IMPROVING PAPER STRENGTH BY GELATION OF NATIVE STARCH AND BORAX IN THE PRESENCE OF FIBERS

Jie Shen, Xiaofan Zhou,* Weibing Wu, and Yuqin Ma

This paper puts forward a novel non-ionic augmentation system, namely, gelation of native starch in the presence of borax and papermaking fibers. Native starch was blended with high concentration pulp and auxiliary agents. After pasting, the starch gel adhered onto fiber surfaces. However, an excess dosage of agents led to a rigid structure and poor gel strength. Starch became gelatinized and then cross-linked by borax and cured as an adhesive layer through the process of pressing and drying under a high temperature. This provided close and uniform contact between starch and fibers. As a result, the strength of the paper was increased after forming.

Keywords: Native starch; Adjuvant; Gel; Strengthening

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INTRODUCTION

Various hydrophilic polyelectrolytes, including starch products, are being used by papermakers to promote inter-fiber bonding and increase paper's dry strength (Hubbe 2006). Starch has been extensively studied because it is an inexpensive raw material in many industrial processes, where it is used mainly as a gelling, thickening, and forming agent.

The most common form of starch used in the industry is as a gelatinised dispersion, which is then mixed with other components in order to obtain a final product (Ortega-Ojeda *et al*. 2004). For most applications, the granules are cooked to the point of pasting by thermal means and processed in solution form (Patel *et al*. 2010). The strength of gels may be affected by subtle differences in starch structure that influence retrogradation, but which have only limited effects on starch pasting properties (Blazek and Copeland 2009).

Two kinds of well-known strengthening mechanisms are as follows: (1) Hydrogen bonding between fibers and electrostatic adsorption are the primary causes of dry strength. More hydrogen bonding points can provide stronger bonding strength. Therefore, dry-strengthening agents can increase the hydrogen bonding force between fibers. (2) In addition, dry strengthening agents containing anion radicals can form coordination bonds with the negative charge of fibers through agents like Al^{3+} (Stratton and Colson 1993).

Stratton and Colson (1993) pointed out that the number of polyelectrolytes on the fiber surface is not enough to form a layer of polymer film between fibers, although polyelectrolytes do improve combination points of fibers. If polyelectrolytes could form a layer of polymer film between fibers, then the combination between fibers would

improve greatly, as well as the strength of the paper. The idea is worth studying. However, strengthening agents currently in use cannot achieve this. Hopefully, that question will be resolved with this proposed method. The proposed method was essentially that native starch and fibers were mixed by a mechanical method. The mixture was pasting in high concentration for 15 minutes. Starch was then wrapped around fibers by adhesive force. The strength of the paper increased due to the film of starch and its redistribution in the process of pressing and drying.

Excess strengthening agent would influence the formation of paper and the balance of wet charge. In this study, a non-ionic strengthening agent (such as potato native starch) was chosen. Native starch formed a gel after a cross-linking agent was added. The gel could be in contact with fiber more closely. Starch dosage could be up to 20% without causing the aforementioned problems.

EXPERIMENTAL

Materials

Old newspaper and adjuvant sodium stearyl lactate (SSL) were supplied by Nanjing Golden Ginkgo Company. Potato starch was from Mongolia. The cross-linking agent (borax) was an analytical reagent.

Methods

Enhancement method

20 gram fibers were mixed with 20% of starch. Other agents and water were then added to adjust the pasting concentration. The mixture was processed by a PFI mill (ZQS_7 Machinery Plant, Shanxi University of Science and Technology) for 40 s. The compound was put in a digester and heated (95 °C to 100 °C) for 15 min. In the process of pasting, the mixture was rubbed to make starch and fibers contact one another sufficiently. When pasting was finished, the mixture was taken out of the digester for further analysis.

Preparation of the standard curve of dissolved starch ratio

The dissolved starch ratio was measured by iodine colorimetry. The specific procedures are found in the literature (Xu *et al*. 1998).

Strength measurement

Tensile breaking strength and bursting strength were tested according to the standard methods used in China (Shi and He 2010).

