# Application of Amphoteric Polyacrylamide Solely or with the Combination of Cationic Starch for Paper Strength Improvement

Peipei Wang,[a] Yangyang Zhu,[a,b] Xiaoyan Wang,[a] Xinyu Zhang,[a] Wenyuan Zhu,[a] Chunli Yao,[c] and Junlong Song [a,*]

Water-soluble amphoteric polyacrylamide (AmPAM) has been widely used in papermaking as one of the agents for the improvement of dry strength. In this investigation, AmPAM was used, solely or with the combination of cationic starch (CS), for the strength improvement of paper sheets made from kraft hardwood fiber (KHW) and recycled old corrugated container (OCC) fiber. The results showed that AmPAM achieved better performance than CS as the dry strength additive of paper on the condition of the same dosage, especially for secondary fibers. AmPAM improved the breaking length of paper sheets made from virgin KHW by 25%, while by 80% for OCC, when at the dosage of 0.5% (wt% to mass of oven dried pulp). When AmPAM was applied with the combination of CS, a negative synergism was observed. Besides strength improvement, there were many additional benefits obtained from adding AmPAM, especially in the absence of cationic starch, *e.g.* decreased slurry conductivity, decreased beating degree, and increased retention. In this aspect, AmPAM is an efficient, multi-beneficial dry strength agent for the papermaking process, especially for secondary fibers.

*Keywords: Amphoteric polyacrylamide; Dry strength; Secondary fiber; Conductivity; Retention*

*Contact information: a: Jiangsu Co-Innovation Center for Efficient Processing and Utilization of Forest Resources, Nanjing Forestry University, Nanjing, Jiangsu, 210037 P.R. China; b: China Light Industry Wuhan Design and Engineering Co. Ltd, Wuhan, Hubei, 430060 P.R. China; c: College of Material Science and Technology, Beijing Forestry University, Beijing, 100083 P.R. China;*
** Corresponding author: junlong.song@njfu.edu.cn*

## INTRODUCTION

The consumption of secondary fiber in the paper industry has greatly exceeded that of chemical pulp or mechanical pulp recently (Göttsching and Pakarinen 2000; Pöyry 2011). In recent years, secondary fiber has composed more than two thirds of the fiber resources for China's paper industry (China-TAPPI 2017).

The bonding ability of secondary fiber decreases as recycle time increases due to the cutting and wearing of fibers subjected during beating or refining, and the hornification that occurs during paper drying (Scallan and Tigerström 1992). When the pulp has been recycled five times, the solids content contains more than 30 to 35% irreversible hornification, and the fiber strength drops 70 to 90% (Nazhad 2005). Strength is an important indicator when evaluating the quality of paper. Therefore, it is necessary to modify secondary fibers for improved strength.

The strength of paper can be improved by increasing the interaction between fibers *via* strength additives. Most studies use cationic starch (CS) due to its positive effect and low price (Formento *et al.* 1994). CS is adsorbed on fibers by electrostatic forces and enhances the connection between fibers, which are negatively charged (Pettersson *et al.* 2006). In addition, CS forms hydrogen bonds with the fibers (Pettersson *et al.* 2006). Additionally, the role of carboxymethyl cellulose (Blomstedt *et al.* 2007), nanofibers (Campano *et al.* 2018), polyampholytes (Song *et al.* 2006, 2013; Zhu *et al.* 2016), and novel biological method (Kumar *et al.* 2018) for improved paper strength have been studied.

Amphoteric polyacrylamide (AmPAM) has been widely used in the wet-end of the papermaking process as a strength additive because of its unique features. AmPAM is a typical polyampholyte, carrying both basic and acid groups along the molecular chain (Dobrynin *et al.* 2004). Basic and acid groups dissociate in an aqueous solution. Consequently, the positively charged groups of AmPAM can anchor on anionic fibers, while the negatively charged groups can interact with the cationic groups from themselves or from other substances in the white water system (Song *et al.* 2010). With this unique feature, AmPAM can interact with fibers without interference from other cations (Song *et al.* 2010). Therefore, AmPAM has been used as a dry strength agent in the paper industry and other fields (Song *et al.* 2006; Silva *et al.* 2009; Song *et al.* 2010; Zhu *et al.* 2015, 2016; Dai *et al.* 2017; Qi *et al.* 2017; Shaikh *et al.* 2017).

