WATER GLASS COMPOUND STARCH USED AS SURFACE SIZING AGENT TO IMPROVE THE STRENGTH OF LINERBOARD

Pengjie Peng,[a,b] Xiaofan Zhou,[a,]* and Jinxia Ma [a]

With the rapid development of the packaging industry, the requirements for physical properties of corrugated paperboard tend to become higher and higher, especially for the strength properties. A water glass-starch compound system was employed as a surface sizing agent to improve the strength of linerboard in this work. The viscosity of water glass-starch compound system, and its impacts on ring-crush strength and bursting strength of linerboard were evaluated. Cobb value and contact angle were used to characterize the waterproof performance of paper after surface sizing. Compared with conventional surface sizing agents, water glass-starch compound system overcame the defects of low coating weight and inadequate stiffness of the sizing layer, allowing ring-crush strength and bursting strength of linerboard to increase by 91% and 50%, respectively. Additionally, the compound system had higher solids content, low viscosity, and good film-forming ability, which will bring a lot of convenience to production.

Keywords: Linerboard; Water glass; Ring-crush strength; Bursting strength; Cobb value

Contact information: a: Jiangsu Provincial Key Lab of Pulp &Paper Science and Technology, Nanjing Forestry University, Box 210037, Nanjing, China; b: National Pulp and Paper Products Quality Supervision and Inspection Center, Station of Product Quality Supervision and Inspection in Putian, Fujian province Putian 351100; Corresponding author: zxiaofan@njfu.com.cn*

INTRODUCTION

Among numerous paper packaging materials, corrugated paperboard is preferred to use as a packaging material due to its light weight, low-cost, high compressive strength, processing and structured adaptability, and other unique attributes. The production of linerboard, as the ancillary product of corrugated board, has grown rapidly in recent years with the increasing demand of the packaging industry, especially the production of high-strength linerboard.

Ring-crush strength, as the most important performance indicator of linerboard, is directly associated with the compressive property of packaging containers. Surface sizing is one of the methods to improve ring-crush strength. Since surface sizing keeps approximately 100% of the sizing liquid on the paper, it overcomes the problem of loss of enhancers when they are added in the pulp, and thus improves the utilization rate. Therefore this approach is quite conducive to the closed recycling of paper machine white water and can be considered environmentally friendly (Qiu 2005).

Starch and synthetic surface sizing agents are often used in paper mills (Lee et al. 2002). However, due to the low coating weight and inadequate stiffness of sizing layer, the increase of ring-crush strength is quite limited (Lehtinen 2005; Exner 2002). Polyacrylamide (PAM) sizing agent is highly viscous but cannot combine with fibers easily. The cost is high and residual monomers are smelly (Kang et al. 2008). Phenolic resin can obviously improve the ring-crush strength of paper, but the problem of high price and difficulty in recycling tend to discourage its use (Xu et al. 2004).

Water glass is the generic term for silicate solutions, such as sodium silicate, potassium silicate, or lithium silicate. Sodium silicate is the most popular water glass, and it is an inexpensive raw material for industrial production. Sodium silicate can be purchased in the form of white or grey-white lumps or powder. When dissolved in water, pure water glass solution is a colorless viscous liquid having a pH in the range from 11 to 13. Furthermore, the composition of water glass can be defined in terms of its module, which is defined as the SiO_2/Na_2O molar ratio. Zhang (1994) demonstrated that the ring-crush strength of linerboard is significantly improved by adding water glass at the wet end. However, a portion of the water glass that failed to combine with fibers resulted in scale formation of the process equipment.

Unfortunately, scaling is one of the main factors affecting the efficiency of paper machine operations, including the length of time the system can be run between shutdowns for system cleanup (Xia 2008). In our previous experiments, we found that ring-crush strength of linerboard can be significantly increased when water glass is used as a surface sizing agent. However, water glass is characterized by low viscosity and high solids content, so the coating weight is hard to control. And when viscosity is too low, the paper may be easily broken. More importantly, water glass has poor water resistance, so the paper is not waterproof.

In order to overcome these deficiencies of water glass as a surface sizing agent, we tried to size instead with water glass-starch combined system. The concept of using a water glass-starch system is not without precedent. In fact, it was applied for a long time in the textile industry (Yao et al. 2003). Water glass, as well as sodium hydroxide, has been used as a decomposition agent of starch. It found that the macromolecular structure of starch was depolymerized in the alkali medium but that the structure of starch granules remained constant (Zhou 1985). Furthermore, starch was absorbed to the surface of silicate acids or colloidal particles in water glass due to hydrogen bonding or electrostatic interactions. And the surface potential energy and solvating power of silicate acids were changed, the stability of silicate acids was also improved. Therefore, starch eliminated or delayed the aging of water glass (Wang et al. 1992).