Images collection of sample

Photomicrographs of the samples were shot with fixed-point by Digital Video microscope under 100X enlargement.

RESULTS AND DISCUSSION

Determination of the Optimum Values of Parameters

Influence of starch dosage

The starch dosage here means the ratio of starch mass to pulp on an absolute dry basis. Starch dosage was changed (other conditions were temporarily selected according to a process of exploration) to analyze its effect on paper strength and the dissolution ratio of starch. The dissolution ratio here means the ratio of the starch dissolved in the water to the total starch amount. A higher dissolved ratio indicates that more starch was lost and less starch was available to be used. So, a lower dissolved ratio is preferred.

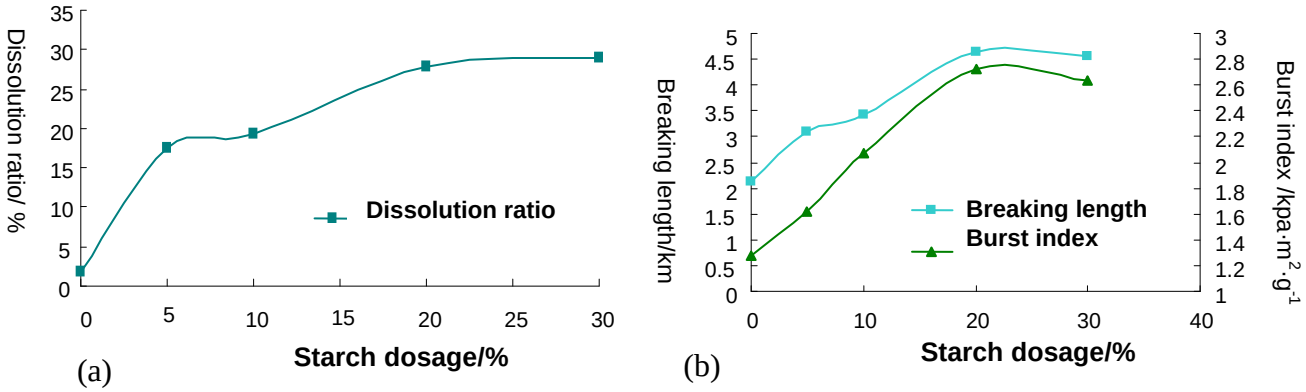


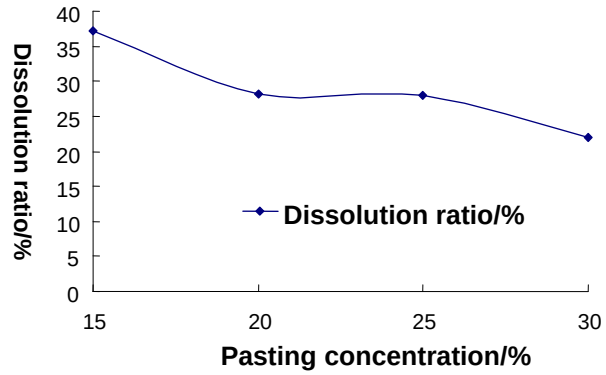
Fig. 1. Influence of starch dosage on (a) dissolution ratio of starch, (b) strength of paper (borax: 0.6%, pasting concentration: 25%, temperature: 95 to 100 °C)

As shown in Fig. 1a, the content of starch in the reclaimed pulp was very low, only about 1.9%. But when the dosage was 5%, the dissolution ratio increased to 17.5%. With the increasing dosage of starch, the dissolution ratio increased quickly at first, followed by a slower, steady rise. The higher the dosage of starch, the thicker the gel accumulated on the surface of fibers was, and there was more starch covering fiber surfaces. At the same time, bonding strength also became higher. As the starch was insoluble in water, the dissolution ratio of starch did not obviously increase. In this experiment, it was found that an excess dosage of starch required much more time to untwine the fibers, and the starch dissolved in water became greater. Thus, the dissolution ratio of starch would increase.

