Etherified dicyandiamide condensation copolymer as a wet-end additive for papermaking

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ABSTRACT

Dicyandiamide-formaldehyde condensation copolymer was synthesized and used as a wet-end additive for papermaking. The retention of fibers and fines was used as a performance index. Factors were evaluated governing the performance of the polymer, including polymer dosage, pH and mixing time. The optimum dosage of the polymer was found to be 0.03\% under the conditions. Overall, the polymer was effective in improving the drainage, as well as the retention of fibers and fines in papermaking process.

Keywords: Dicyandiamide-formaldehyde; Retention; Drainage; Papermaking

1. INTRODUCTION

In the paper industry, retention and drainage additives are widely used. Basically, retention and drainage additives can be divided into four categories: cationic, anionic, amphoteric and nonionic.\textsuperscript{1} Dicyandiamide formaldehyde condensation copolymer (DDF) is a cationic polymer. It has high positive charge density, and it can promote the flocculation of fines and fibers. As a result of the use of retention and drainage polymers, fines can be efficiently trapped in fiber networks.\textsuperscript{2} At the same time, fines would not tend to block the spacing in the fibrous layer, while water can flow through the fibrous layers freely. Dewatering can also be improved.

However, free formaldehydes are present in commercially available DDF. These toxic components come from (a) excess formaldehyde of the starting materials, and (b) positive ion-types condensation polymerization obtained from the polycondensation. The reaction is also reversible.\textsuperscript{3} Under the conditions of acid, alkali and high temperature, N–hydroxy methyl structure can break and release free formaldehydes. As a result, DDF does not find its use as retention and drainage aid for papermaking.

In this study, dicyandiamide-formaldehyde polymer was synthesized as a functional additive for papermaking, and the reaction pathways were explored. Drainage and fines content in the white water were used as the performance indices to evaluate the performance of the polymer under varying process conditions.

2. Experimental

2.1 Materials

The materials used in the current study are: dicyandiamide (analytical reagent, Tianjin Bodi Chemical co., Ltd), formaldehyde (analytical reagent, Sinopharm Chemical Reagent Co., Ltd), ammonium chloride (analytical reagent, Tianjin Bodi Chemical co., Ltd), urea (analytical reagent, Tianjin Hengxing Chemical Reagent Co., Ltd), methanol (Tianjin bo di chemical co., Ltd), pulp from Oji Paper.

2.2 Methods

(1) Dicyandiamide, formaldehyde, and ammonium chloride were added into a four-neck flask with reflux condensing tube and stirrer. The mixture was heated in water bath for a given period of time. The boiling exothermic phenomenon occurred, and the temperature was kept at a constant level after the boiling exothermic phenomenon.

(2) Dicyandiamide formaldehyde condensation copolymer and methanol were added into a four-neck flask with reflux condensing tube, stirrer, and thermometer. The pH was adjusted to 2 and the temperature was 50 °C, heated in water bath for 2 to 4 h. By using vacuum distillation, formaldehyde and methanol were recycled. Formaldehyde was then “caught” by urea.

(3) Bleached hardwood pulp (360 g) and water (23 L) were added into a Valley Beater, and the pulp was then refined. The degree of beating was measured according to the standardized method GB/3332-2004. The refined pulp had a beating degree of 43 °SR. Most of the water of was removed, and the wet pulp was then sealed and conditioned for more than 24 h.

(4) The conditioned pulp was disintegrated and then diluted to 0.5\%. DFR-05 was used to determine fibers/fines retention and three parameters were evaluated, including dosage of DDF, pH, and mixing time.
(5) Paper sheets with a basis weight of 75 g/m² were formed. Filler addition level was 20%, based on the dry mass of pulp. Paper sheets were then conditioned for 24h under controlled conditions.

(6) In order to investigate the distribution of calcium carbonate in the paper sheets, three groups of paper samples were observed using a scanning electron microscope.

3. RESULTS AND DISCUSSION

3.1 Process optimization for synthesis of dicyandiamide-formaldehyde condensation copolymer

The dicyandiamide formaldehyde condensation copolymer was synthesized with dicyandiamide, formaldehyde, and ammonium chloride as starting materials, and furnish retention was used as a performance index, and the process conditions were optimized. Then, several factors affecting retention, including dosages of starting materials, temperature, and reaction time. The results indicated that optimum retention was achieved when the molar ratio of dicyandiamide to formaldehyde, and to ammonium chloride was 1:2.1:0.9, temperature was 60°C, and the reaction time was 2.5 h. The removal of formaldehyde were also studied, and the results showed that formaldehyde content was less than 0.124% when the molar ratio of dicyandiamide to methyl alcohol was 1:2.8, that of dicyandiamide to urea was 1:0.04, temperature was 50 °C, and reaction time was 4 h.

3.2 Impact of polymer dosage

The dosages of DDF were 0.01%, 0.02%, 0.03%, 0.04% and 0.05%, respectively. The results are shown in Figure 1.

