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IMPACT OF CATIONIC POLYACRYLAMIDE FOR A NEW KIND OF PULP ULTRASONIC WHEAT STRAW ON ALKYL KETENE DIMER SIZING

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ABSTRACT

As a new kind of pulp that can protect the environment by conserving wood resources, ultrasonic wheat straw pulp has received increasing attention. It is prepared by the mechanical effect of ultrasound, the effect of cavitation, and thermal effect, and it does not require a large amount of chemical additives. Different pulp methods yield differences in performance. The conventional method of sizing is difficult to achieve the ideal of wheat straw pulp ultrasonic sizing effect. This work examined the effects of additives and surface charge on sizing by studying ultrasonic wheat straw pulp with 0.25% alkyl ketene dimer (AKD) added in the form of a commercial emulsion without separate retention aids. As a retention aid cationic polyacrylamide (CPAM) contents were prepared and added to fiber suspensions at the wet end of the papermaking process. The relationship between CPAM and the zeta potential of papermaking furnish and sizing degree, the strength properties of the paper sheet, and the factors that affected measuring the zeta potential were investigated. As the CPAM content increased, the surface morphology, the zeta potential and the strength properties of the paper sheet presents a curve.

KEYWORDS: Ultrasonic wheat straw pulp, CPAM, AKD sizing, surface charge.

INTRODUCTION

Environmental protection has been one of the main drivers of sustainable developments in the pulp and paper industry, resulting in more focus on non-wood resources. However, some properties of non-wood raw materials are inferior to those of wood materials. Therefore, it is necessary to find a method that enhances the performance of non-wood raw materials. Performance additives such as sizing agents are used in paper making to give paper or board specific properties. Sizing agents are added to pulp furnish (a complex mixture of pulp fibers, pulp fines, and other additives such as fillers and retention aids) to reduce the rate at which liquid penetrates the final paper product. Traditionally, sizing is performed at a pH below 6 using alum and rosin. Given that there are many advantages in producing paper under neutral or alkaline conditions, there is pressure to change to a sizing agent that is stable under these conditions. Alkyl ketene dimer (AKD) is one such sizing agent.

AKD is popular internal sizing agents, which by definition produce paper with hydrophobic properties. AKD is a waxy, water-insoluble solid that any emulsion be formedabove its melting temperature in the presence of surfactants. After cooling to room-temperature, liquid AKD droplets become solid particles (Mohlin et al. 2003, Mohlin et al. 2006), that engage in a solid-water interfacial interaction for sizing. Thus, there exists an opportunity to prepare stabilized AKD dispersions (Yang et al. 2016), which may avoid the adverse effect of surfactant on paper sizing and environmental problems caused by surfactant bioaccumulation.

Otherwise, there has been little published work on the effect of surface charge on AKD sizing performance.

The charge on pulp fibers is generally believed to result from the ionization of acidic surface groups (Jian et al. 2006), such as carboxylic and sulphonic acids and catecholic and phenolic hydroxyl groups and it can promote the swelling process (Scallan et al. 1983) and can strongly influence the papermaking properties of the fibers. Under papermaking conditions, the carboxylic and sulphonic acid groups are the major contributors to surface charge. Commercial AKD emulsions are prepared as a stabilized emulsion by the dispersion of the AKD wax in water containing a cationic polymer (usually cationic starch). In commercial operations, retention aids are also added to assist AKD retention, but the pulp, the kind of retention aid and reaction condition have great influence on the sizing degree of AKD (Lindström et al. 2007, Johansson et al. 2004)

The mechanism of AKD retention is the combination of negative charge on the surface of the fiber. A study by Isogai et al. (1997) reported that deposition or retention of AKD can be prevented by blocking carboxyl groups in the pulp with non-ionic methylamide groups. This is clear evidence that the degree of surface charge on pulp fibers affects the sizing performance of AKD.

There are numerous ways of measuring the sizing performance of treated handsheets. The Cobb test, which involves determining the amount of liquid absorbed by paper in a given time, is the one most commonly used methods in mill situations as it gives a simple, quick measure of the degree of sizing. Measurement of the contact angle formed by a liquid drop in contact with the surface of paper also measures the sizing performance. The Cobb test and contact angle, however, are not only influenced by the performance of the sizing agent. Other factors include the size of the pores in the paper and its surface roughness.