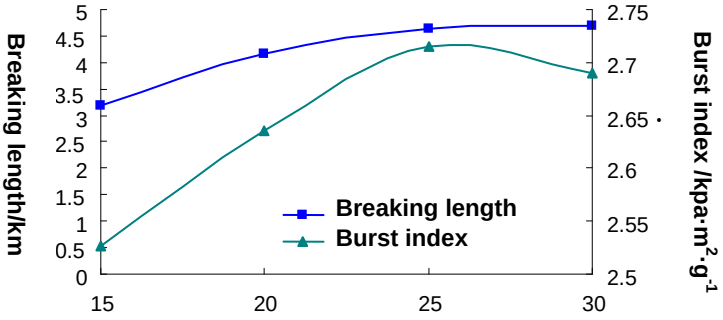
With the increasing dosage of starch, paper strength first increased and then decreased. The strength was maximized at 20% starch dosage, as Fig. 1(b) shows. Under that condition, breaking length and burst index increased by 90.95% and 112.50%, respectively. The mixture without uniform dispersion may result in non-uniform formation and low paper strength.

Influence of pasting concentration

Different pasting concentrations of starch would cause great differences in viscosity. According to Deng *et al.* (2005), when pasting concentration was 40% to 50%, the dissolution ratio of native starch was about 17%. Because of the restriction of treating equipment, pasting concentration could only reach 30% in this study.



(a)



(b)

Fig. 2. Influence of different pasting concentration on (a) dissolution ratio of starch, (b) strength of paper (borax: 0.6%, pasting concentration: 25%, temperature: 95 to 100 °C)

The dissolution ratio of starch dropped with increasing pasting concentration (Fig. 2(a)). With increasing pasting concentration, the stickiness of starch also increased. So, the adhesive force between starch and fibers was increased after pasting. As a result, the dissolution ratio was reduced. However, starch can be dissolved in water easily after pasting, so the dissolution ratio stayed at a high level even at 30% pasting concentration.

It was observed that there were trends of increasing the breaking length and burst index with increasing pasting concentration (Fig. 2(b)). When concentration reached 25%, the breaking length of paper with added starch increased by 90.95% compared to the blank sample. The burst index was improved by 112%. When the pasting concentration was 30%, the curve of breaking strength tended to be steady, but bursting strength decreased. If the pasting concentration was too high, absorbable moisture was reduced and starch could not be completely pasted. So, a pasting concentration of 25% was chosen.

Solubility Reducing of Starch after Being Disposed

The method evaluated in this paper was found to enhance the strength of paper dramatically. However, there were still problems, such as a high dissolution ratio, a heavy loading of the recirculated process water (whitewater), and high product cost. In order to solve these problems, methods for reducing the dissolution ratio of starch and improving the paper strength were put forward, as described below.

Influence of cross-linking agent borax on dissolution ratio of starch and strength of paper

A cross-linking agent can form chemical bonds between linear molecules. The mixture as a whole is thus formed into network structures. As a result, strength and elasticity increase. Starch formed a gel when it was pasting and then borax was added. The gel was insoluble in water and antiseptic. A certain amount of borax was able to increase the viscosity of starch. However, an excess dosage of borax led to a rigid gel structure and poor strength, and reduced its anti-shear ability further.