The structures of AmPAM, *e.g.*, molecular weight (MW), charge density, and type of ionic monomer used, have significant impacts on its performance. Sezaki *et al.* (2006a,b) synthesized a series of AmPAMs with various charge densities but with the same charge ratio and similar MW (~3000 kD) and thoroughly investigated their colloidal behaviors thoroughly. When AmPAMs were added to the pulp slurry for dry strength improvement, it was found that the best dry strength of the paper sheets was achieved by AmPAMs with a moderate charge density (Song *et al.* 2006). The mechanism of how AmPAMs interact with fiber and the conformation of AmPAM layer adsorbed on the fiber surface were unveiled by a quartz crystal microbalance with dissipation monitoring (Song *et al.* 2010). Higher MW did not necessarily improve the paper tensile strength (Abdelmouleh *et al.* 2002). In our previous study, it was found that the optimum MW for strength improvement was around 350 kD (Zhu *et al.* 2016).

In this paper, the dry strength improvement performance of AmPAM and CS, which is another widely used but much cheaper dry strength agent in the paper industry, was compared. The possibility of application of both agents together was also explored. Some other tests associated with the application of AmPAM, *e.g.*, conductivity of the system, retention, and beating degree of fiber, were also assessed.

## EXPERIMENTAL

### Materials

Bleached kraft hard wood (KHW) fibers were provided by Asia Symbol (Shandong, China). Recycled OCC fiber was obtained from Shanying Paper Co. (Anhui, China). A commercial cationic starch (CS) was purchased from Zhucheng Xinmao Corn Starch Co. (Shandong, China). Prior to application, the gelatinization of CS was conducted as follows: CS (2 wt%) was dispersed in water initially, and then heated to 95 °C and kept at this temperature for 15 min; continually stirring was maintained during the process. After cooling, the aqueous CS solution was diluted to a concentration of 1 wt %.

An AmPAM sample with MW of around 350 kD was synthesized in the laboratory as described by Zhu *et al.* (2016).

All other common chemicals were ordered from Nanjing Chemical Reagent Co., Ltd (Nanjing, China). All chemicals were used as received, without further purification.

### Handsheet Preparation and Performance tests

Prior to handsheet preparation, bleached KHW was beaten with a laboratory Hollander beater (TD6-23 Valley Beater, XianyangTongda Light-Industry Equipment Co., Ltd. Xianyang, China) to a beating degree of 35°SR (GB/T 3332-1982). Whereas for the recycled OCC fiber, the pulp was used as received and the beating degree was measured to be 15° SR. During handsheet preparation, a 1000 mL of slurry (with 0.2% oven-dried fiber) was blended with AmPAM, CS or the combination solution and stirred for 5 min. Handsheets were prepared in an automatic rapid Köthen Sheet Machine Mold (Frank-PTI, Birkenau, Germany) with a basis weight of 68 $g/m^2$ for virgin KHW while it was 130 $g/m^2$ for recycled OCC fiber. The wet handsheets were dried for 15 min.

The breaking length using standard GB/T 12914 for handsheets was measured on a tensile machine (Qingtong Instrumental Co., Ltd. Hangzhou, China). Before measurements were taken, the handsheets were stored at 23 °C and 50% humidity for more than 48 h. The handsheets were cut into pieces with a width of 15 mm and length of more than 150 mm. The pulling force at tensile failure of the paper sheet was recorded to calculate the breaking length.