As shown in Figure 1, the retention increased with increasing dosage of DDF, and then it decreased. The highest retention was achieved when the amount of DDF was 0.03%. Particles dispersed in the water would become negatively charged. The reason behind the charge characteristics of filler particles is related to ion adsorption; On the other hand, it is caused by the lattice defects; for example, ions on the lattice isomorphous substitution can lead to imbalance of the charge, and as a result a net electrical charge is generated. Filler particles with negative charge and fibers with same charge can repel each other. After the addition of cationic retention and drainage aids, the main interaction between the colloidal particles and the cationic particles is electrostatic adsorption, and the reduction in zeta potential is due to the electrical neutralization of the two types of particles. The maximum degree of condensation occurred when the cationic particles was equal to the colloidal particles in water. And if the dicyandiamide formaldehyde polymer charge is too high, it would result in reversal change of the colloidal system, thus negatively affecting retention.

3.3 Impact of pH

The pH of papermaking stock was adjusted to 6, 7, 8, 9 and 10, and the results are shown in Figure 2.

As shown in Figure 2, the retention of filler particles increased with increasing pH, and maximum retention was achieved at pH 7. Actually, the charge and reactivity of dicyandiamide-formaldehyde is pH-dependent. Specifically, the negative charge increased with increasing pH due to enhanced ionization of –COOH. Meanwhile, the capacity of dewatering in papermaking is weakened as a result of the generation of a considerable amount of anionic impurities, which can negatively affect sheet formation. Dicyandiamide-formaldehyde polymer contains a large number of activity groups, such as -CONH₂, -NH₂⁺, -CN, -NH₂, =N⁺H₂, which could be abundantly consumed, leading to the reduction of charge density of dicyandiamide-formaldehyde polymer in the aqueous system. The weakened effect of charge neutralization could have an adverse impact on the retention of fines and fillers. In a study on the use of dicyandiamide formaldehyde polymer as a decolorizing agent, good charge neutralization performance was achieved at various pH values, and enhanced dissociation of active groups could contribute to better retention at a high pH.
3.4 The influence of mixing time on Retention

The mixing time was adjusted to 10s, 20s, 30s, 40s and 50s. The results are shown in Figure 3.

![Figure 3. Relationship between mixing time and retention.](image)

As shown in Figure 3, with the increase of mixing time, retention increased and then decreased. Maximum retention was reached at a mixing time of 30 s. The key mechanism of retention is the colloidal aggregation, which involves flocculation of fines and fibers. The addition of DDF was able to promote the flocculation of fibers together with fines. After adding DDF, negative charges that existed on fiber fines and fillers were neutralized to reduce the exclusive inter-particle forces, and flocculation occurred through collisions.10 The “patch” mechanism showed that, with the addition of cationic particles, negatively charged fibers adsorbed a number of positive charges. Thus, the electrostatic attraction occurred between fibers and negatively charged particles, thereby causing flocculation. These processes occurred gradually upon the addition of DDF.11 If the flocculation time was too long, flocculates would be small due to the function of dispersive force, resulting in a reduction in filler retention.

3.5 Impact of polymer additive on Drainage

The drainage curves for several sets of experiments are shown in Figure 4.

![Figure 4. Relationship between drainage time and weight.](image)

![Figure 5. SEM pictures of paper sheets (A-blank, B-PAM, C-DDF)](image)
The retention aids can play an important role in drainage/dewatering process. There is strong adsorption between fibers, fines, and cationic polymer, when the cationic polymer is in contact with the pulp, where the polymer is quickly absorbed to fiber surface, and infiltrated into the fiber micro hole, so that the charge and polarity of the fiber surface are reduced, which is difficult for water molecules’ wetting and achieving directional arrangement on the fiber surface. The decrease of the specific surface area of fibers and fiber fines leads to the decrease of the adsorption of water molecules. In addition, the clogging of the small fibers can be reduced, and the dewatering can be easier. As seen from Figure 4, after adding retention and drainage aid, the drainage performance of the papermaking stock was improved, but it was not obvious. PAM was better than DDF in terms of drainage. The performance of DDF may be improved by increasing its molecular weight.

3.6 Impact of mixing time on retention

In order to further understand the role of dicyandiamide-formaldehyde condensation copolymer in retention of fines. Three groups of paper sheets were measured by SEM. These paper sheets are blank sheets, DDF-containing sheets, and PAM-containing sheets. It should be noted that the polymer dosage relevant to the paper sheets was 0.05%, based on the dry mass of pulp. As seen from the SEM images in Figure 5, polymer addition resulted in an increase in the size of the particles in the fiber network and a reduction of the gap between fibers.

4. CONCLUSION

In this work, a functional dicyandiamide-formaldehyde condensation copolymer was successfully synthesized, and the process conditions for the synthesis were optimized. The prepared polymer was employed as a retention and drainage aid in the papermaking process, and various governing factors were investigated. The results showed that this polymer performed well as a retention aid, although it was not as effective as polyacrylamide in improving drainage.

ACKNOWLEDGMENTS

This work was financially supported by Shandong Provincial Natural Science Foundation of China (ZR2017MC032), open fund of Key Laboratory of Biomass Energy and Materials of Jiangsu Province (JSBEM201808), the Undergraduate Training Programs for Innovation, the Entrepreneurship in Qingdao University of Science &Technology (201601008), and the Science and Technology Major Project (Emerging industries) of Shandong Province (2015ZDXX0403B03).

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