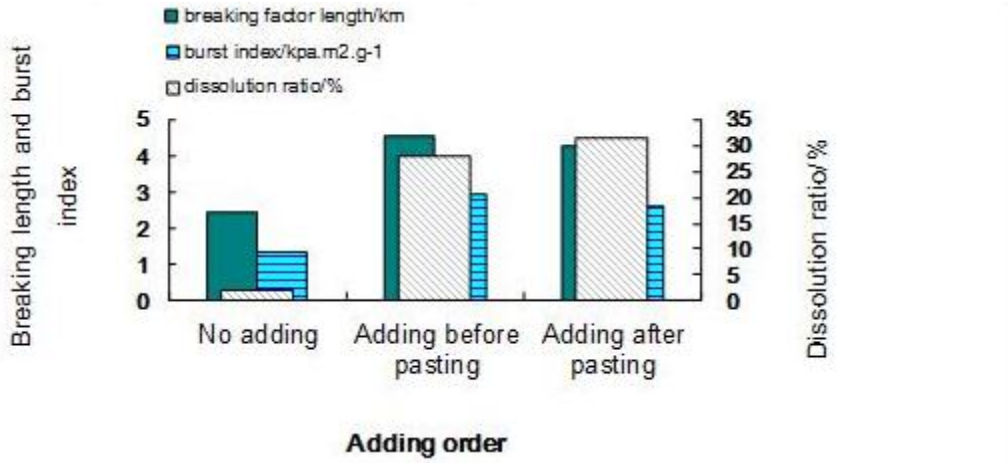
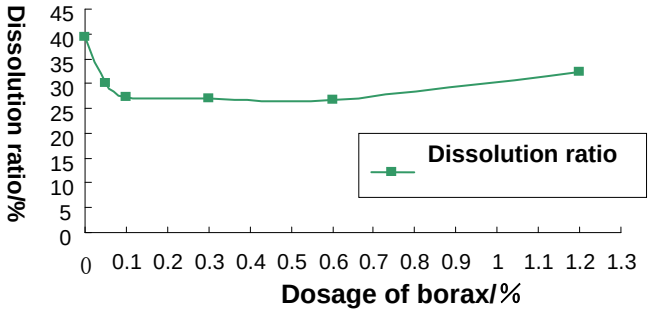


Fig. 3. Influence of the adding order of the cross-linking agent borax on strength and dissolution ratio (starch dosage: 20%, pasting concentration: 25%, borax dosage: 0.6%, concentration: 0.01 g/ml, temperature: 95 to 100 °C. The first blank sample was just added starch.)

As can be seen from Fig. 3, the dissolution ratio of starch and paper strength presented different trends for different orders of addition. Breaking length was increased by 90.95%, and burst index was increased by 122.92% when borax was added before pasting. However, breaking length only increased by 75.30% and burst index increased by 99.69% if borax was added after pasting. This may be because borax could not contact with starch fully at a high concentration. Therefore, adding borax before pasting was chosen for the subsequent experiments.

As shown in Fig. 4(a), with the increasing dosage of borax, the dissolution ratio of starch first decreased and then increased. It reached the lowest point at 0.6% borax dosage. This may have been caused by the excess dosage of borax making starch gel form a rigid structure, thus decreasing its strength. The anti-shear ability of starch gel also decreased. As a result, the amount of starch that was washed away increased.

It is apparent that borax could improve the strength of paper to some extent (Fig. 4(b)). However, when the dosage of borax was more than 1.2%, the strength slightly decreased. The reason was mentioned above. Accordingly, the optimal dosage of borax was judged to be 0.6%.



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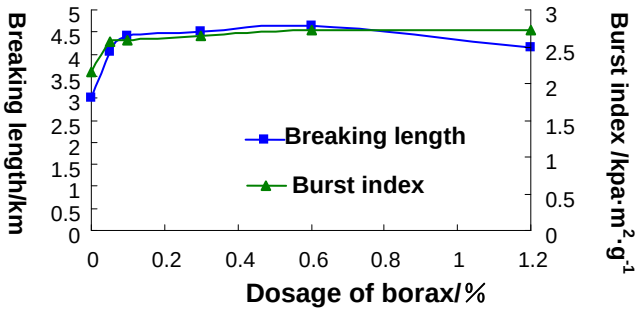
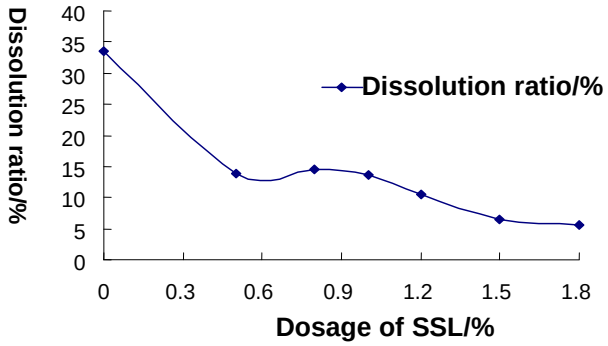


(b)

Fig. 4. Influence of different dosages of borax on (a) dissolution ratio of starch, (b) strength of paper (starch dosage: 20%, pasting concentration: 25%, temperature: 95 to 100 °C. The first blank sample was just added starch.)

