Preparation, Application, and Mechanism of Starch Modified Dicyandiamide Formaldehyde Polymer–Bentonite Microparticle Retention and Drainage Aid System

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Modified dicyandiamide formaldehyde polymer (MDDF) and calcined bentonite were used to produce a MDDF-bentonite microparticle retention system. The authors investigated its retention, drainage-aid effect, and its mechanism through measuring the pulp charge density, particle size of the fine particles, and other factors. The results revealed that under neutral conditions and the addition of 0.08% MDDF and 0.3% bentonite, the initial floc was broken *via* high-speed shearing. Meanwhile, the inorganic filler was added, and the retention effect of the MDDF-bentonite system was close to that of the cationic polyacrylamide (CPAM)-bentonite system. The MDDF-bentonite system exhibited a patch-bridging mechanism. First, the authors added cationic polymer to form a sizeable initial floc, which was then dispersed at high shear force. Then, the authors added inorganic fillers with opposite charges. A smaller floc with more compact structure reformed and was distributed on the wet paper sheet so that more fillers and fine fibers remained on the paper, thus improving the retention efficiency. Because the charge density of MDDF is higher than that of CPAM, the addition of MDDF enabled the pulp system to become closer to the isoelectric point, and the drainage effect was better than that of CPAM.

Keywords: Modified dicyandiamide formaldehyde polymer; Microparticle retention system; Patch-bridge; Retention and drainage-aid mechanism

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INTRODUCTION

The process of paper forming uses the greatest amount of water used during the whole process of paper and paperboard production. Recovered paper can increase the content of fine fibers. The most common and effective solution to the modern paper industry is to offer retention and drainage aids to the wet end (Gill 1991).

Wang and Xiao (1997) confirmed that dicyandiamide formaldehyde polymer is a kind of polymer with positive charge density, thus making it suitable as a flocculant and decolorant in sewage treatments. However, Geng *et al.* (2016) argued that the molecular weight of the dicyandiamide polymer is extremely small, and the number of functional groups on the chain was relatively low, which results in small flocs and slow settlement. Dicyandiamide-formaldehyde has evident advantages, but its shortcomings limit its application in various fields. Therefore, the modification of dicyandiamide polymer has become the focus of many researchers.

He *et al.* (2016) used the dicyandiamide-formaldehyde polymer as the retention and drainage aid in the papermaking process. The dicyandiamide-formaldehyde polymer enables a good retention effect, but it performs poorly as a drainage aid, thus requiring further modification. Dicyandiamide-formaldehyde polymer also has a positive charge, unlike cellulose, filler, and fines. To keep the filler and the fine fiber as much as possible in the pulp using the charge neutralization mechanism, dicyandiamide-formaldehyde polymer can be modified through various means, such as the introduction of acrylamide for compounding and grafting modified starch (Li *et al.* 1990; Zeng *et al.* 2004; Zhang *et al.* 2014), to increase molecular weight and charge density. These methods can increase the ability of the adsorption bridge between the polymer and cellulose.

The traditional single retention system widely used in paper forming sometimes has low retention efficiency, resulting in paper formation, opacity, and other flawed aspects (Heard *et al.* 1998; Zhang and Hu 2002, 2004; Hou *et al.* 2004; Antunes *et al.* 2008). In 1996, Wagberg *et al.* (1996) studied the flocculation kinetics of the cationic polyacrylamide (CPAM)-bentonite microparticle retention system. It was believed that the flocculation of the microparticle retention system was acting as a bridge between bentonite and CPAM adsorbed on the fiber. The microparticle retention system has a better flocculation effect than the CPAM single retention system, and the microparticle retention system requires a higher amount of CPAM than the CPAM single retention system to achieve the maximum flocculation effect. This is probably because the fiber of the microparticle retention system needs sufficient CPAM coverage and due to the absence of the configuration change after the covering. Therefore, the microparticle retention system can be re-flocculated after breakup of the fiber flocs by hydrodynamic shear. The addition of a suitable amount of high-charge-density, low-molecular-weight cationic organics to the pulp can improve the flocculation efficiency of the microparticle retention system. These organic materials were added to the pulp and adsorbed on the fiber, thereby acting as a barrier and resulting in the CPAM chain being more effective.

In 2009, Cho *et al* (2009) studied the action mechanism of microparticle retention systems. The number of fines passing through the 200-mesh screen was measured to determine the retention efficiency of the system. Experiments found that bentonite produces a strong bond between the CPAM adsorbed on fibers due to the highly negatively charged surface of the bentonite. Therefore, strong adsorption of prominent CPAM was observed on the fiber. Bentonite is characterized by the large specific surface, good adsorption, ion exchange-ability, and nontoxicity (Zhou *et al.* 2015). Moreover, the bentonite material has apparent anionic charge, which is more readily adsorbed on CPAM than other particulate materials. The paper strength loss upon the addition of precipitated calcium carbonate filler particles was significantly mitigated by adding bentonite, which may provide an alternative strategy for improving the strength properties of mineral-filled paper grades (Antunes *et al.* 2015; Fan *et al.* 2015).

Dicyandiamide, formaldehyde, ammonium chloride, acrylamide, and cationic starch were used as the primary raw materials in this research to synthesize a novel cationic polymer, modified dicyandiamide formaldehyde (MDDF), to increase charge density and molecular weight through graft modification. Then, the synthetic modified by grafting polymer MDDF was combined with bentonite. The application of retention and drainage aid was explored from four aspects, which include MDDF addition, bentonite amount, change of shear rate, and change of pulp pH. Furthermore, the mechanism of action was analyzed by measuring the charge density, the particle size of the filler in pulp and whitewater, and *via* scanning electron microscopy. This provided a new type of microparticle retention and drainage aid system for papermaking wet end chemistry.