The objective of present study was to improve the stiffness of linerboard by sizing with a water glass-starch system. In addition, Cobb value and contact angle were used to characterize the waterproof performance of paper after surface sizing. The desired results were achieved. The system could increase the ring-crush strength of corrugated paper by 91%. And the $Cobb_{60}$ was 60.8g/m^2, a value far below that of the base paper (138.6 g/m^2). The purpose for this study was to find a new-type surface sizing agent for improving the stiffness of linerboard, in addition, to explore the prospective uses of grass fibers as raw materials, or uses of light weight base paper for high-strength linerboard.

EXPERIMENTAL

Materials

Linerboard (120 g/m^2) with no internal or external sizing (Wuxi & Rongcheng Paper Co., Ltd.) was used as substrate. The ring-crush strength and bursting strength were 6.3N*m/g and 1.13Kpa*g/m^2, respectively. Corn oxidized starch with 0.02% of carboxyl group was provided by ECH Shanghai Emperor of Cleaning Tech Co., Ltd. Water glass with a solids contents of 56%, and module of 3.25, was provided by Guangzhou Liqiang chemical plant.

The non-ionic high hydrogen silicone oil emulsion (solids content of 50%), and the potassium zirconium carbonate waterproofing agent were provided by Nanjing Huatuo Electromechanical Co., Ltd.

Methods

Starch solution was prepared as follows: approximately 10 g of starch was dispersed in 90 mL water. And then the starch suspension was cooked in a water bath at 95 ^{o}C for 30 minutes under vigorous stirring. Based on the amount of water glass, 33%, 50%, or 67% of starch were respectively taken to be compounded with water glass, afterwards mixed with a strong constant speed mixer. The viscosity of the compound system was measured by rotational viscometer (NDJ-79, Kunshan Shun Debbi Instrument Co., Ltd.) at 70 ^{o}C, and the measurement was compared with the starch viscosity. Starch (33%) and silicone oil (5%), both calculation based on the water glass dosage, were taken to be compounded with water glass, and stirred evenly. Cobb value, surface contact angle, and the stiffness of the paper were all measured.

Surface sizing was performed by K-type coating method. The coating weight was controlled by adjusting the power and speed used in the sizing process. All sheets were dried on a standard drier set at 105 ^{o}C for three minutes, and then stored in a conditioned environment (23 ^{o}C and 50% RH) for at least 24 h until further analysis. The coating weight was calculated after drying and conditioning as,

$$\text{Coating weight } (\text{g}/\text{m}^2) = (ME_{\text{sized paper}} - ME_{\text{paper}})/A_{\text{paper}} \qquad (1)$$

where $ME_{\text{sized paper}}$ represents the mass of the dried sizing paper conditioned under standard condition (23 ^{o}C and 50% RH), ME_{paper} is the initial mass of the paper sheet conditioned, and A_{paper} is the area of one side of the paper sheet (Byoung et al. 2000). Paper surface contact angle was measured with a contact angle meter, and the liquid used was distilled water. The camera focal length was adjusted first, and then a small water droplet was dropped on the paper surface with a micro injector. Images were captured after the liquid droplet contacted the paper surface at 5 seconds, and finally the contact angle was measured. Scanning electron microscopy was used to characterize the surface morphology changes after surface sizing.

Ring crush strength was measured according to standard ISO 12192. Bursting strength was measured according to standard ISO 2758. Cobb value was measured according to standard ISO 535.

RESULTS AND DISCUSSION

Viscosity Comparison

Viscosity is an important technical parameter of surface sizing agents. Viscosity affects not only the sizing process, but also the sizing weight. It can be seen from Fig. 1 that water-glass viscosity (45 mPa·s) was much lower than that of either the compound system (190 mPa·s, 280 mPa·s, 300 mPa·s) or starch (370 mPa·s). The viscosity of the water-glass-starch mixture would be increased accordingly with the amount of starch added. When the dosage of starch added was more than 50%, the viscosity (300 mPa·s) was increased to be close to that of starch solution. The reason is that the degree of polymerization of starch decreased in the alkaline medium and it therefore exhibited a viscosity reduction (Zhou 1985). Adding starch can improve the leveling of glue, the uniformity, and thickness of the layer. Furthermore, the film forming property is also improved obviously (Lehtinen 2005). Such results indicate that starch improved the film-forming ability of water glass. The solids content of compound system was 41% in the case of compounding water glass with 33% starch; however, the viscosity was only 190 mPa·s. Due to high solids content, low viscosity, and good film-forming ability, the compound system can provide not only ideal conditions for controlling the coating weight, but also can save in the amount of steam, reducing the load on the drying equipment (Lee et al. 2002; Wang et al. 2011).