Influence of SSL on dissolution ratio of starch and paper strength

According to the literature (Qian 2005), use of the agent SSL as a kind of emulsifier can result in the formation of an insoluble spiral complex with amylose of the starch and slow down the crystallization rate and aging rate of starch.



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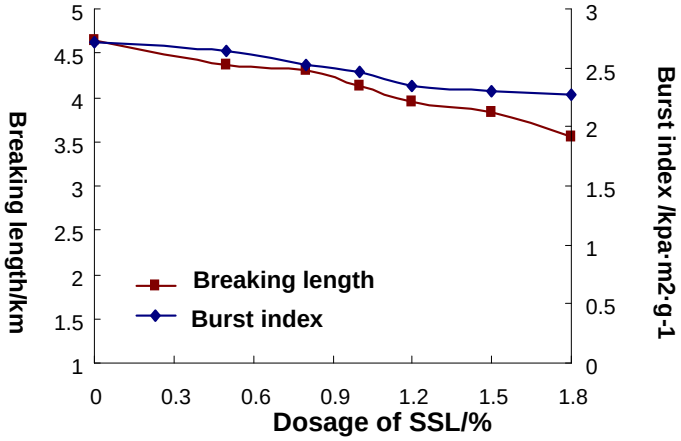

(b)

Fig. 5. Influence of different dosages of SSL on (a) dissolution ratio of starch, (b) strength of paper (borax dosage: 0.6%, starch dosage: 20%, pasting concentration: 25%, temperature: 95 to 100 °C. The first blank sample contained just borax.)

As shown in Fig. 5, with the borax dosage held constant, both the dissolution ratio of starch and paper strength dropped with an increasing dosage of SSL. The dissolution ratio decreased to 13.54% when SSL was 1.0%. As for strength, when the SSL dosage was 1.8%, breaking length still was increased by 46.50%, and the burst index increased by 77.34%. It could be concluded from the data that SSL played a significant role in water resistance. By using both borax and SSL it was possible to obtain both good strength and a low dissolution ratio.

The problem that the starch gel would adhere on the handsheet surface could be solved by adding adjuvant. Such addition also could solve problems of roller sticking and blanket sticking in practical production. 1.5% was chosen as the optimal dosage of SSL. Here, mainly the dissolving starch ratio was considered.

Optical Microscope Pictures of Samples

The mechanism of enhancement was analyzed with use of an optical microscope and compared with the adsorption mechanism of cationic starch. In order to make an overall analysis, images of pulp processed with different dosages of starch were collected. The samples were dyed with KI-I_2.