EXPERIMENTAL

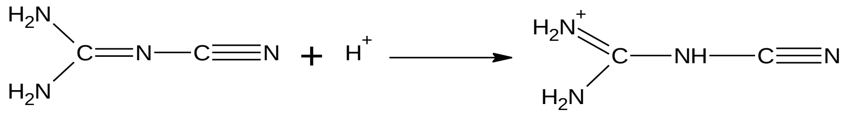
Materials

The equipment used included a beater (ZT4-00; Zhongtong Experimental Equipment Co., Ltd., Xingping, China), a fiber standard dissociation device (GBJ-A; Yueming Small Test Machine Co., Ltd., Changchun, China), a dynamic water filter (DFR-05; BTG PLC, Eclépens, Switzerland), a pattern picker (ZT6-00; Zhongtong Experimental Equipment Co., Ltd., Xingping, China), an infrared spectrometer (SPectnllTIR; American PE Company, Waltham, USA), a streaming current detector (PCD-03; BTG PLC, Eclépens, Switzerland), an emission scanning electron microscope (JSM-6700F; JEOL Co., Ltd., Tokyo, Japan), and a laser particle size tester (Mastersizer3000; Malvern Instruments Co., Ltd., Malvern, UK).

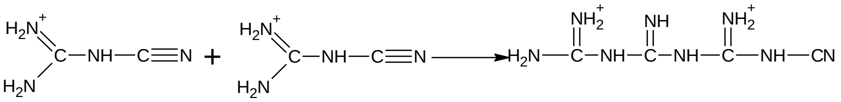
The chemicals used were dicyandiamide (Bodi Chemical Co., Ltd., Tianjin, China), formaldehyde (37%), anhydrous ethanol, ammonium persulfate (APS), sodium bisulphite (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), acrylamide (Ebene Chemical Reagents Co., Ltd., Shanghai, China), and CPAM (Wanhua Chemical Technology Co., Ltd., Shandong, China). The above chemicals were all analytically pure. Moreover, pulp (Leaves Bleached Hardwood Kraft Pulp (LBKP): Northern Bleached Kraft Pulp (NBKP) = 70:30) was purchased from Prince's Paper Industry (Nantong, China). Corn starch (food grade) was obtained from Juneng Gold Corn Development Co., Ltd. (Shandong, China). Bentonite (calcium bentonite, calcined) was provided by Huayu Bentonite Co., Ltd. (Shandong, China). Additionally, the distilled water was self-made.

Synthetic route of starch modified dicyandiamide formaldehyde polymer

Starch-modified dicyandiamide-formaldehyde polymer was synthesized according to Zhang *et al.* (2018). First, the cyano group in dicyandiamide reacted with its amine group and the amino group of the acrylamide molecule (Formulas 1, 2, and 3). Then, the formaldehyde molecules reacted with the amine groups to form hydroxymethyl (Formula 4). Next, there were dehydration condensation reactions between hydroxymethyl and hydroxymethyl, or the hydroxymethyl and amido groups (Formula 5). Afterwards, a cationic macromolecule with a terminal group of C=C was formed (Formula 6). Finally, the graft copolymerization of starch and cationic macromolecule with terminal group C=C was initiated under the action of initiator (Formula 7). The principle of the reaction is shown in Fig. 1.

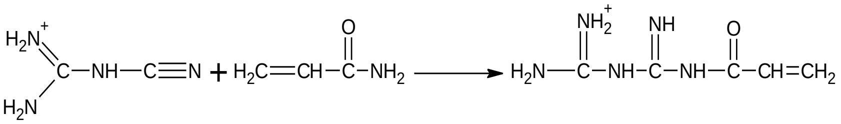


(Formula 1)



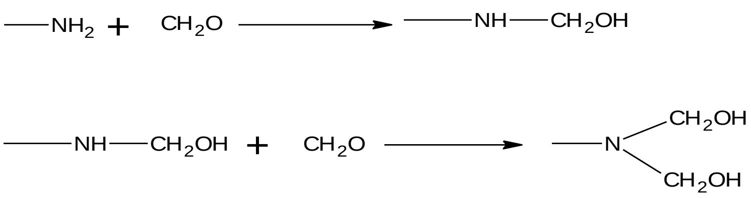
$$(H_2N)_2C^{+}{=}\text{—}NH{-}C{\equiv}N + (H_2N)_2C^{+}{=}\text{—}NH{-}C{\equiv}N \longrightarrow H_2N{-}\overset{NH_2^+}{\overset{\|}{C}}{-}NH{-}\overset{NH}{\overset{\|}{C}}{-}NH{-}\overset{NH_2^+}{\overset{\|}{C}}{-}NH{-}CN$$

(Formula 2)



$$(H_2N)_2C^{+}{-}NH{-}C{\equiv}N + H_2C{=}CH{-}\overset{O}{\overset{\|}{C}}{-}NH_2 \longrightarrow H_2N{-}\overset{NH_2^+}{\overset{\|}{C}}{-}NH{-}\overset{NH}{\overset{\|}{C}}{-}NH{-}\overset{O}{\overset{\|}{C}}{-}CH{=}CH_2$$

(Formula 3)



$$—NH_2 + CH_2O \longrightarrow —NH—CH_2OH$$

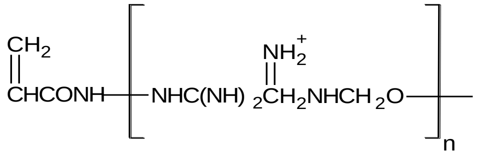
$$—NH—CH_2OH + CH_2O \longrightarrow —N(CH_2OH)_2$$

(Formula 4)

$$—CH_2OH + HOH_2C— \longrightarrow —CH_2O—CH_2— + H_2O$$

$$—CH_2OH + H_2N— \longrightarrow —CH_2—NH— + H_2O$$

(Formula 5)



$$\overset{CH_2}{\overset{\|}{CHCONH}}\left[NHC(NH)_2\overset{NH_2^+}{\overset{\|}{}}CH_2NHCH_2O\right]_n$$

(Formula 6)

$$StOH \longrightarrow StO^{\cdot}$$

$$StO^{\cdot} + M \longrightarrow StOM^{\cdot}$$

$$StO(M)_a^{\cdot} + StO(M)_b^{\cdot} \longrightarrow StO(M)_{a+b}OSt$$

(Formula 7)

Fig. 1. Synthetic principle of the starch modified dicyandiamide formaldehyde polymer

Methods

Preparation of cationic starch with a high degree of substitution

A certain amount of cornstarch and distilled water was added to a four-neck flask equipped with a condenser reflux tube, thermometer, stirrer, and a dropping funnel. The temperature was raised to 55 °C, and the alkali was added. Then, heating was continued to 70 °C and maintained for 10 min. Afterwards, the cationic etherification agent (3-chloro-2-hydroxypropyltrimethylammonium chloride) was added. The pH was subsequently adjusted, and a highly substituted cationic starch solution was obtained. The product was then washed with anhydrous ethanol, filtered three times, dried, and ground to acquire a solid cationic starch.