From a global perspective, the full utilization of native or local wheat straw to produce biomass-based products is of strategic significance (Petrik et al. 2013, Backer et al. 2013). Ultrasonic wheat straw pulp production technology fits well into the above concept by virtue of its high-yield production (approximately 70%) (Xing et al. 2010). Furthermore, because ultrasonic wheat straw pulp provides high-bulk and high-opacity paper sheets (Hu et al. 2015), it has found increasing application in many paper grades (Georgieva et al. 2008). Its physical strength, however, is lower than that of chemical pulp, which hinders widespread application. While ultrasonic wheat straw pulp retains the advantages of the traditional chemistry wheat straw pulp, its strength and optical properties are better than those of traditional chemistry wheat straw pulp.

CPAM as retention and drainage aid to the pulp in addition to fill all kinds of additives have a good retention effect, has a wide range of applications (Jin et al. 2003, Shan et al. 2012).

CPAM with positive charge can effectively neutralize the negative charge of the surface of the pulp (Vanerek et al. 2000), in the fiber and filler in the directional arrangement of macromolecular structure, therefore, a gap channel is formed to help improve the effect of intervention.

The effect of CPAM on filler retention is obvious, so it has been widely used. The amount of CPAM added in this paper has been studied. The effect of different amount of CPAM on the performance of AKD has been studied.

Ultrasound has a strong penetrating ability and can penetrate various gases, liquids, solids, plasmas and so on. Ultrasonic treatment can produce mechanical effects (such as ultrasonic crushing), thermal effect, chemical effect, biological effect, which can change the properties or state of the material, so ultrasonic wave can be used as an important means of processing and treatment. Water molecules can penetrate into the crystalline region of cellulose and the effect of surface acoustic cavitation results in amorphous cellulose molecular chain amorphous and crystalline defects area are quickly separated so, the reactivity of the fibers can be increased during the second drying process.

Ultrasonic pulping technology is a new technology, material with water forming concentration is 3% to 30% of the raw material liquid, ultrasonic assisted adding weight of 0.1% to 1% of the raw material liquid additives; and then heating the raw material to 50°C to 180°C after opening, ultrasonic generator, ultrasonic power is 0.25 to 1 kW / cubic, the frequency is 15 to 80 KHz, ultrasonic interval in raw materials liquid, reaction for 1 to 5 hours.

Pulping and bleaching simultaneously; the quantity of equipment and energy consumption is greatly reduced, saving investment, low production cost; the yield of pulp bleaching and high efficiency, good product quality; pulp washing process, less water consumption; less waste water, chemical oxygen demand (COD) and low chroma, without persistent toxic AOX and other pollutants, the pollution load of small, environmentally friendly (Liu et al. 2009). To study the ultrasonic wheat straw pulp and wheat straw pulp from traditional chemical crystallization from different perspectives, in order to further explore the optimal dosage of additives in the process of paper making.

The primary aim of this study was to gain a better understanding of the effect of additives in the process of AKD sizing. The secondary aim was to extend the understanding of the factors affecting AKD sizing.

MATERIALS AND METHODS

Materials

Ultrasonic wheat straw pulp was supplied by Anyang Paper Industry Co., Ltd. (Henan, China) (solid content of 15%). Cationic polyacrylamide (CPAM) (molecular weight of 8 million grams per mole, charge density of 2.47 mmol.g-1) was supplied by Xilong Chemical Co., Ltd (Guangdong, China)). The ash, extractives, pentosane, and lignin contents were determined according to GB/T 742 (1989), GB/T 2677.6 (1994), GB/T 745 (1989), and GB/T 747 (1989), respectively (Tab. 1).

Tab. 1: The chemical composition (Based on mass) of the ultrasonic wheat straw pulp.