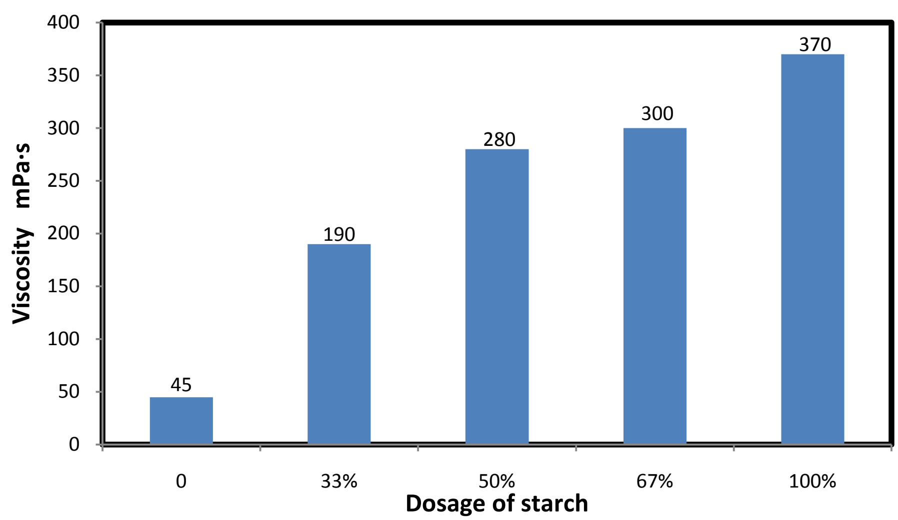

Fig. 1. Viscosity of water glass starch compound system

Comparison of Paper's Water Resistance

The strength of linerboard can be significantly increased by sizing with water glass, but the water resistance tends to be very poor. In previous experiments, we made considerable efforts to overcome the poor resistance to water. The results showed that paper sizing with a water glass-starch mixture may get good waterproof property. Details are shown in Table 1, where it can be seen that the Cobb value of paper sizing with water glass (135.7 g/m^2) was even higher by comparison with base paper (131.2 g/m^2). The problem is that a water glass film adsorbs water easily (Zhu et al 2001).

Without water repellent, the Cobb value of paper sizing with a water glass-starch mixture was slightly lower, compared with base paper. Adding potassium zirconium carbonate waterproofing agent into the compound system, the waterproof performance of paper was slightly improved. This means that the potassium zirconium carbonate waterproofing agent could react with oxidized starch containing hydroxyl and carboxyl groups to form a waterproof membrane. But the water glass included in the system could still adsorb water easily and be soluble in it, so that the improvement of waterproof performance of paper was limited.

Table 1. The Cobb Value of Paper Surface Sizing by Water Glass-Starch Compound System With, or Without Water Repellent

Type	Coating weight （g/m^2）	$Cobb_{30}$ (g/m^2)
Linerboard	0	131.2
Water glass	5	135.7
Water glass-starch	5	129.5
Water glass +5% water repellent	5	128.5
Water glass-starch +5% water repellent	5	95.7

Table 2. The Performance Indicator of Paper Surface Sizing

Type	Coating weight （g/m^2）	$Cobb_{30}$ (g/m^2)	$Cobb_{60}$ (g/m^2)	Contact angle(5s)
Linerboard	0	131.2	138.6	0°
Water glass+5% silicone oil	5	126.8	130.6	95 °
Water glass+33% Starch+5%silicone oil	5	27.1	60.8	101 °

Table 2 indicates that if a certain amount of silicone oil was added into water glass, the Cobb value would be reduced only to a limited extent, so that the requirements of usage could not be met sufficiently. But once a the amount of silicone oil added into the compound system had been increase sufficiently, the Cobb value would be far lower, and in addition, the paper contact angle was also greater than 100 degrees, indicating that moisture could hardly spread on the surface. This meant that the paper had good waterproof performance. Therefore, the water glass-starch, mixed with the addition of 5% silicone oil, was employed as a surface sizing agent to improve the strength and water resistance of linerboard in the following analysis and discussion.

The Impact of Water Glass-starch Mixture on the Strength of Linerboard

As shown in Fig. 2, the water glass-starch compound system had a lower enhancement effect on paper ring-crush strength than water glass by itself. And with the increase dosage of starch, the enhancement effect was further reduced. Furthermore, the enhancement effect of the compound system was better in contrast with starch. Surface sizing with water glass, the ring-crush strength of paper was increased progressively with increasing coating weight. However, sizing with water glass-starch, the ring-crush strength of paper first was increased to reach a peak value, and then it was decreased. The more starch was added, the sooner and smaller the peak value became. The peak value was improved up by 91% when water glass was compounded with 33% starch.