### Drainage and Retention

The drainage properties of the pulp suspension were measured with a DDA Apparatus (Dynamic Drainage Analyzer, AB AkribiKemikonsulter, Sweden). The pulp was diluted to a final consistency of 2 g/L. Then, 10 mL of NaCl solution (0.01 mol/L) was added and stirred for 10 min at 500 rpm. A known amount of AmPAM was then added into the suspension, and mixed for another 15 min. Finally, the stirring stopped while the drainage valve was simultaneously opened, and the drainage time was recorded.

### Ions Removal Performance of AmPAM

The pulp suspension with a consistency of 2% was deliberated with a laboratory Valley Beater (TD6-23, Xianyang Tongda Light-Industry Equipment Co., Ltd. Xianyang, China). NaCl solutions were added into the system to adjust the medium conductivity to 500 or 5000 μS/cm to mimic the wet-end system in low and high ions, respectively. A known amount of AmPAM was added into the system and the conductivity was recorded again. The ions removal performance of AmPAM was evaluated by the conductivity reduction of the pulp slurry.

## RESULTS AND DISCUSSION

### Comparison of the Dry Strength Performance of AmPAM with that of Cationic Starch for Virgin Hardwood Pulp and Recycled OCC Pulp

The breaking length is used as an indicator of the dry strength of paper sheets added with AmPAM and/or CS. AmPAM and CS were employed to improve the dry strength of the paper sheets made from virgin KHW or recycled OCC pulp. The breaking length of the paper sheets made of virgin KHW and recycled OCC fiber was plotted as a function of AmPAM and CS dosage in Fig. 1.

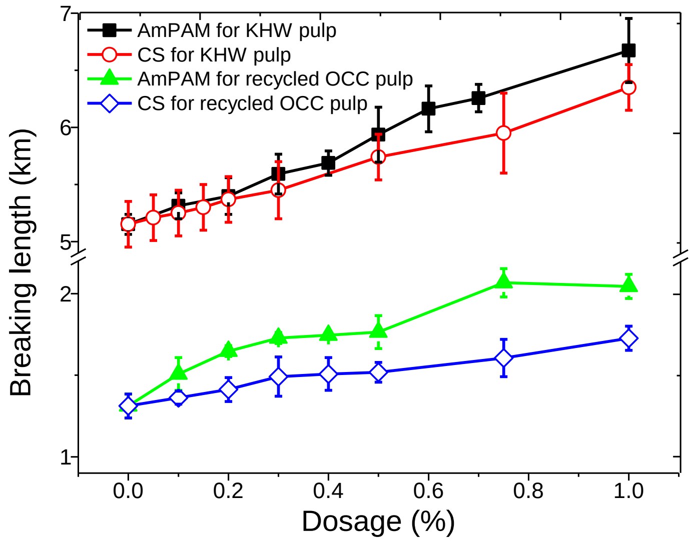


**Fig. 1.** Comparison of the breaking length of AmPAM and CS samples for KHW and recycled OCC pulp

Figure 1 shows that the breaking length of paper sheets increased with the dosage of additives. Either AmPAM or CS created inter-fiber bonds, and therefore, with the dosage increment, more bonds were formed, reflecting in a higher breaking length. This was consistent with the trends reported in the literature (Hubbe *et al.* 2007a; Hamzeh *et al.* 2013). However, there were some differences between virgin KHW and recycled OCC pulp, and between AmPAM and CS.

Comparing the dry strength performance of AmPAM with that of CS, the former improved the breaking length of the paper sheet greater than that of CS. AmPAM improved the breaking length of virgin KHW by 25% at a dosage of 1%, while that value for CS was only 20% at the same dosage. AmPAM is more soluble than CS in water. Its molecular chain is more extended, and therefore, more $–NH_2$ groups that are extended outward can connect to the –OH group on fibers to form hydrogen bonds. There are both anions and cations on the AmPAM chain, and the anions can be connected to the fibers by other cations in the pulp to enhance the binding force of the paper. At the same time, cations can form hydrogen bonds directly with the fibers.

