

NOVEL STARCH SOLUTION PREPARED FROM THE STARCH IN NaOH/THIOUREA/UREA AQUEOUS SOLUTION AND ITS APPLICATION AS SURFACE SIZING AGENT

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Novel starch solutions were prepared by dissolving starch in NaOH/thiourea/ urea aqueous solution, and they were further used as a surface sizing agent at high solids content in papermaking to improve the surface strength of papers. Two methods were adopted to dissolve the starch. In method A dry starch granules were directly added into the prepared solution. In method B a starch slurry was mixed with the prepared solution. The results revealed that method B was more effective than method A to achieve a lower viscosity of the starch solution. Dissolving temperature played an important role in dissolution of the starch. The viscosity values decreased with a decrease in the temperature of sample preparation. The starch dissolved in 4 wt% NaOH – 3 wt% urea – 3 wt% thiourea aqueous solution at -10°C were optimized to do the further application experiments. This kind of starch solution had lower viscosity and reached better viscosity-temperature stability, the viscosity was stable over a broad range of temperatures, and it also can be stored for over one month under room temperature. The surface sized papers with them had outstanding surface strength. Moreover, the prepared starch solutions were investigated by infrared spectroscopic analysis and scanning electron microscope, respectively, showing the structure of the starch solution.

Keywords: Starch; NaOH/thiourea/urea aqueous solution; Surface sizing

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INTRODUCTION

After fibers and fillers, starch is the third most important raw material in the manufacture of paper. When starch is used as a dry-strength additive for paper, it either is added to the stock in the paper machine, or it is used as a surface sizing agent, in which case a starch solution is applied to the surface of the dried paper. The purpose of external application of starch solution onto dried paper or surface sizing is to provide resistance to penetration of liquids, to give better surface properties, and to improve certain physical properties of the paper sheet (Lee et al. 2002).

Through surface sizing both surface strength and internal strength are targeted at the expense of an over-dried paper prior to the sizing operation. A great deal of drying capacity is required to remove the last moisture bound into the sheet. There may be a possibility to reduce the drying capacity requirements by increasing the solids content of the starch size and decreasing the viscosity of the starch solution through modification (Lehtinen 2005). In our laboratory novel starch solutions were prepared by dissolving

starch granules in NaOH/thiourea/urea aqueous solution. This kind of starch solution achieved lower viscosity and reached better viscosity-temperature stability, increasing the solids content of starch size to 30%, thus reducing the drying capacity requirements.

The present research takes advantage of recent developments in cellulose dissolution techniques. Several new solvent systems have been developed to dissolve cellulose in recent years. In particular, Zhang et al. have developed a novel solvent for cellulose, namely a 7 wt% NaOH 12 wt% urea aqueous solution pre-cooled to minus 12 °C. It is particularly noteworthy that new solvent systems, such as aqueous NaOH/urea, NaOH/thiourea, and LiOH/urea aqueous solutions, have been used to dissolve cellulose at low temperature (Cai and Zhang 2006; Cai et al. 2007a; Ruan et al. 2004; Cai and Zhang 2005). These solvents are attractive because cellulose can be easily and quickly dissolved in them, producing stable cellulose solutions (Yan et al. 2007).

Since the starch polymer is chemically much like cellulose, the difference lies in the construction, which gives these two materials different properties. The difference is in the way glucose monomers are bonded together. The bonds between glucose units are called glycosidic bonds. In starch all glycosidic bonds are oriented in the same way, whereas in cellulose the orientation of two consecutive bonds is opposite. Combined with the character of the glycosidic bond, this is the reason for cellulose exists as a straight polymer chain, while starch is coiled. Cellulose forms fibers, which are partly crystalline; starch is totally amorphous and forms granules (Lehtinen 2005). Taking inspiration from cellulose dissolution techniques, a NaOH/thiourea/urea aqueous solution was used to dissolve starch.

Starch solutions have two main functional properties: viscosity and stability. A concentrated solution of starch has a propensity for retrogradation as it cools, which is seen as a rise in viscosity, as turbidity, or as a thickening of the solution. Retrogradation limits the application of starch in papermaking industry. In our laboratory a novel NaOH/thiourea/urea aqueous solution was adopted to dissolve starch at minus 10 °C. This type of starch solution does not need to be cooked and also has lower viscosity, better viscosity-temperature stability, and there is no retrogradation as it cools. It was used as surface sizing agent to improve the surface strength.

4wt % NaOH - 3 wt% urea - 3 wt% thiourea aqueous solution is inexpensive, and it has a low toxicity. According to MSDS descriptions, China MAC (Maximize Allowable Concentration) showed no limitation, whereas for LD50 there was no information, all indicating that NaOH/thiourea/urea has low toxicity. There is no chemical reagent volatile and evaporation during the process of the dissolution of starch at low temperature; therefore the gaseous environment would not be affected if mass production were implemented. The present research shows that the solvents constitute a stable system that is hard to recover.

EXPERIMENTAL

Materials

Surface sizing tapioca starch was supplied by SMS Company (Thailand). NaOH, thiourea, and urea were provided by NanJing Chemical Reagent Co. Ltd. Base papers

(60g/m²) with no internal or external sizing were provided by UPM-Kymmene (Changshu) Paper Industry Co., Ltd.