Synthesis of starch grafted dicyandiamide oxymethylene polymers

A total of 10 g of the preceding cationic starch product was added to a four-necked flask equipped with a stirrer, a condenser reflux tube, and a thermometer. The product was gelatinized at 80 °C for 30 min and was cooled down to 40 °C. Initiator and acrylamide monomer was then added under N_2 protection. After the reaction, the product was heated up, and the molar ratio of 1:4 of dicyandiamide and formaldehyde were added. The solution was added to a four-necked flask, and the required amount of methanol and urea were also added to the mixture to perform etherification blocking and the capturing of free formaldehyde (Guo and Peng 2012). The starch grafted product was obtained. A total of 20 g of product was removed and repeatedly washed with 60 mL of anhydrous ethanol. After washing, the obtained solid was dried and weighed.

Infrared spectrum measurement of products

The infrared spectrum of products was tested using the KBr pelletizing method. The product was ground into solid powder, and a small amount was added to KBr powder for pressing. Then, the infrared spectrum of the KBr sheet was measured by the infrared spectrometer.

Product charge density determination

The product was diluted 100,000 times and evaluated by titration, using the streaming current device (Peng and Garnier 2012). The titrant was the potassium salt of polyvinylsulfate having a concentration of -.001 ml/L.

Pulp preparation

The metered pulp board made by coniferous wood and hardwood were taken into the pulper, and 23 L of water was added to soak the pulp boards for a period before beating. The degree of the beating was determined according to GB/T 3332 (2004).

Performance testing of retention aid drainage

The retention efficiency needed to be measured using a dynamic water filter. The wet pulp with a dry fiber mass of 5 g was added to a fiber disintegrator. The ratio of the raw material pulp was LBKP:NBKP = 70:30. The solution was defibrized for 5 min and diluted with water. The amount of filler added was 20% of the total dry fiber and diluted to 1000 mL. The pulp with the consistency of 5 g/L was added to the dynamic water filter, and the additive addition point, stirring time, and stirring speed was set. Then, the pulp retention efficiency and the drainage curve were measured.

Whitewater particle size measurement

Appropriate upper layers of pulp and whitewater with different additives, agitation rates, and stirring times were obtained separately, and the size distribution of the particles was determined by using a Malvern Mastersizer 3000 laser particle size analyzer at a system temperature of 25 °C. Moreover, the particle size test conditions were set according to the standard operating procedure (SOP). The particle refractive index was 1.486, the particle absorption rate was 0.1, water acted as the dispersant, and the dispersant refractive index was 1.330.

Papermaking

An appropriate amount of pulp was placed in a defibrizer to defibrize at 3000 rpm, the paper basis weight was 80 g/m^2, and the amount of filler added was 20% of the total dry fiber. The wet paper was dried in a rotary drum dryer with a drum temperature of 120 °C and a drying time of 30 s.

Scanning electron microscope

The paper sheet was cut into a square, and the surface structure of the sample was preserved as much as possible. Then, the sample was cut to a size of approximately 1 cm, fixed on a sample plate, and subjected to conductive treatment to maintain the sample in a conductive state. The JSM-6700F scanning electron microscope was used for analysis.

RESULTS AND DISCUSSION

Infrared Spectrographic Analysis of Starch Modified Dicyandiamide Formaldehyde Polymer

As shown in the first infrared curve in Fig. 2, there was an apparent absorption peak of C-H stretching vibration in the vicinity of 2937cm^{-1}, and the absorption peak of C-O stretching vibration at 1000 cm^{-1} to 300 cm^{-1} was found, thus implying the successful synthesis of cationic starch.

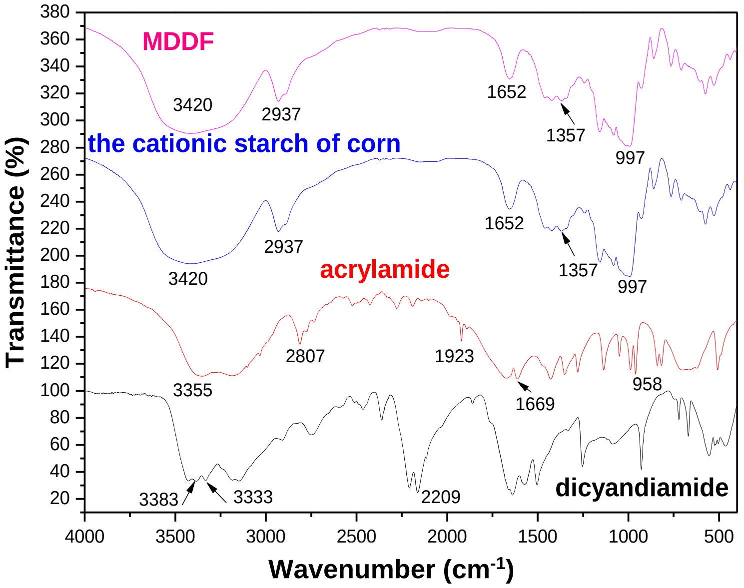


Fig. 2. IR spectra of dicyandiamide, acrylamide, cationic corn starch, and MDDF

There was also a stretching vibration absorption peak of the N-H similar to dicyandiamide near 3426 cm^{-1}, and there was a stretching peak of group "=N+=" at 2198 cm^{-1}, which was located in the middle chain section of the dicyandiamide formaldehyde polycondensate, indicating the reaction of dicyandiamide to formaldehyde. The C-H stretching vibration absorbance peak was the same as cationic starch near 2933 cm^{-1}, there was an N-H vibration similar to that of the acrylamide monomer near 1640 cm^{-1}, and there was an absorption peak of the C-N stretching vibration like dicyandiamide within the range of 1000 to 1350 cm^{-1}. It was deduced that starch and acrylamide monomer reacted with dicyandiamide formaldehyde, so that the product was a starch graft dicyandiamide formaldehyde polymer.