Additives worked more efficiently for recycled fibers than virgin KHW. Compared with the control, AmPAM and CS improved the breaking length of the paper sheets made of recycled fiber by 80% and 40%, respectively. The difference can be explained by the difference in surface chemistry between virgin and recycled fibers. The surface of the virgin fiber is smooth, fibrillated, and soft; thus enough hydrogen bonding can be formed by themselves without the aid of additives. On the contrary, there are many changes taken place on the surface of recycled OCC fiber, such as hornification during paper sheet drying, reduction in the external surface area, and reduced flexibility, leading to a decrease in fiber binding force (Hubbe *et al.* 2007b). Therefore, the additives are more effective when used on low quality pulp. However, it seemed the effect was saturated when the dosage of AmPAM for recycled OCC pulp was above 0.75%, reflecting in a leveling-off effect in the breaking length at high AmPAM dosages.

## Application of AmPAM Combined with CS

In paper mills, both CS and AmPAM are common additives used as dry strength and retention agents. CS can improve both retention and strength, and so does AmPAM. To evaluate whether there was a synergic effect when both additives were used in the wet-end system in papermaking, the strength performance of the paper handsheets (expressed as breaking length) made from recycled OCC pulp was plotted against the additive dosage (fixed 1% CS and varied AmPAM dosage) and reported in Fig. 2(a). With the dosage of AmPAM increasing from 0 to 0.5%, the breaking length of the paper handsheets increased slightly from 1.72 to 1.81 km. The hollow symbols presented in the chart were the expected values of both additives used separately, *e.g.* the expected breaking length of paper sheets produced at the condition of 1% CS and 0.5% AmPAM was 2.17 km, representing the total contributions of recycled OCC pulp without a strength agent (1.31 km), 1% CS (0.41 km), and 0.5% AmPAM (0.45 km). It is obvious that the practical performance was much worse than the expected performance. This suggests that there was a negative synergic effect when both AmPAM and CS agents were used together.