Different Dissolution Methods

Two different methods were used in this research for dissolution:

A: The NaOH/thiourea/urea aqueous solution was prepared initially at a certain proportion. E.g. 10% 6#A was made as follows: 4wt% NaOH – 3 wt% urea-3 wt% thiourea aqueous solution was prepared by mixing of NaOH, urea, thiourea, and distilled water (4:3:3:90 by weight), and then the mixture was cooled for 30 min at minus 10 °C. The starch granules were directly added into the solution and then stirred with a glass rod for 3 min. In order to mix up the starch granules with the NaOH/thiourea/urea aqueous solution adequately, the mixture was dispersed in the homogenizer at 1000r/min speed for 2 min.

B: The water used to make the aqueous solution was divided into two parts. One part of the water was used to prepare the NaOH/thiourea/urea aqueous solution, and the rest was used to prepare the starch slurry. E.g. 10% 6#B was made as follows: 4wt% NaOH – 3 wt% urea-3 wt% thiourea aqueous solution was prepared by mixing of NaOH, urea, thiourea, and distilled water (4:3:3:60 by weight), and then cooled for 30 min at minus 10 °C. Starch slurry was prepared by mixing of starch granules and distilled water(10:30 by weight) for 1 min. The final step is to mix the starch slurry with the prepared solution and then stir the mixture with a glass rod for 3 min.

Viscosity Measurement

The viscosity of starch was measured by RVDV-I+ viscometer from Brookfield.

Surface Sizing

Surface sizing was performed using a K-type coating method. The sizing weight was controlled by adjusting the power and speed in the sizing process. All sheets were dried on a standard drier set at 105 °C for three minutes and then stored in a conditioned environment (23°C and 50%RH) for 24h until further analysis.

Surface strength was measured according to standard ISO 3783 by AIC2-5E IGT tester.

FT-IR Analysis

FT-IR analysis was carried out with an IR-360 instrument from Thermo Nicolet. Samples were frozen in a refrigerator for 24 h and then placed into a Power dryer (R507, Heto) for 48 h before being observed by the infrared detector.

Microscopy of Starch Samples

Granule micrographs were obtained with a FEI QUANTA 200 Scanning Electron Microscope (SEM). The starch was sprinkled onto a double-backed adhesive carbon tab stuck to a circular aluminum stub. The stub with gold coated starch was then placed in the SEM chamber, which was evacuated before the electron beam was turned on. SEM images of each sample were taken at 400× magnification, 1500× magnification, 3000× magnification, and 10000× magnification.

RESULTS AND DISCUSSION

Influence of Different Methods on Viscosity

Viscosity is an important index for the characterization of starch properties. An important goal of our research was to achieve a lower viscosity of starch solution. The viscosity of starch in different NaOH/thiourea/urea solvent solutions is shown in Table 1, where A stands for using method A to get the 10% solid content starch solution at minus 10 °C, and B stands for using method B to get the 10% solid content starch solution at minus 10 °C). The results reveal that method B was more effective than method A at the same temperature and dissolution system. When using the same dissolution method and dissolution system, a lower temperature promotes starch dissolution. From Table 1, sample 6#B (the starch dissolved by method B in 4wt% NaOH – 3 wt% urea-3 wt% thiourea aqueous solution at -10°C) was optimal for use in the subsequent application experiments.

Table 1. Viscosity of Starch Solution at Room Temperature

	NaOH (%)	Urea (%)	Thiourea (%)	Water (%)	A Viscosity (mPa.s)	B Viscosity (mPa.s)
1#	8	6	6	80	76.3	25.2
2#	8	4	4	84	75.4	24.5
3#	8	2	2	88	66.7	23.2
4#	6	3	3	88	60.3	22.4
5#	6	2	2	90	50.4	21.6
6#	4	3	3	90	38.6	16.9
7#	4	2	2	92	43.6	38.7

Influence of Temperature on Viscosity

Figure 1 shows the viscosity of 10% solid content 6#B starch solutions prepared at different temperatures. The results reveal that, at high temperature from 0°C to 25°C, the viscosity of starch solution hardly changed and also reached higher viscosity compared with starch solution prepared in lower temperature.

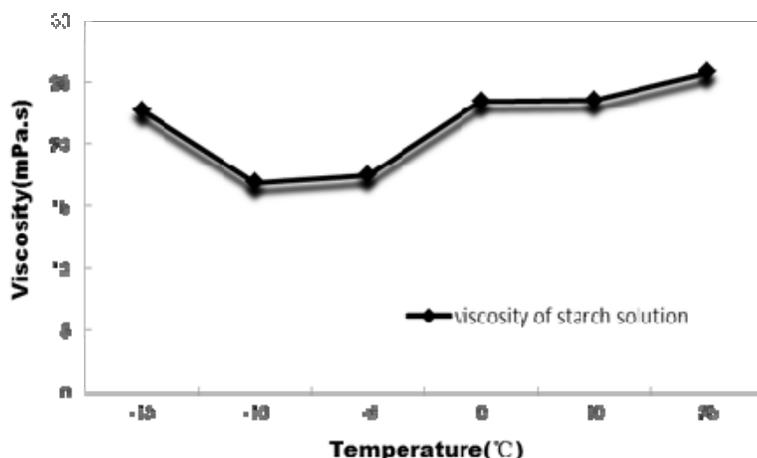


Fig. 1. Viscosity of 6#B starch solution prepared at different temperatures

By decreasing temperature from 0 °C to minus 10 °C, the viscosity of the starch solution became lower and lower, proving that the lower temperature was good for the starch dissolution. However, as the temperature went down to minus 15 °C, the viscosity became higher than at -10 °C, and there was some ice in the starch solution. The presence of ice crystals may be the reason why the viscosity of starch solution became higher. It follows that the starch solution had dissolved completely at minus 10 °C.