As shown in the uppermost curve in Fig. 2, there was an apparent absorbance peak of C-H stretching vibration in the vicinity of 2937cm^{-1}, and the absorbance peak of C-O stretching vibration at 1000 cm^{-1} to 300 cm^{-1} was found, thus implying the successful synthesis of cationic starch. There was also a stretching vibration absorbance peak of the N-H similar to dicyandiamide near 3426 cm^{-1}, and there was a stretching peak of group "=N+=" at 2198 cm^{-1}, which was located in the middle chain section of the dicyandiamide formaldehyde polycondensate, indicating the reaction of dicyandiamide to formaldehyde. The C-H stretching vibration absorbance peak was the same as cationic starch near 2933 cm^{-1}, there was an N-H vibration similar to that of the acrylamide monomer near to 1640 cm^{-1}, and there was an absorbance peak of the C-N stretching vibration like dicyandiamide within the range of 1000 to 1350 cm^{-1}. It was deduced that starch and acrylamide monomer reacted with dicyandiamide formaldehyde, so that the product was a starch graft dicyandiamide formaldehyde polymer.

Influencing Factors of Grafting Polymers-bentonite Retention and Drainage Aid System

Influence of MDDF dosage on grafting polymers–bentonite retention and drainage aid system

Under the alkaline condition, at 19 °C a total of 5 g of dry pulp and filler that accounted for 20% of the dry pulp were poured into the DFR-05 dynamic water filter, and the speed of the mixing chamber was adjusted to 700 rpm for 10 s. Then, a certain amount of MDDF was added, and the speed was adjusted to 800 rpm for 20 s. The rotational speed was set to 1500 rpm for a total of 60 s, and 0.3% bentonite was added. Finally, the rotational speed was set to 750 rpm for 15 s, the preset procedure was turned off, and the pulp retention measurement was initiated.

As shown in Fig. 3 as curves a and b, a bentonite amount of 0% was equivalent to a single retention system.

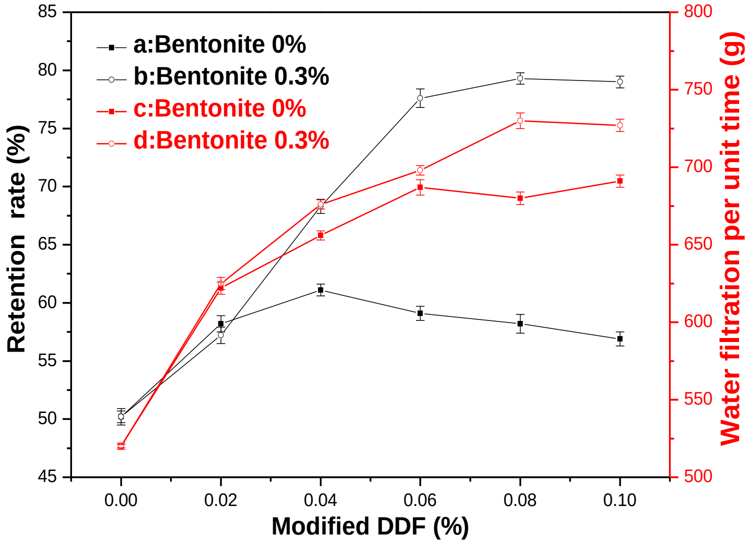


Fig. 3. Effect of MDDF addition on the retention efficiency of the microparticle retention system

Compared to the microparticle retention system with the MDDF dosage of 0.3, the retention effect of fines was considerably less than 20% to 30%. When the dosage of MDDF was relatively low, the retention effect of the microparticle retention system was nearly the same as that of the single retention. This finding could be have been attributed to MDDF consumption by the electrostatic neutralization reaction with the anionic substances in the pulp when the added MDDF amount was relatively small. Hence, such an amount of MDDF was impossible to be bridged with the subsequent addition of bentonite. The increasing amount of added MDDF, which was attached to the fiber in the form of a chain ring tail, increased the contact with the fine material in the paper and formed a sturdy and compact bridging layer, thus improving the retention and drainage effect.

As shown in Fig. 3 (see curves c and d), compared with the single retention system, the amount of drainage in the unit time considerably increased when the MDDF system was added with bentonite. When the addition of MDDF was 0.08%, and the amount of bentonite was 0.3%, the internal drainage content reached 727 g in 60 s, which was not relatively different from that of the CPAM system, evidently improving the drainage performance of the paper material. This finding was attributed to the addition of bentonite with the large specific surface area, small floc formation, evident uniformity, and complex water preservation. Therefore, the drainage rate notably accelerated compared with the large floc system.

Retention System

Effect of bentonite dosage on graft polymer-bentonite retention and drainage system

Table 1 shows that for a certain amount of MDDF, with an increase in the amount of bentonite, the retention efficiency of paper increased, and the greatest effect was observed when the amount of bentonite was 0.3%. When the amount of bentonite was further increased, the effect was no longer changed. This finding was attributed to the addition of MDDF, which has high molecular weight and low charge density. The original floc was dispersed by increasing the high shear force caused by the rotational speed, and the cationic material dispersed in the paper was combined with the negative bentonite. The specific surface area of bentonite is large, and the bridge union was more compact than the original floc by electrostatic attraction. Therefore, the fine fibers and fillers were evenly maintained in the paper. If few cationic polymers were present, then the addition of cationic materials would combine with negatively charged materials, which would no longer play a role in the bentonite added later.