Composition	Extractive	Cellulose	Pentosan	Lignin	Kappa number
Content (%)	1.08	66.76	12.28	4.31	11.71

Experimental procedure

The pH of the stock was approximately 7.0, as measured by a Sartorius PB-10 acidometer (Gőttingen, Germany). The consistency of the stock was 1% (w/v), and the time interval between the addition of AKD and the fillers was 10 min. Before manufacturing, the paper, pulp, and chemicals were mixed in an agitator (IKA Eurostar, Staufen, Germany), and then CPAM was added to the pulp as follows: 25°C, 30 min, pH 6.5 to 7.5. The dosages for the additives were 0.2, 0.4, 0.6, 0.8, and 1.0% on oven dry basis, and every treatment was repeated three times. Including the blank test, with no fixative treatment, six pulp samples were tested.

X-ray diffraction (XRD)

X-ray diffraction analysis was carried out using a Shimadzu model XRD 6000 (Kyoto, Japan) (CuKα radiation with a graphite monochromator, 30 kV, and 40 mA). The patterns were obtained between 5° and 45° 2θ with 0.05° steps at a speed of 2°·min^{-1}. The degree of crystallinity was calculated as the ratio of the intensity differences in the peak positions (Eq. 1),

$$Cr = \frac{Fc}{Fa+Fc} \times 100 \qquad (\%) \qquad (1)$$

where: F_c - the intensity for the crystalline region,
F_a - the corresponding quantity for the amorphous region.

Surface morphology

The ultrasonic wheat straw pulp samples with different CPAM content were coated with a thin layer of gold, sprayed with metal, and mounted on aluminum stubs with conductive adhesive tape prior to FESEM analysis. A US 8020 model scanning electron microscope (FEI Company, Hillsboro, U. S. A) was used to observe the fiber surface morphology. The working conditions included a working distance of 20 mm, accelerating voltage of 1 kV, and illuminating current of 0.7 Na.

Zeta potential

The surface charge of the fibers was evaluated using zeta potential measurements by a FPA Fiber Zeta Potential Analyzer (AFG Analytic GMBH, Darmstadt , Germany).

Handsheet preparation and testing

A total of 0.25% AKD sizing agent (as the solid mass of the AKD emulsion) and 0.2, 0.4, 0.6, 0.8, and 1.0% CPAM (0.1% water solution) was added, while mixing, to a ultrasonic wheat straw pulp of 40° SR. All of the chemical dosages were as solid mass percentages based on pulp fibers. Laboratory paper sheets (handsheets) were formed with a sheet former. There are numerous ways of measuring the sizing performance of treated handsheets. In this study, measurement of the contact angle formed by a liquid drop in contact with the surface of paper gave a measure of sizing performance.

Eighty g·m^{-2} handsheets were produced in a standard KRK handsheet machine for the six different samples from a suspension containing 0.25% AKD on an oven dry pulp mass basis, which is within the normal range for papermaking. The AKD emulsion was added to the pulp before sheet forming and formed sheets were cured for 2 h at 105°C.

The Fibro 1100 dynamic adsorption tester (DAT) MkII (Beijing, China) was used to measure the average dynamic contact angles of the AKD-sized handsheets, as described previously (Kwok et al. 1998). Water was used as the test fluid with a drop size of 4.0 µL. The contact angle used to characterize the sheets was recorded 1.0 s following contact of the drop with the paper.

RESULTS AND DISCUSSION

XRD analysis

Fig. 1 presents the XRD spectra of traditional chemical wheat straw pulp and ultrasonic wheat straw pulp samples. The traditional chemical and ultrasonic wheat straw pulp showed a maximum at 18° 2θ (cellulose crystal diffraction, 101), a region that is characteristic of amorphous cellulose.

The most obvious diffraction peak (002) of the cellulose crystal was near 22° 2θ, whereas two small diffraction peaks (040) occurred near 29° 2θ and 34° 2θ. The diffraction profile changed minimally for the ultrasonic wheat straw pulp, possibly caused by a new diffraction peak at 27° 2θ that made the cellulose crystal change. The traditional chemical and ultrasonic wheat straw pulp showed 32.0% and 35.4% crystallinity, respectively. Thus, after ultrasonic treatment, the crystallinity of wheat straw had an obvious improvement; water molecules penetrated to the cellulose on the surfaces of the crystalline and amorphous areas.