Comparison of Viscosity between Dissolved Starch Solution and Cooked Starch Solution at Different Temperature

Viscosity is an important technical parameter for surface sizing agents. Viscosity affects not only the sizing process, but also the amount of material transferred to the paper at the size press. In papermaking, surface sizing starch must to be cooked when it is used, the viscosity of starch changes a lot during the cooking process (the starch was added at room temperature, and the viscosity was monitored when the temperature was raised) and cooling process (the viscosity was monitored after cooking). But in our research, the 6#B can be used as a sizing agent directly after dissolving, no need of cooking, and the viscosity of 6#B was more stable even with changes in temperature. So we compare the viscosity of 6#B and surface sizing starch during cooking process and cooling process which are presented in Figs. 2 and 3 (Cooked starch is the surface sizing starch that is commonly used in papermaking mills). As shown in Fig. 2, during the cooking process the granules of cooked starch started to swell at 40 °C to 50°C, and after that the starch polymers started to dissolve. As temperature increases, the viscosity of cooked starch first increases, and then decreases. By contrast, the viscosity of 6#B starch solution decreases slowly as temperature increases, so the viscosity of 6#B is stable when it is heated.

Figure 3 shows that the cooked starch had a propensity for retrogradation as it cools, which was seen as a rise in viscosity. Retrogradation limits the applications of starch in the papermaking industry, e.g. by limiting the time of storage of cooked starch.

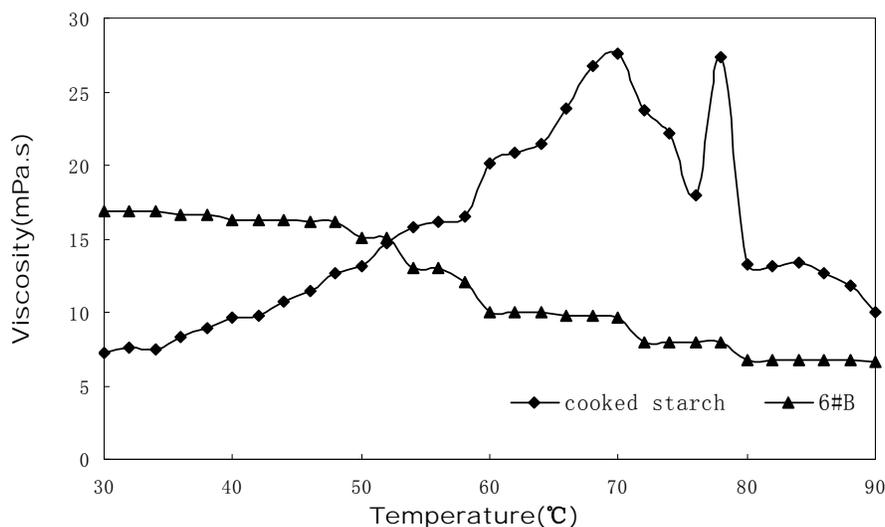


Fig. 2. Viscosity of cooked starch and 6#B starch solution at different temperatures

The viscosity of dissolved starch was almost the same when it cooled, so better viscosity-temperature stability of dissolved starch solution was achieved, and it also had the lower viscosity, which reveals that the dissolved starch solution can be widely used in a large range of temperature, and it also can be stored for over one month at room temperature, bringing more convenience for papermaking applications.