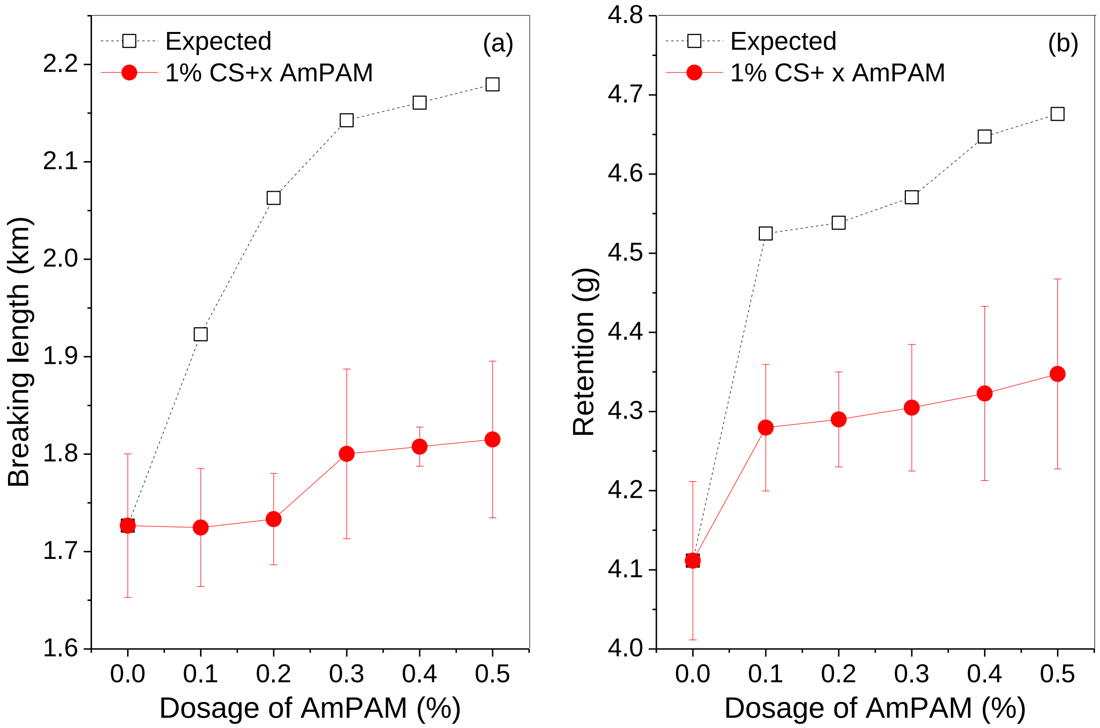


**Fig. 2.** (a) Breaking length and (b) Retention performance of AmPAM used with the combination of 1% CS

In the same manner, the retention performance of AmPAM used with the combination of 1% CS is reported in Fig. 2(b). The retention performance was expressed by the retained paper sheets weight after additive addition when the initial fiber weight was 5 g. The retention exhibited a sharp jump from 4.12 to 4.28 g when the dosage of AmPAM increased from 0 to 0.1%. After that dosage, the retention increased steadily from 4.28 to 4.35 g. The similar negative synergic effect was observed in breaking length that occurred in the practical retention performance test when both agents were used together and was worse than the expected values.

AmPAM bears both basic and acid groups and its net charge is close to neutral. It is well known that pulp fibers carry some negative charges, while CS carries some positive charges. AmPAM can be attracted by both fiber and CS. When AmPAM was applied in combination with CS, the negatively charge groups of AmPAM would interact with the positively charged CS. Hence, AmPAM lost its capacity to form a 3D network to link fibers together, which contributes much to the superior strength improving performance of amphoteric additives (Song *et al.* 2006). These may be the reasons why there was negative synergism observed when both AmPAM and CS were applied in the wet-end system.

However, the effect was investigated only when both agents were used together. The influence of AmPAM dosage on the breaking length and retention when they were used sequentially is an issue that needs to be investigated further in the future.

## Additional Benefits Obtained by the Application of AmPAM

Water drainage is a parameter of energy consumption in the pressing and drying process. The beating of pulp is a common mechanical method to improve the strength of paper. However, drainage becomes slower during the course of refining. In Fig. 3(a), the beating degree, which is an indication of the slow drainage, decreased with an increasing dosage of additives. Compared to the control, the beating degree decreased 1 to 4°SR after AmPAM addition. This means that the additives like CS and AmPAM can modify drainage in the papermaking process and improve the strength of paper. This may be due to the adsorption of AmPAM and fine fibers, which leads to a decrease in the degree of dispersion, and a decrease in the degree of beating (Lu *et al.* 2010).