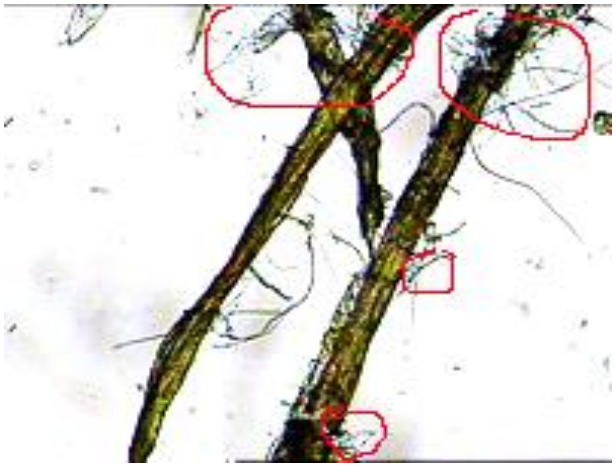

Fig. 6(a). 2% cationic starch absorbing on fibers

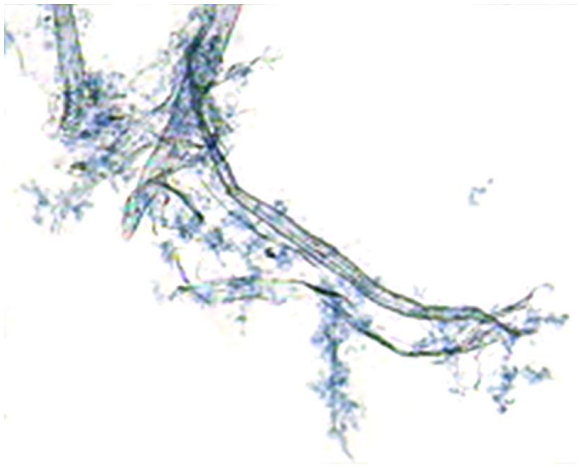

Fig. 6(b). Excess cationic starch absorbing on fibers

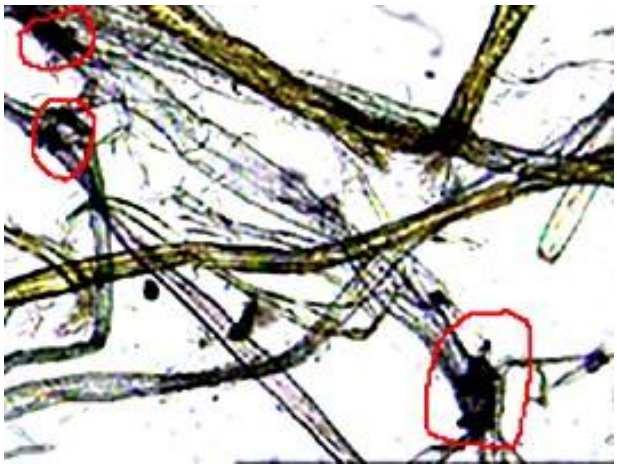

Fig. 6(c). 2% dosage of native starch

Fig. 6(d). 5% dosage of native starch

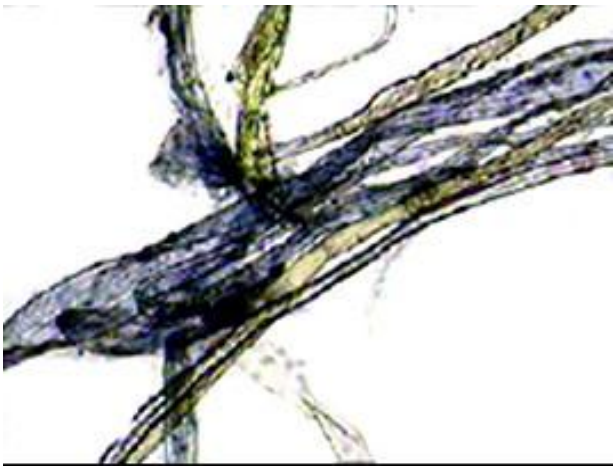

Fig. 6(e). 10% dosage of native starch

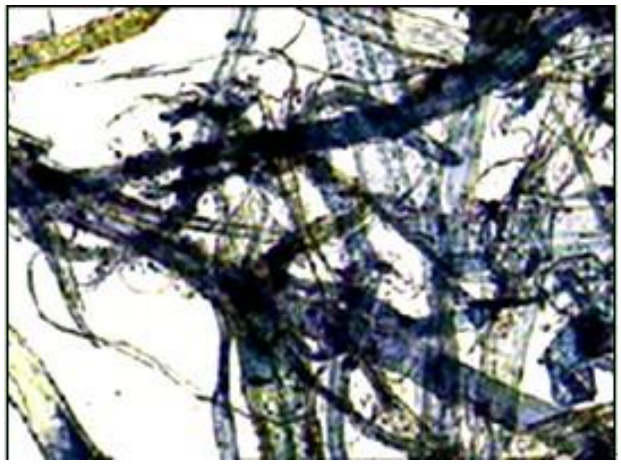

Fig. 6(f). 20% dosage of native starch

As Fig. 6(a) shows (light blue parts in red circles), very little cationic starch could adsorb on fibers' surfaces when 2% cationic starch was added to the pulp (0.5% concentration). After pasting, cationic starch with cationic charge would adsorb on the surfaces of fibers with negative charge (Wagberg and Bjorklund 1993). An excess dosage of cationic starch could make starch absorb on fibers in a greater quantity (Fig. 6(b)).