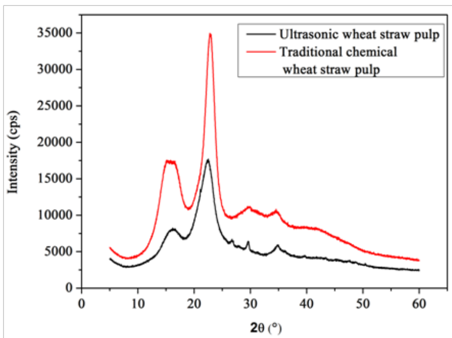

Fig. 1: XRD patterns of ultrasonic wheat straw pulp and traditional chemical wheat straw pulp

The result of acoustic cavitation makes the cellulose chain of the non crystalline region and the region with crystalline defects quickly break off, and the degree of freedom increases, so when dry again, the degree of crystallinity increase. Due to the limited impact force generated by the cavitation bubble collapse, the impact on the crystal surface was not large. Specifically, the crystallization of the intact crystal was not affected, so the degree of crystallinity increased rapidly.

The maximum radius of the cavitation bubble was much larger than the size of the crystal region. Previously, the cavitation bubbles were not circular; the near side was flat crystal. Therefore, the collapse of a cavitation bubble fired at the crystal liquid on the surface, initially its rate of power increasing, and then decreasing. These changes were conducive to the crystallization of cellulose molecules, to the movement of the crystal's surface, to crystal growth, and to the rise is crystallization degree. Thus, crystal size subsequently increased slowly. Therefore, the subsequent addition of additives in the slurry in the fiber penetration will have an impact.

Effect of the CPAM content on the morphology of fibers

Fig. 2 shows the morphology of ultrasonic wheat straw pulp fibers with various additive contents.

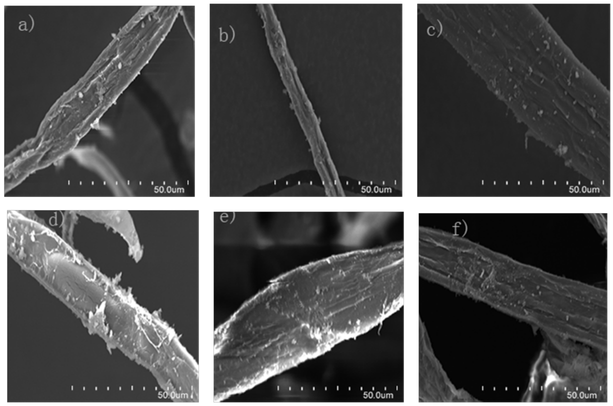

Fig. 2: SEM images of the fiber with various CPAM contents

When the CPAM content was low (0 and 0.2%, based on oven-dried pulp), it had few fiber additives; the same was true at 0.4% CPAM content (Fig. 1c). As the additive content increased further to 0.6% and 0.8% (Fig. 1d, e), the pulp fibers appeared to have amorphous materials on their surface. The cationic CPAM, easily adsorbed on the fiber, we can see that the ultrasonic added amount of wheat straw pulp when CPAM is 0.6% adsorbed on the fiber had the best effect.

Zeta potential

Zeta potential is the value of the surface charge of the fibers. The results of this study are shown in Fig. 3.

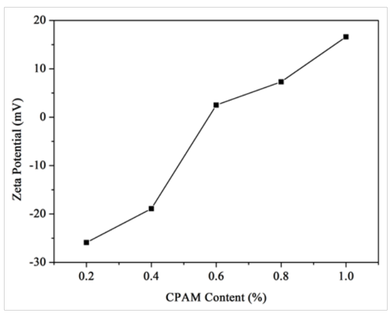

Fig. 3: The effect of CPAM content on the zeta potential of ultrasonic wheat straw pulp samples.

By increasing the additive content in the pulps, the negative charge density on the surface of the fiber increased markedly. When the additive content was 0.2%, the zeta potential was -25.9 mV. When the additive content was 1.0%, the zeta potential increased to +16.6 mV, an increment of nearly 164%. Positively charged AKD droplets adsorbed onto the negatively charged fiber via electrostatic attraction. For this reason, the fiber with stronger negative charge had higher AKD adsorption capacity (Lindström and Glad-Nordmark 2007).