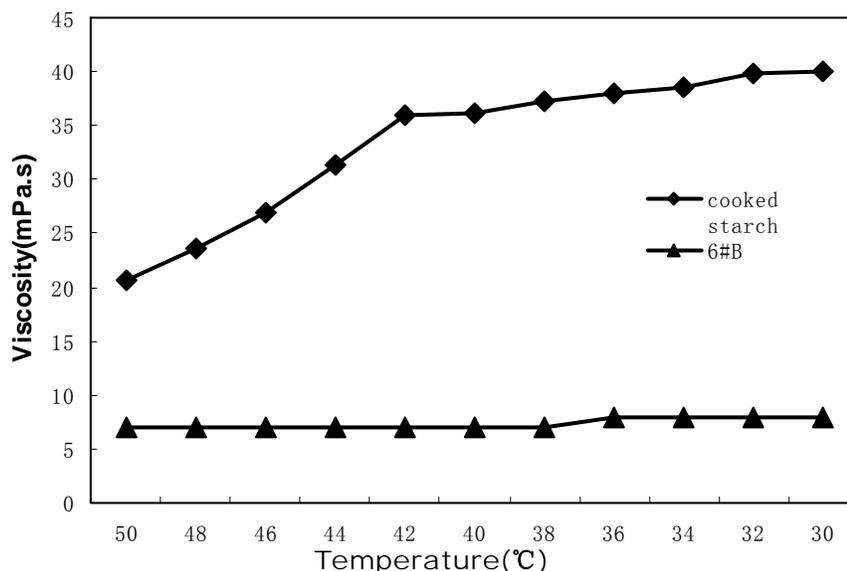


Fig. 3. Viscosity of cooked starch and 6#B starch solution as it cools

Influence of Different Starch Solutions on Surface Strength

The target of surface sized papers was to produce more stable paper with clear printing of fine characters and without a need for additional printing press washings due to linting. The linting tendency can be reduced by improving the surface strength of paper (Sang and Liu 2004). In our lab, the base papers were provided by UPM-Kymmene (Changshu) Paper Industry Co., Ltd. The IGT surface strength results were almost $0.7\text{m}\cdot\text{s}^{-1}$.

The surface strength was compared for the two kinds of surface sized papers at different size amounts, which were coated with 10% cooked starch and 10% 6#B. Table 2 shows that increasing the size amounts resulted in improved surface strength in both cases. When the papers were coated at the same size amount, the 6#B paper had higher surface strength.

The viscosity with high solids content of non-modified surface sizing starch was too high, and it was impossible to use for surface sizing. But the dissolved starch solution had good properties in surface sizing process at high solid content up to 30%. As shown in Table 3, the surface strength of base paper increased substantially after coated with 10%, 20%, and 30% of 6#B. Reducing the drying capacity requirements can be targeted by increasing the solids content of the dissolved starch size to 30%.

Table 2. IGT Surface Strength of Surface Sized Paper at Different Size Amount

Size amount (g/m ²)	IGT surface strength of surface sized paper with 10% cooked starch(m.s ⁻¹)	IGT surface strength of surface sized paper with 10% 6#B(m.s ⁻¹)
0.5	0.9	1.5
1.0	1.2	2.0
2.0	1.8	2.6
3.0	2.0	3.0

Table 3. IGT Surface Strength of Surface Sized Paper with 10%, 20%, and 30% of 6#B

The solid content of 6#B (%)	IGT surface strength of surface sized paper with 6#B(m.s ⁻¹)
10	2.6
20	2.9
30	3.2

FT-IR Analysis

Figure 4 shows FT-IR spectra of starch granules (a), 10% cooked starch (b), and 10% 6#B (c). Infrared spectroscopy was used to analyze the hydrogen-bonded network structure in water clusters, indicating that the envelopes associated with hydrogen bonds (3000 to 3600 cm⁻¹) blue-shift with increasing cluster size (Asbury et al. 2004). As shown in Fig. 4, there was a broad band for all samples, and those of 10% cooked starch (b) and 10% 6#B (c) were significantly blue-shifted. The blue-shifted peak (a to c) and increased intensity prove that the hydrogen-bonded networks structure and cluster size in NaOH-urea-thiourea aqueous systems increased gradually. In other words, the low temperature promoted the formation of the hydrogen-bonded network among NaOH, urea, thiourea, and water molecules. The rapid dissolution of starch in precooled (-10°C) 4wt % NaOH - 3 wt% urea - 3 wt% thiourea aqueous solution could be associated with the formation of a new hydrogen-bonded network structure in the system. The NaOH “hydrates” could be more easily attracted to starch chains through the formation of new hydrogen-bonded networks at low temperatures (Cai and Zhang 2007). This is the likely reason why the dissolved starch solution had lower viscosity, better viscosity-temperature stability, and also was able to improve the surface strength after being coated on the dried paper. Moreover, a shoulder peak (3200 to 3400 cm⁻¹) appeared in the FT-IR spectra of 10% 6#B (c), which was due to NH stretch in urea and thiourea. Figure 4(c) shows many peaks associated with urea and thiourea.

SEM Observation

Examples of SEM images for the granules of surface sizing starch used in our research are shown in Fig. 5(a through c), while Fig. 5(d through f) shows the corresponding SEM images from 10% 6#B. As shown, the surface sizing starch granules were oval and polyhedral shape with smooth surfaces, but the surface of granules from 10% 6#B were filamentous, and there was also a lot of filamentous material scattered in solution. 10% 6#B had a larger specific surface area, and this kind of surface can be expected to promote interaction with other materials. In the future, novel retention agents or other functional materials may be made from them.