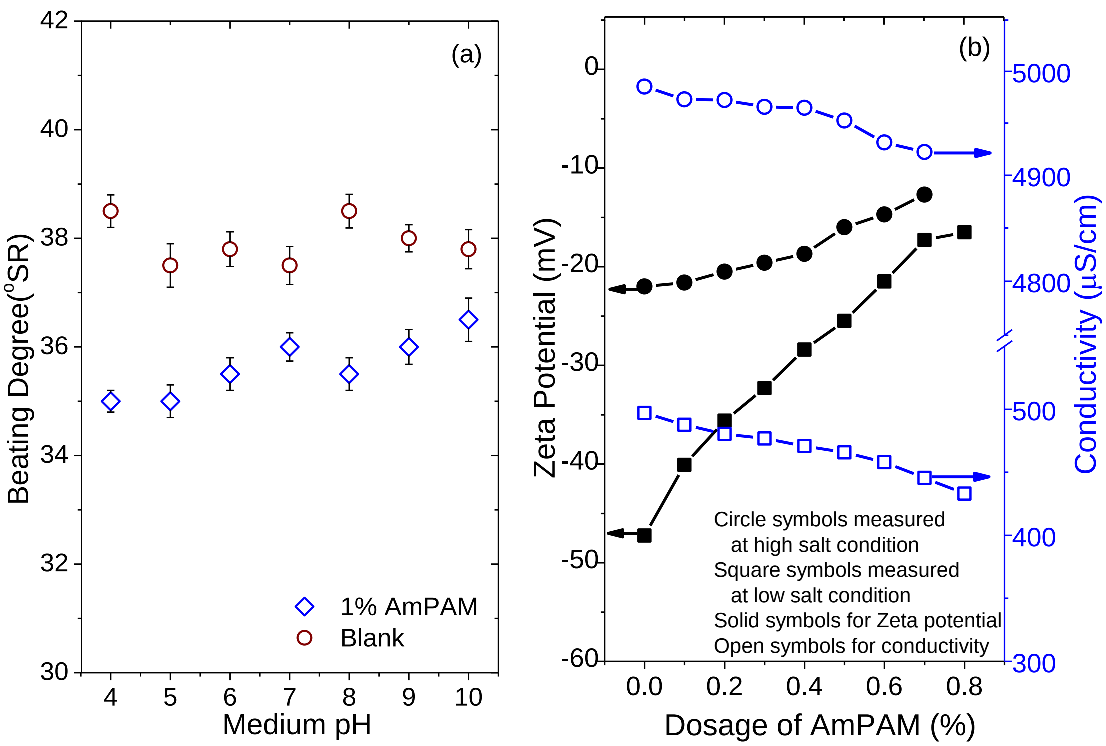


**Fig. 3**. (a) Beating degree of original pulp and pulp with 1% AmPAM and (b) Change in zeta potential and conductivity of fiber in pulp slurry

Figure 3(b) shows the changes in zeta potential of virgin fibers and conductivity of the 1% slurry with the AmPAM dosage at low and high salt conditions. Figure 3 shows that zeta potential decreased with increasing dosage of AmPAM, due to AmPAM being adsorbed onto fiber surface. Charge density of fiber decreased, leading to a zeta potential decrease. Unlike other additives, the zeta potential of fiber didn’t reverse to positive when AmPAM was used. Even at a dosage of 3%, the zeta potential of fiber was close to -10 mV. This is the reason why the strength of the papersheets increased with AmPAM dosage monotonously.

The capacity of ion catching of AmPAMwas exhibited in the right axis of Fig. 3(b). The proper approach to assess the ion catching capacity of AmPAM is to use white water from the mill process. Here, white water was mimicked by the addition of NaCl to the desired conductivity, 500 and 5000 μS/cm, respectively for low and high salt conditions. The conductivity dropped linearly with the dosage of AmPAM. Roughly, the conductivity of the system can be reduced by 80 μS/cm when 1% AmPAM was used. This ion removal effect caused by polyampholyte addition was also observed by Ayoub *et al*. (2013) in the case of polyelectrolyte complexes. The cited study even found that the ion removal by polyampholytes was more efficient for monovalent ions than divalent ions. The ion removal was attributed to replacement of intra-polyelectrolyte charge group associations with monomeric ion-polyelectrolyte ion associations as the ionic strength was increased (Ayoub *et al*. 2013). In this investigation, the cationic groups of AmPAM can bind to fibers, while the anionic groups on AmPAM can adsorb ions (mainly positive) in the wet-end system. This shows that AmPAM can remove some ions out of the wet-end system due to its balanced structure, and can be beneficial to void ion accumulation in the closed white water system.

## CONCLUSIONS

1. As a paper dry-strength additive, AmPAM was more effective than CS when used solely, especially for recycled fiber.
2. A negative synergism was observed when AmPAM was applied in combination with CS in the wet-end system on the conditions tested in the investigation.
3. Besides dry-strength improvement of the paper sheets, many benefits in drainage, retention, and ion removal can be obtained by the AmPAM application.

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