosage of AKD in pulp fibers is 0.2%).

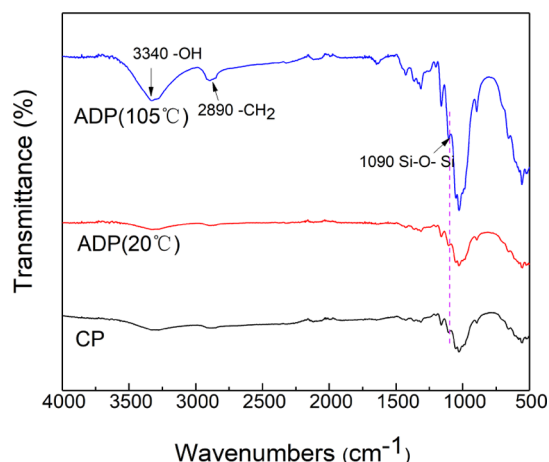


Figure 8. FTIR spectra of the CP and ADP at different temperatures of 20 and 105 °C (the dosage of AD is 8%; i.e., the dosage of AKD in pulp fibers is 0.2%).

showed better sizing and retention performance using the CPAM or CPAM/bentonite retention system. The chemical reaction forming ketones during AD sizing may not be indispensable. The sizing mechanism of AD mainly depended on numerous hydrophobic sites and the microsurface structure

of the paper sheet caused by AD. Meanwhile, we observed an interesting “sticky” hydrophobicity phenomenon in the paper sheet filled with AD. This study also provides a facile method to prepare the “sticky” hydrophobic paper sheet and enlarges its application in some nontraditional application fields.

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Author Contributions

The manuscript was prepared through the contributions of all authors. All authors have approved the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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