The method used in this paper was different from conventional enhanced methods, and its mechanism was different from the adsorption mechanism of cationic starch. In Fig. 6(c), it can be seen that native starch could not adhere on fiber surfaces uniformly when its dosage was 2%. It could only form a thin layer, and small adhering particles were present. When the dosage of native starch was increased to 5% (Fig. 6(d)), fibers in circle A could be wrapped uniformly by more starch. Blue-black hairy material in circle B was judged to be starch adhering on the cottony fiber surfaces. When the dosage of native starch was increased to 10% (Fig. 6(e)), after being dyed, fibers wrapped by starch became blue, and the others were yellow. Obviously, it could be predicted from the depth of dyeing that more native starch was wrapped on fiber surfaces, forming a thicker layer. Yellow fibers indicated that not all of the fibers could be wrapped by starch in the process. Continuing the increase in the dosage to 20%, more fibers were wrapped by starch, and the joining layer was much thicker (Fig. 6(f)).

According to the analysis above, native starch could form a gel with the help of other agents, and the gel could wrap the fiber surfaces. The coverage ratio increased with increasing starch dosage. The strength increased as well. When the mixture was in an aqueous solution, the gel on fiber surfaces was not easily dissolved in water. In the pressing and drying process, starch gel became cross-linked and contacted with fibers more closely and uniformly at a high temperature. Thus, the paper strength increased, as shown in Fig. 7. Because of the hydroxyl groups, the starch increased the connection strength and quantity between fibers after adhering on fiber surfaces. Thus, it has been demonstrated that the method evaluated in this study helped increase bond strength and quantity between fibers.

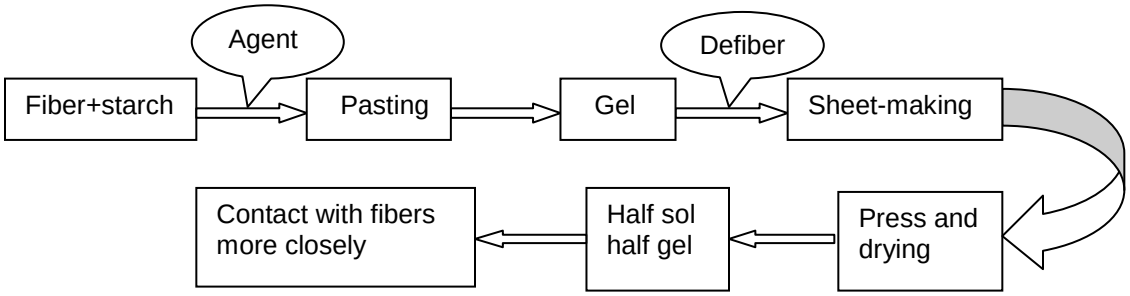

Fig. 7. The basic process

CONCLUSIONS

1. The strength of paper and the dissolution ratio of starch increased with an increasing dosage of potato native starch. However, an excess dosage worked against untwining of the fibers. Strength increased with increasing pasting concentration of starch, while the dissolution ratio dropped progressively. Starch worked against untwining of the fibers when the concentration was greater than 25%. At that time, strength decreased and dissolution ratio increased instead. It could be concluded that the optimal pasting concentration and starch dosage were 25% and 20%, respectively.
2. When borax dosage was increased, the dissolution ratio of starch dropped and strength of paper also rose. The best effect was achieved at 0.6% borax dosage. The effect on dissolution ratio of starch and strength of paper became negative when a higher borax dosage was added. It was better to add borax before pasting rather than after.
3. If sodium stearyl lactate (SSL) and borax were used jointly, then the dissolution ratio of starch would drop farther. However, a great negative impact on strength was observed if the SSL dosage was too great. Therefore, 1.5% SSL dosage was judged to be optimal.
4. The enhancing principle of the starch application method used in this work was not adsorption, but adhesion on fiber surfaces. In the pressing and drying process, gelatinized starch in a pseudo-plastic form was distributed more uniformly and wrapped more closely with fibers. It also increased paper strength.

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