Table 1. Effect of Bentonite Addition on Retention Efficiency of Microparticle

Grouping	1	2	3	4	5	6
Bentonite Addition (%)	0	0.1	0.2	0.3	0.4	0.5
Retention Efficiency (%)	50.2	56.8	66.8	78.6	78.2	77.9

The results showed that the optimum dosage of bentonite changed with the addition of the modified polymer. The adsorption of bentonite and cationic polymer will generally reach the maximum when the cationic polymer reaches the maximum coverage on the fiber. The system remained unchanged as the amount of bentonite or polymer increased.

Effect of pulp pH on grafted polymer–bentonite retention and aid drainage system

The amount of added MDDF was 0.08%, the amount of added bentonite was 0.3%, the speed of the stirring paddle was 700 rpm for 10 s, the speeds were 800 rpm for 20 s, 1500 rpm for 60 s, and 750 rpm for 15 s. The system pH was changed, and the pH value of the system was separately adjusted with aluminum sulfate and sodium hydroxide. The retention of the fine components is shown in Table 2.

Table 2. Effect of pH on Retention of Microparticle Retention System

Grouping	1	2	3	4	5	6
pH	10	9	8	7	6	5
Retention Efficiency (%)	79.4	78.9	78.6	79.6	74.4	69.8

As shown in Table 2, the retention of fines in the alkaline and neutral conditions was maintained at a high value. Meanwhile, in acidic conditions, the retention efficiency was reduced. This finding could have been due to the presence of -COO- as the primary charge group of the fiber under medium alkaline conditions. Therefore, the pulp was negatively charged. After the cationic MDDF was added, the pulp was adsorbed together in the form of a chain ring-tail with the fiber under the action of neutralization and increased the system retention efficiency. In acidic conditions, the surface of the pulp was partly in the form of -OOH, and there was less net negative surface charge of the pulp to interact with cationic substances. Therefore, the retention efficiency decreased. Furthermore, under acidic conditions, $CaCO_3$ as a filler was partially decomposed, with the release of Ca^{2+} ions, which was not conducive to filler retention in the paper.

Analysis of the Mechanism of Action of Graft Polymer-bentonite Retention System

The charge density of grafted polymers

After the grafted product was diluted 100,000 times, the charge density of the grafted product was measured with a PCD-03 particle charge detector. The results are shown in Table 3.

Table 3. Charge Density of Graft Products

Sample	MDDF	CPAM
Charge Density (meq/g)	3.9	2.0
Molecular Weight	3.0×10^6	5.0×10^6

Table 3 reveals that the charge density of modified graft polymer was low and its molecular weight was slightly lower than CPAM. Liu and Liu (2005) argued that the molecules of high molecular weight, low-charge density polyelectrolytes, are curled. The polymer molecules are adsorbed on the fibers in an “extended” configuration when added to the pulp and are present in the pulp in the form of a chain ring-tail (Fig. 4). The configuration of the chain-ring and tail increased the contact area of the polymer with the negative particles in the pulp. This configuration was easier to flocculate with the fibers or fine components in the form of bridging, forming what is called the bridging mechanism (Feng *et al.* 2018).

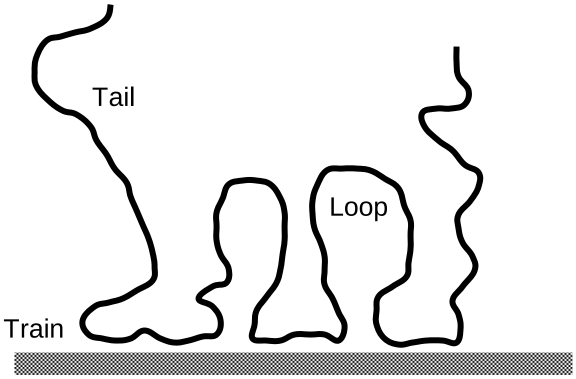


Fig. 4. Schematic diagram showing the loops and tails of an absorbed polymer with an extended conformation

Compared with CPAM, the MDDF has a relatively large charge density. If the charge density is extremely low, then there are few bonding points with fibers, fine fibers, and fillers. Moreover, the adsorption is weak, which is not conducive to the formation of initial flocs and subsequent bridging.

Particle size analysis

Table 5 and Fig. 5 show the particle size distribution of particles and flocs in different times and position sizes measured *via* the Mastersizer3000 laser particle size analyzer, in which the refractive index of the particles was 1.486, and the dispersant was water. The Mie scattering model was used to detect the particle size. The different treatment methods for the five groups of curves in Fig. 5 are shown in Table 4. Curves 1 and 2 showed that after the addition of high molecular weight MDDF, negative fibers, fillers, and fine fibers were rapidly attracted to form the initial floc due to the positive charge of MDDF. From the comparison of the specific surface areas of the particles between the blank group and the two groups with the additives in Table 5, it was not difficult to find that when the MDDF was added to the pulp, the floc had a specific surface area of 198.4 m^2/kg, larger volume, and no shear resistance. After high-speed shearing for 60 s, the specific surface area of the floc in the pulp increased to 199.8 m^2/kg, meaning that the initial floc was broken into small volume pieces, thus exposing additional short-chain cationic polymers in the pulp. Therefore, the addition of bentonite microparticles with high negative surface charge was adsorbed together with a polymer and was connected by the synergistic action of electrostatic neutralization and a non-static section to combine the fragments through bridging. From the comparison of the specific surface areas of the particles with the single retention system in Table 5, in the microparticle retention systems, a bridge with small size and considerable strength was formed to improve the retention efficiency of the fine components in the pulp. Simultaneously, the size of the distribution coefficient in the pulp was observed, and the distribution coefficient of the microparticle system was 1.419, which was the smallest of the three groups of pulp. The overall distribution width of the floc particles in the solution was narrow, and the size was relatively concentrated. Given that the specific surface area was smaller than the single system, the floc was fine and uniform, thereby improving paper formation and drainage to some extent.