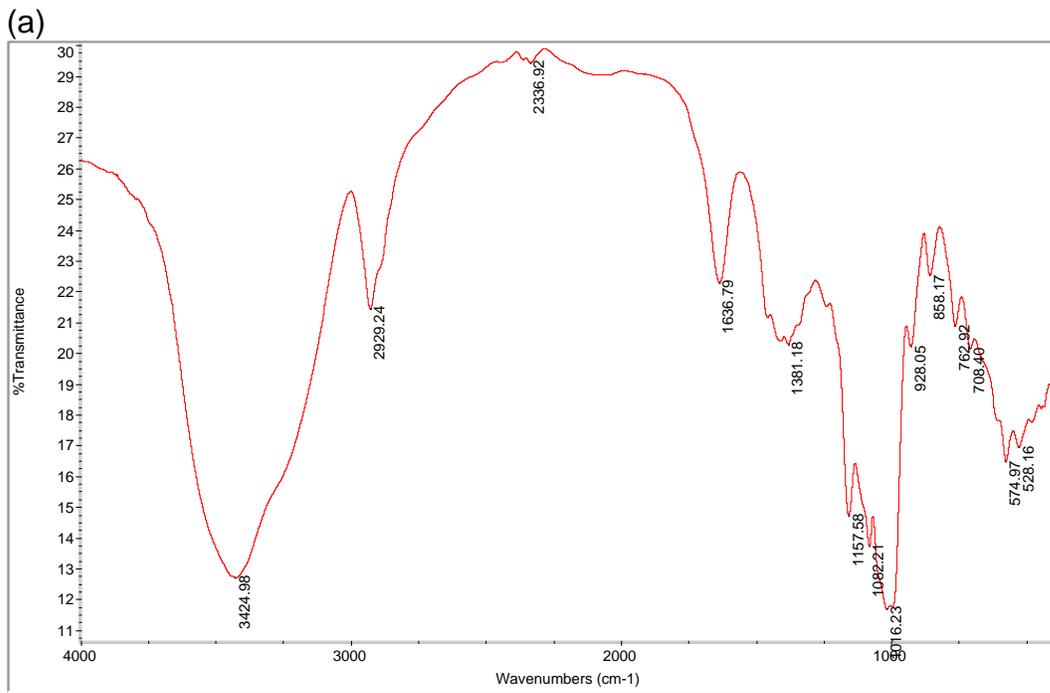


Fig. 4(a). Infrared spectrogram: (a)spectrogram of starch granule; (b) spectrogram of 10% cooked starch; (c) spectrogram of 10% 6#B

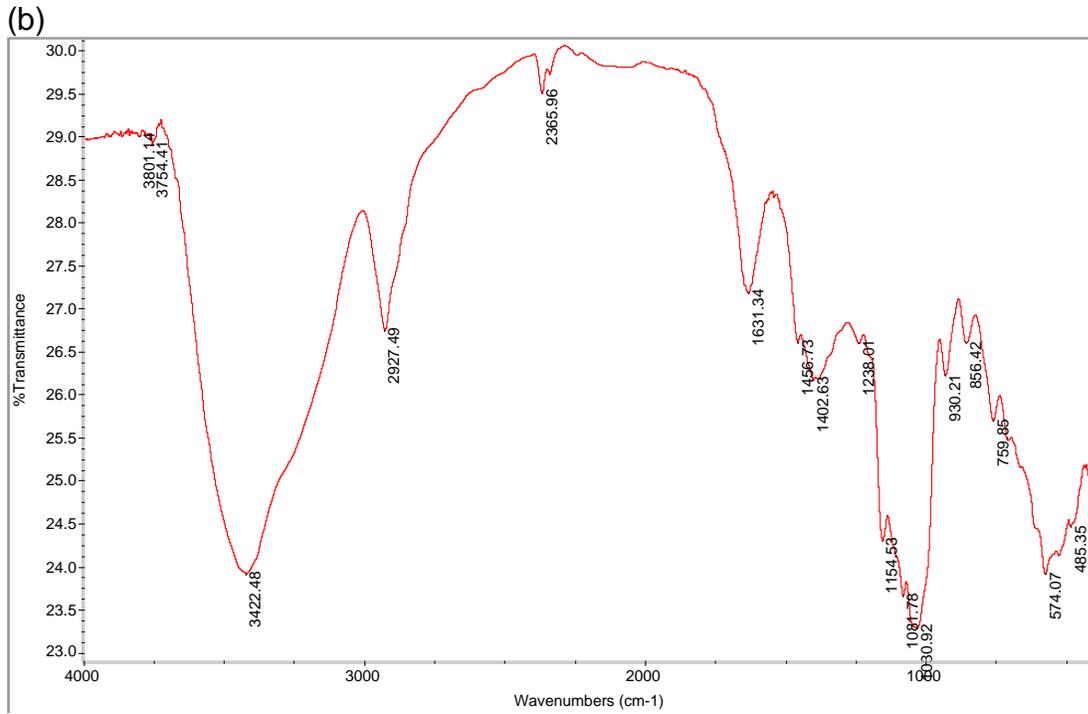


Fig. 4(b). Infrared spectrogram: (a)spectrogram of starch granule; (b) spectrogram of 10% cooked starch; (c) spectrogram of 10% 6#B