Degree of sizing

As shown in Fig. 4, when the amount of AKD was 0.25%, with increasing the amount of CPAM, the paper measured the contact angle, we can see that the hydrophobicity of the paper at first increase and then decrease, indicating that the sizing performance of CPAM addition on the AKD there is a certain effect, when added the amount of CPAM in the 0-0.6%, can be seen from figure ABCD contact angle increased, the hydrophobicity of strong, indicating that the adsorption of high AKD, good sizing effect so that the water resistance of the paper is good, but with the added amount of CPAM added, when increased to 0.8% and greater than 0.8%, the contact angle small, hydrophobic weak, so the amount of the concentration of CPAM under the condition of AKD sizing performance of adverse effects, therefore, from the perspective of water resistance, the optimal dosage of CPAM is 0.6%.

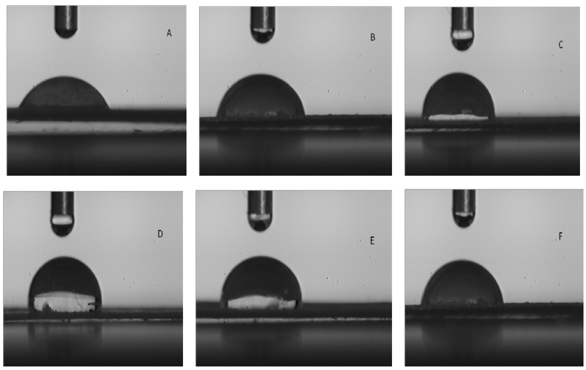

Fig. 4: Effect of different CPAM contents of the contact angle on the paper sizing efficiency.

Effect on properties of paper

As shown in Fig. 5, when the CPAM content is 0.6%, Zeta potential is most close to the isoelectric point, and the sizing degree reached the highest, but the tensile index began to decrease so the results revealed that to use the ultrasonic wheat straw pulp only may has no obvious effect on improving the properties of paper, but can increase the sizing degree.

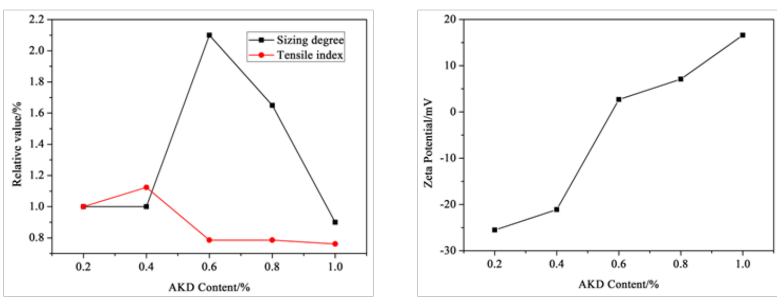

Fig.5: Relative value and Zeta potential of different AKD content.

In order to solve this problem, it may be a good choice to add some softwood or hardwood pulp to improve paper properties. Therefore, through this study, we have successfully found that ultrasonic wheat straw pulp has unique morphology and structural characteristics, and explored the Zeta potential sizing and degree of sizing during papermaking are greatly affected by the addition of CPAM, It is a great help to the application of ultrasonic wheat straw pulp and the amount of additive used in papermaking process..

CONCLUSIONS

1. The crystallinity of ultrasonic wheat straw pulp increased compared with the traditional chemical wheat straw pulp.
2. Scanning election microscope images revealed that the presence of CPAM in the pulp changed the morphology of the fiber efficient. When the CPAM content increased to 0.6%, the surface of the fiber was almost completely covered with amorphous material.
3. As the CPAM content increased from 0.2% to 0.8%, the zeta potential negative charge density of the fiber increased by more than 133.6%. When the amount of CPAM was 0.6% and the Zeta potential was 2.7mV, the effect of AKD was the best.
4. When the CPAM content increased, the absolute value of the negative charge on the surface of the pulp fibers increased rapidly. CPAM had a great effect on changing the negative charge on the surface of the ultrasonic wheat straw pulp fibers, which have a great effect on the sizing performance of AKD.
5. As a new kind of pulp, ultrasonic wheat straw pulp are superior to other kinds of pulp in pulping process and conditions, but only the use of ultrasonic wheat straw pulp made high quality paper still exist some problems, so the research in the future can be used with proper copying with other pulp or further application of the wet end.

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