Table 4. Different Processing Methods of the Five Sets of Curves

Grouping	MDDF	Sampling Position	Shear Rate	Bentonite
1	+	Online pulp	1500 rpm High-speed	+
2	+	Online pulp	Low-speed	/
3	/	Whitewater	Low-speed	/
4	+	Whitewater	Low-speed	/
5	+	Whitewater	1500 rpm High-speed	+

Table 5. Particle Size Detection Data

Grouping	Pulp			White Water		
	Blank	Single	Microparticle	Blank	Single	Microparticle
Specific Surface Areas (m^2/kg)	215.6	198.4	199.8	441.9	275.2	336.3
Consistency	0.628	0.627	0.612	0.505	0.468	0.430
Distribution Coefficient	1.469	1.456	1.419	1.101	0.934	0.857
D (50) (μm)	1.19	2.64	1.45	0.936	0.879	0.600

Curves 3 and 4 of Fig. 5 revealed that the particle size was smaller in the whitewater under the net added with the MDDF than that of the group without MDDF, which showed that merely the addition of MDDF had a specific improvement effect on pulp retention and the fine components in the whitewater under the net decreased. However, for the specific surface area in the pulp, the single system resulted in smaller particle size than the particulate system, demonstrating that the flocs decreased after the high shearing force; the initial floc volume was relatively large, and it was resistant to shear, causing damage to paper evenness. Table 5 shows the specific surface area of the fine components in whitewater passing through the screen as 336 m^2/kg in the microparticle retention system, which was considerably reduced compared with the blank group of 442 m^2/kg. This indicated that only a small amount of the components of the small particles reached in the whitewater through the nets, and it was beneficial to the closed circulation of the whitewater. Based on the difference in particle consistency between those groups in Table 5, the consistency of the fine components and the particle size of the filler in the whitewater of the blank group was 0.505, which was larger than that of the single system and the microparticle system. This finding could have been attributed to the fact that the small components were relatively large, the overall retention was weak, and the particle size distribution was off-centred in the whitewater of the blank group, which made the distribution broad. Meanwhile, the deviation in particle size within the microparticle retention group was small, the distribution was relatively uniform, and the floc volume in the pulp solution was small. A dense layer of flocculation was formed in-between to increase the retention of the fine components in the pulp.

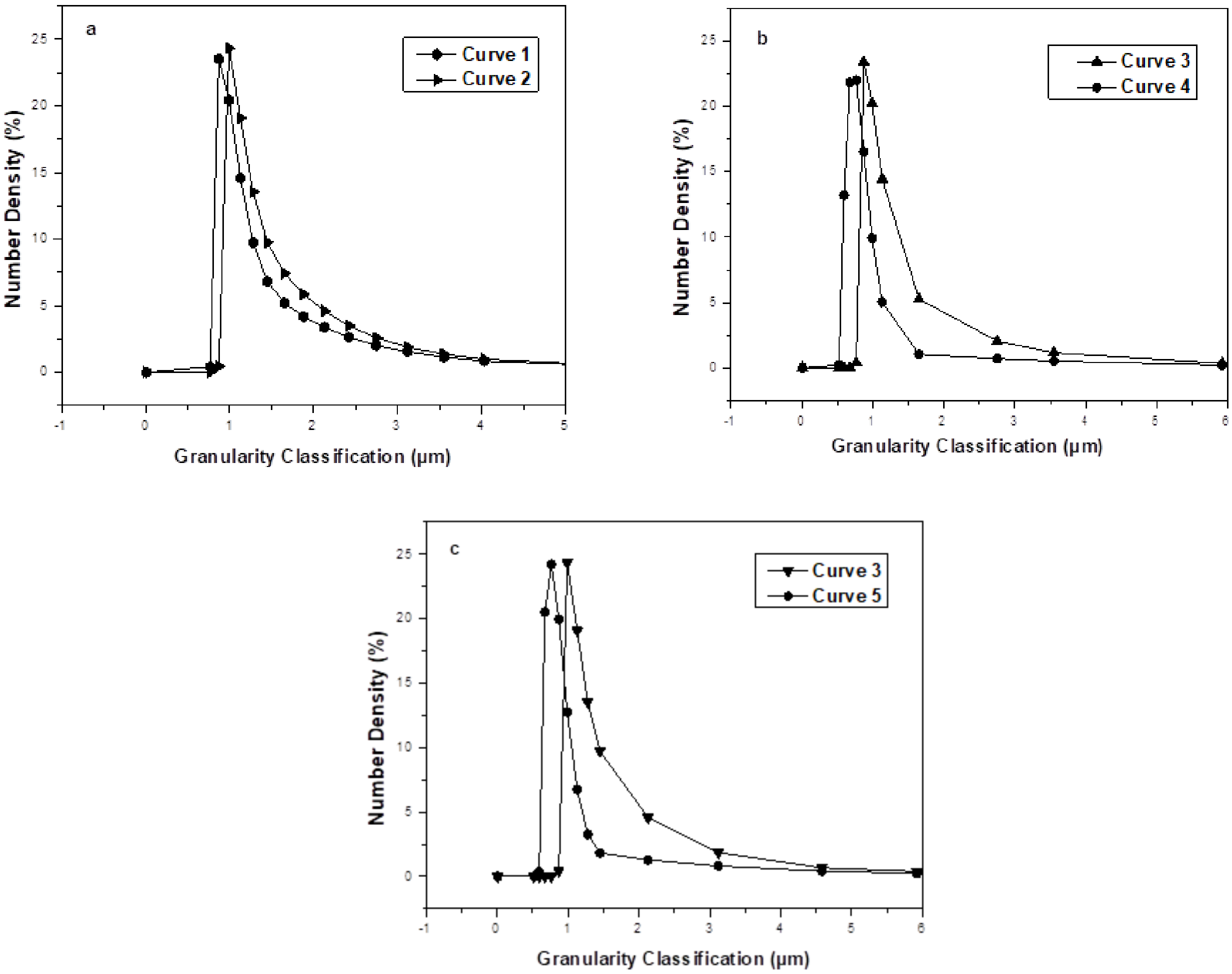


Fig. 5. Particle size distribution in paper materials at different times and position: a) Particle size distribution in the slurry after adding MDDF and MDDF and bentonite retention system; b) Particle size distribution in whitewater after adding MDDF and blank group; c) Particle size distribution in whitewater after addition of MDDF microparticle retention system and blank group