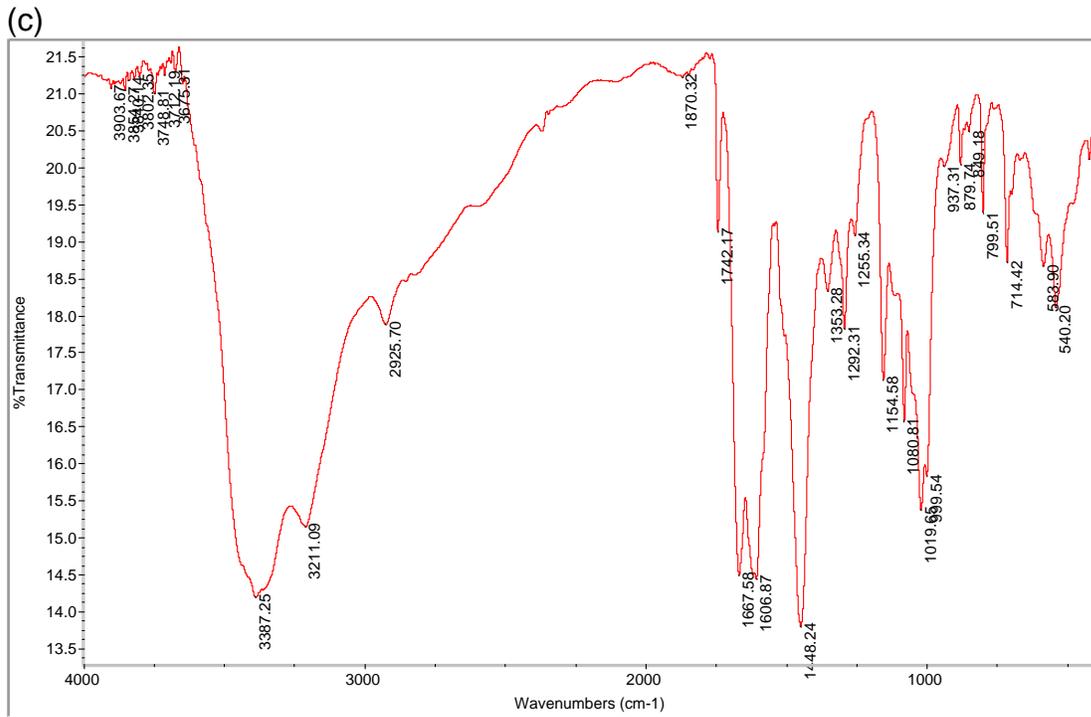


Fig. 4(c). Infrared spectrogram: (a) spectrogram of starch granule; (b) spectrogram of 10% cooked starch; (c) spectrogram of 10% 6#B

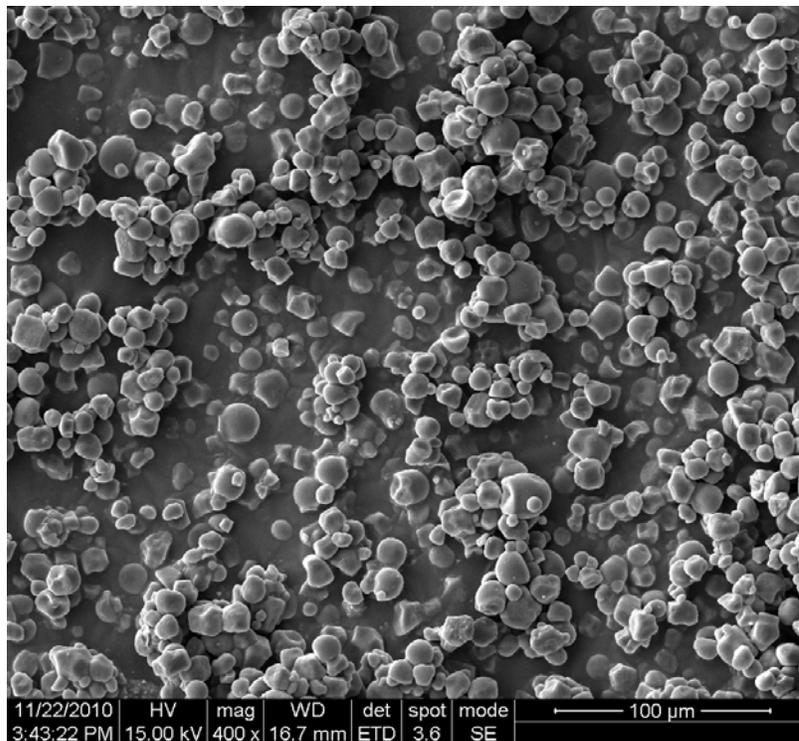


Fig. 5 (a). Scanning electron micrographs of starch particles used in the research: (a) through (c) cooked starch; (d) through (f) 6#B solution starch