SEM analysis

A large number of papers prepared by various retention systems were analyzed using SEM. The authors randomly selected four pictures for Fig. 6. Figure 6A and 6B show the papers produced by the microparticle retention system, which were enlarged 800× and 500× *via* scanning electron microscopy, respectively. Figures 6C and 6D were papers created by the single retention system, which were enlarged 800× and 500×, respectively. Figure 6 clearly shows that the paper produced by the microparticle retention system was remarkably improved in terms of its evenness, the filler distribution was uniform, and the retained fine components were noticeably increased. Moreover, the fibers demonstrated orderly bonding, indicating considerable improvement in paper performance. In the paper's pattern of the single retention system, the distribution of fibers was disorganized, and the distribution of the filler was not uniform. Such nonuniformity in paper can lead to problems during pressing and drying of the paper web, during converting of the paper, and during end-use processes, such as printing.

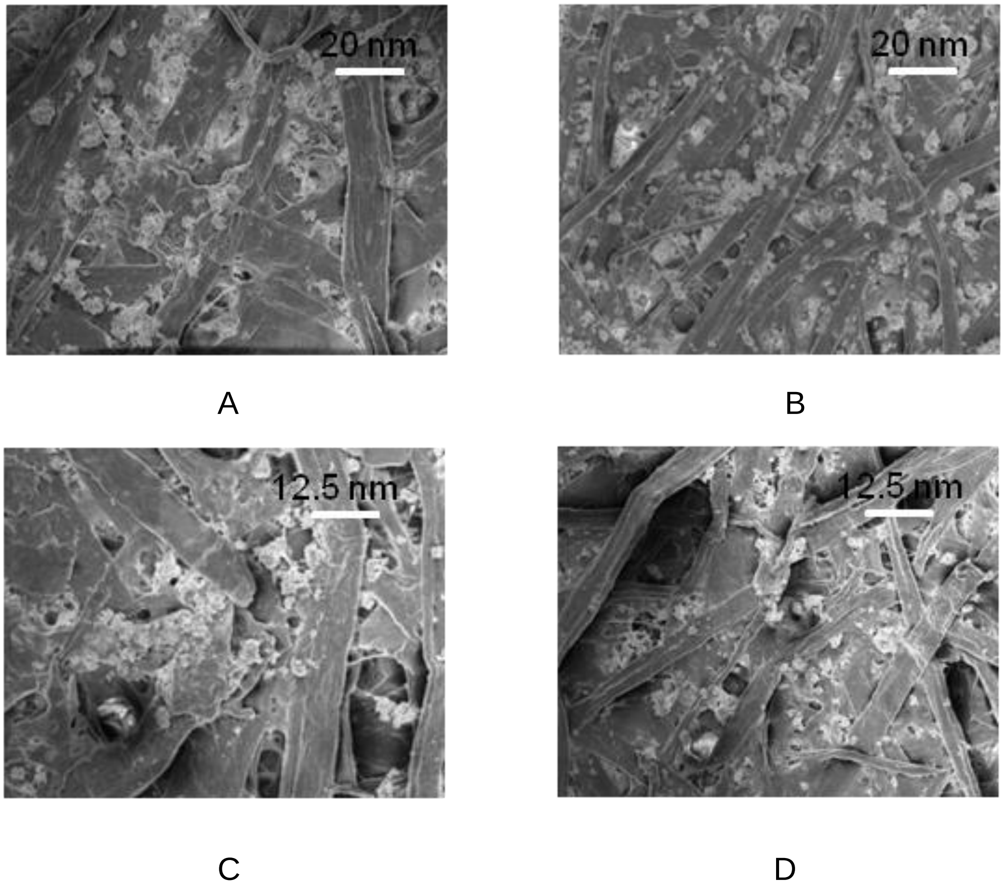


Fig. 6. SEM images of papers manufactured under different retention systems

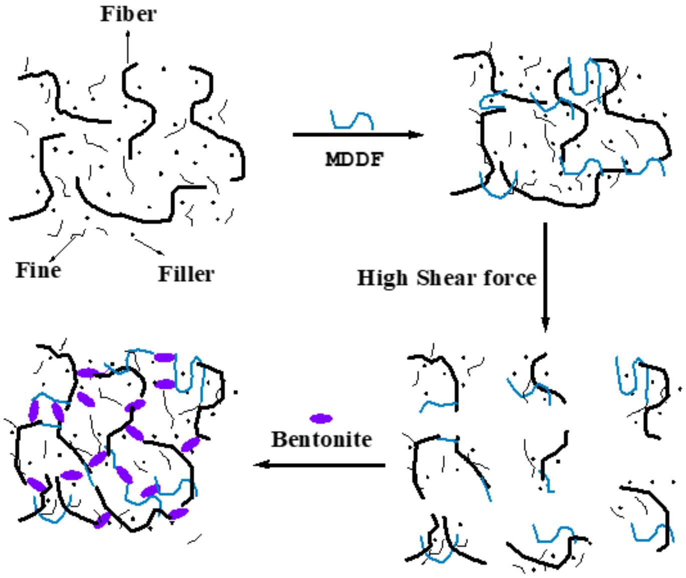


Fig. 7. Mechanism of the microparticle retention system

Figure 7 provides a schematic description of a proposed overall mechanism of action of the modified graft polymer. The cationic polymer was added to the pulp and existed in the form of chain rings and chain tails and adsorbed on the fibers to form a sizeable initial floccule. Then, the initial flocculation was broken by the high shear force, exposing more cationic polymer active sites. Adding bentonite particles with large specific surface area facilitated adsorption in-between to form a uniform and dense "bridge" layer while improving the retention of the fine components, which enhanced the formation of paper degree and the drainage performance.

In contrast, adding bentonite formed a complex network with excess free cation polymer in the pulp. Although the flocculation effect was not as strong as bridging, it could still partially improve the retention of fine components, reduce the content of excess polymer in pulp, and decrease waste materials in whitewater.

Analysis of the Mechanism of Graft Polymer–bentonite Drainage System

The prepared pulp was added to the dynamic water filter and switched to the drainage module. The blank group, 0.08% MDDF group, and CPAM group (molecular weight: 5 million) were measured to determine the drainage aid performance. The amount of added filler was 20% total dry fiber, and the weight of the drainage was measured through a 60-mesh net within 60 s. The results are shown in Fig. 8. As shown, the drainage curve within 60 s when the single retention agent MDDF and CPAM were added, and the drainage curve of the MDDF-bentonite system and the CPAM-bentonite system within 60 s. It is apparent that compared with the blank group without the drainage aid, the drainage aid effect considerably increased after the drainage aid was added, and the drainage increased to 185% within 60 s. Moreover, for the MDDF system, whether it was a single or a microparticle system, the effect of drainage was superior to that of the CPAM system.

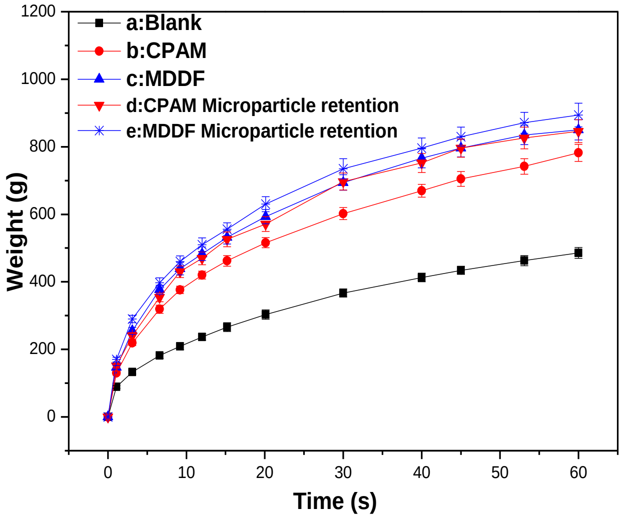


Fig. 8. Water drainage curve of unit retention in 60 s

Figure 9 shows that after the addition of two kinds of retention aids, namely, MDDF and CPAM, the zeta potential in the pulp both changed from negative to positive with an increased amount of additives, and the change of zeta potential could explain the changes in the drainage performance of the different drainage aids. Figure 9 also reveals that when the zeta potential of the pulp was near the isoelectric point 0, the retention effect of the pulp and the effect of water drainage were satisfactory. Therefore, the amount of MDDF added was approximately 0.08%, which corresponded to the best doses explored in Figs. 1 and 2. Observing Fig. 9, the absolute zeta potential of the pulp decreased after the addition of two kinds of drainage aid. However, the effect of MDDF to reduce the zeta potential was considerably greater than that of the CPAM. A possible reason for such a result was the higher charge density of MDDF than that of CPAM (molecular weight: 5.0×10^6, charge density: 2.0 meq/g), which led to the larger change in the zeta potential of the pulp. Figure 9 also shows that when the zeta potential was close to zero, the water drainage performance was improved. Moreover, the zeta potential continuously increased to a positive value when the addition of the drainage aid was sustained, at that time, the fibers in the pulp absorbed additional cationic charge but no considerable improvement was observed in the retention and drainage aid performance, such phenomenon was practically pointless. Hence, MDDF with higher charge density demonstrated superior water drainage performance to CPAM.

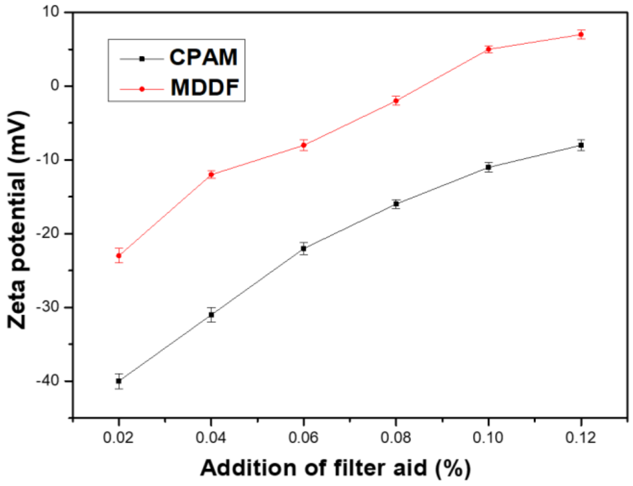


Fig. 9. Change of zeta potential with the number of additives added

CONCLUSIONS

In this study, synthetically modified dicyandiamideformaldehyde polymer was used as the primary raw material to form the MDDF-bentonite microparticle retention system. The retention and drainage aid effects were determined after adding calcined bentonite. The mechanism was inferred by measuring the pulp charge density and the particle size of the fines. The following conclusions were obtained:

1. Under the neutral condition in which the amounts of MDDF and bentonite added were 0.08% and 0.3%, respectively, the initial floccule was broken *via* high-speed shearing. Then, the inorganic filler was added and the water filtration capacity reached 727 g in 60 s. Thus, the retention effect of the MDDF-bentonite system was close to the retention effect of the CPAM-bentonite.
2. The mechanism of the MDDF-bentonite system was inferred through particle size analysis and charge density measurement. For the patch-bridging mechanism, the cationic polymer was first added to form a sizeable initial floccule. Then, the floccules were broken up under high shear conditions. At that time, inorganic fillers with opposite charges were added. Small flocs were reconstituted and distributed on the wet paper web. The filler and fine fibers remained on the paper and improved the retention.

The pulp system became close to the isoelectric point after the addition of MDDF due to its higher charge density than CPAM, which led to the superior effect of water drainage.

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