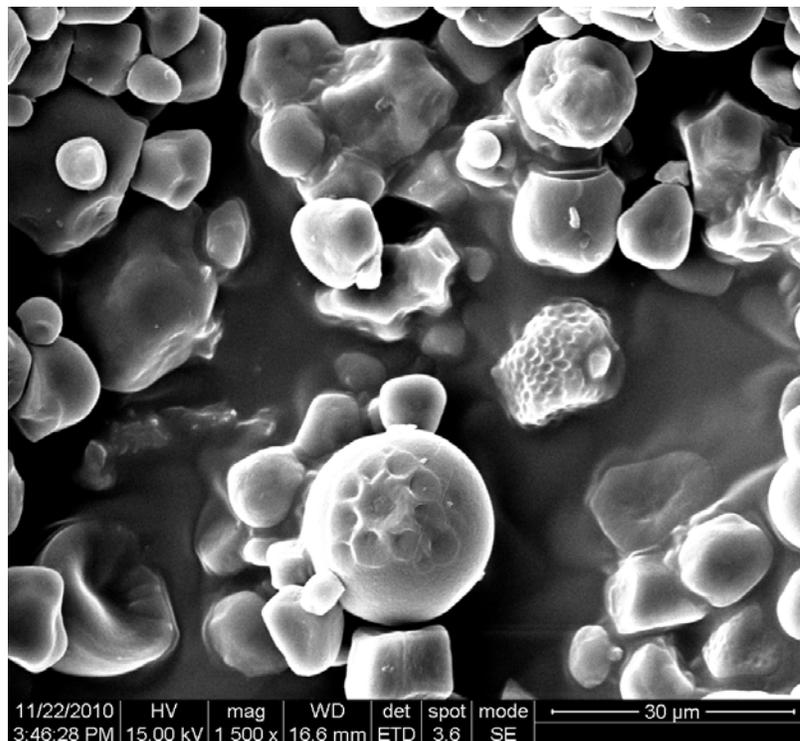


Fig. 5 (b). Scanning electron micrographs of starch particles used in the research: (a) through (c) cooked starch; (d) through (f) 6#B solution starch

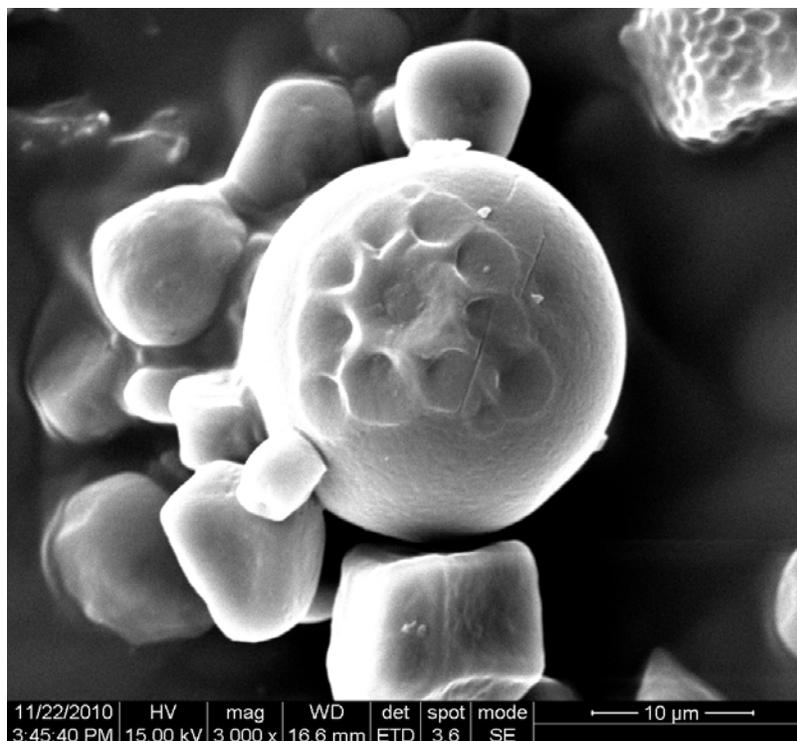


Fig. 5 (c). Scanning electron micrographs of starch particles used in the research: (a) through (c) cooked starch; (d) through (f) 6#B solution starch

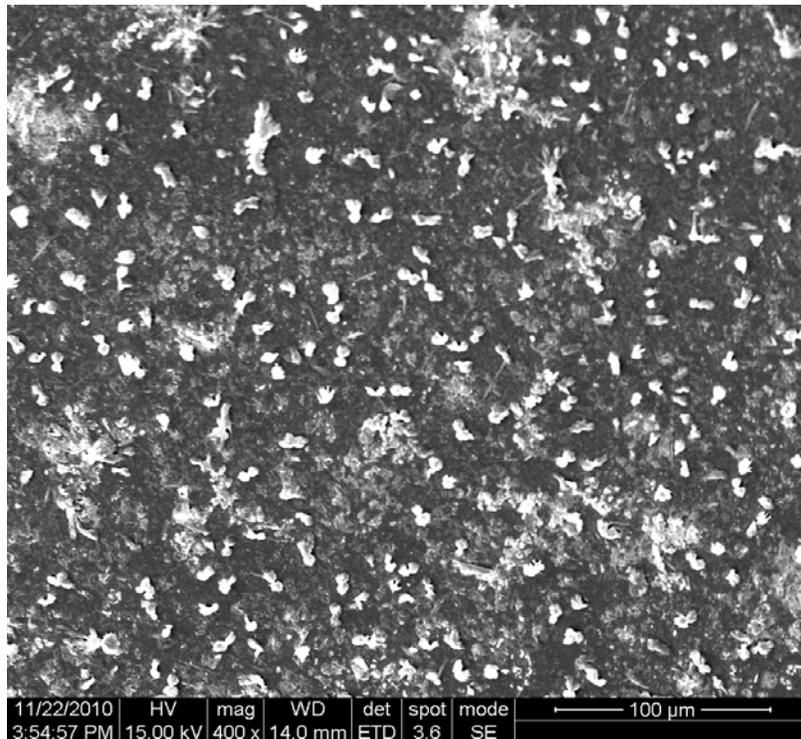


Fig. 5 (d). Scanning electron micrographs of starch particles used in the research: (a) through (c) cooked starch; (d) through (f) 6#B solution starch

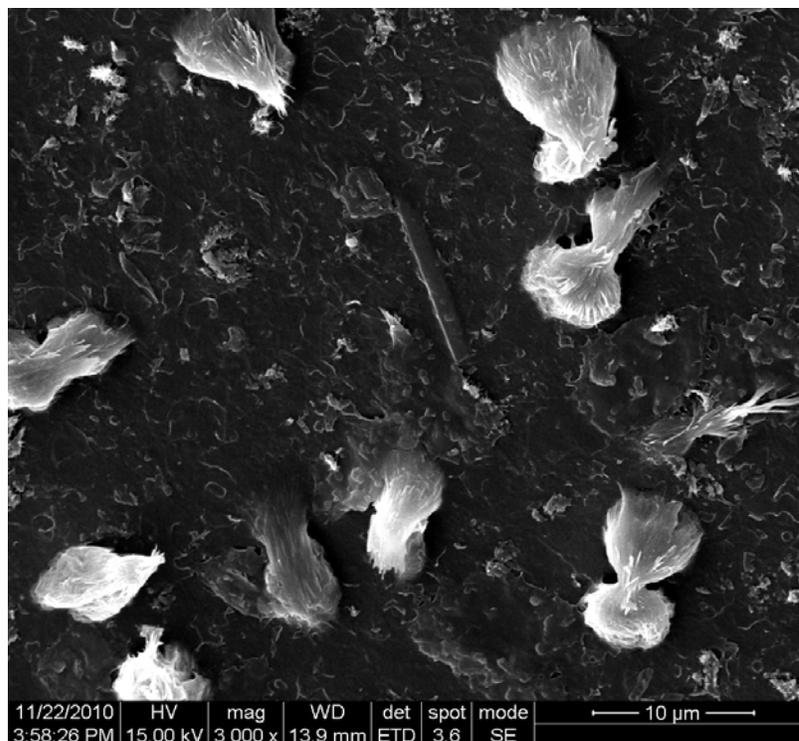


Fig. 5 (e). Scanning electron micrographs of starch particles used in the research: (a) through (c) cooked starch; (d) through (f) 6#B solution starch

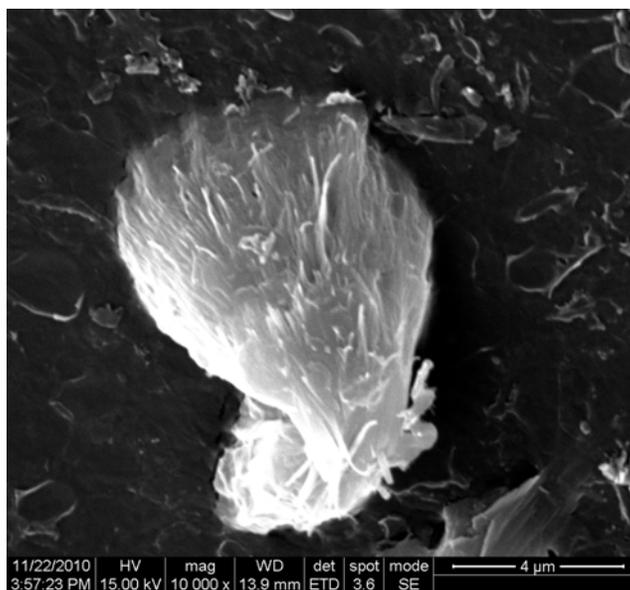


Fig. 5 (f). Scanning electron micrographs of starch particles used in the research: (a) through (c) cooked starch; (d) through (f) 6#B solution starch

CONCLUSIONS

1. Two feasible methods were explored to dissolve starch. In method A the starch granules were directly added into the prepared solution, whereas method B entailed mixing the starch slurry with the prepared solution. The results revealed that method B was more effective than method A to achieve a lower viscosity of starch solution. The condition 6#B (prepared from 4 wt% NaOH – 3 wt% urea – 3 wt% thiourea aqueous solution at minus 10 °C) was optimized to do the application experiments.
2. The 6#B starch had lower viscosity and better viscosity-temperature stability when it was compared with the cooked starch at different temperatures.
3. When the papers were coated at same size amount, the 6#B paper had higher surface strength than paper prepared with the cooked starch. The surface strength of base paper increased substantially after coating with 10%, 20%, 30% 6#B. Reducing the drying capacity requirements can be targeted by increasing the solids content of dissolved starch size to 30%.
4. Low temperature promoted formation of a hydrogen-bonded network of NaOH, urea, thiourea, and water molecules. The rapid dissolution of starch in precooled (minus 10 °C) 4 wt% NaOH - 3 wt% urea - 3 wt% thiourea aqueous solution could be associated with the formation of new hydrogen-bonded network structure in the system, which was at a highly stable state at low temperatures. The NaOH “hydrates” could be more easily attracted to starch chains at low temperature through the formation of hydrogen-bonded networks.
5. The pH of 6#B was higher than 8. For this reason the papermaking team should be cautious when considering 6#B for use as a surface sizing agent when the acidic dry or wet strength agents are being used in the papermaking process. If the whole papermaking process is alkaline, then it is suitable to use 6#B as a sizing agent.

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