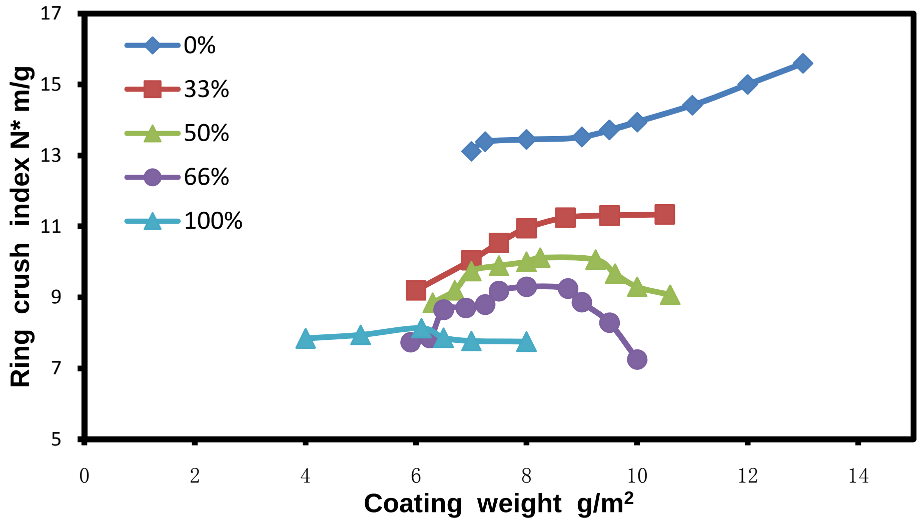

Fig. 2. Impact on ring-crush strength, and the legend indicates the percentage of starch in the formulation

From Fig. 3 it can be seen that the maximum bursting strength was achieved by surface sizing with starch. And a rising trend with growing coating weight was shown. Water glass-starch had a weaker enhancement effect on bursting strength than starch. Although water glass-starch and water glass had significant effect on bursting strength, water glass-starch had a better effect than water glass alone. When sizing with water glass-starch at less than or equal to 6 g/m^2 coating weight, there was an obvious trend that bursting strength increased with increasing dosage of starch. But it began to decline as the coating weight increased above 6 g/m^2. As coating weight grew, its trend of changes was the same as that of water glass surface sizing. But the more starch was added, the peak appeared earlier, and the peak value became larger. Comparing with base paper, the peak value was improved up to 50% when water glass was compounded with 66% starch.

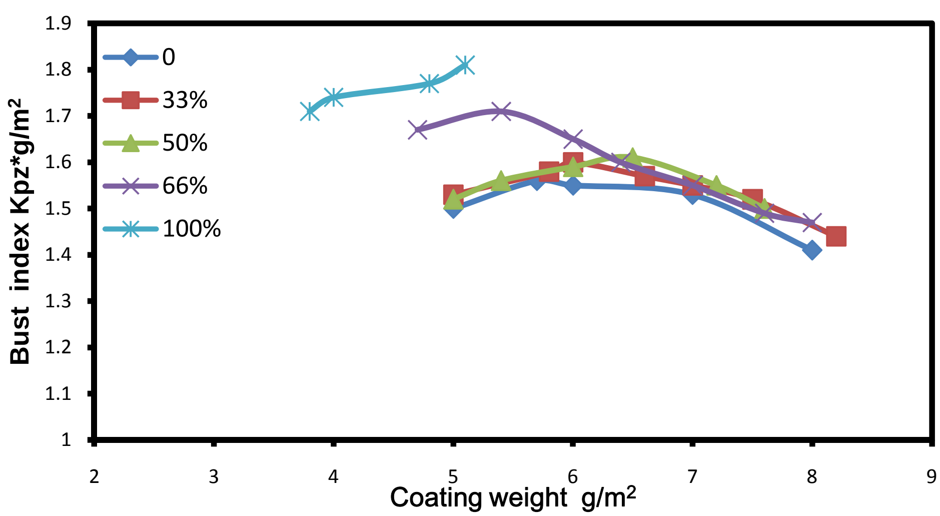

Fig. 3. Impact on burst strength, and the legend indicates the percentage of starch in the formulation

It can be seen from Figs. 2 and 3 that the values of ring-crush strength and bursting strength of linerboard sizing with water glass-starch both ranged between those of sizing with water glass and starch. The ring-crush strength of linerboard sizing with water glass-starch was remarkably increased in comparison to sizing with starch alone, and yet, it became lower than that of sizing with water glass. The reason is that the strength of water glass film (41.0 Mpa) is nearly 2 times that of a starch film (23.5Mpa) (Wang et al. 1994; Jansson et al. 2004; Tong et al. 2004). Furthermore, the strength of the compound film ranged between the two (Iler 1952; Xu 2008; Jansson et al. 2004). The ring-crush strength increased to a peak value, and then began to decrease with increasing coating weight. The problem is caused by the highly brittle nature of a water glass film, which can crack easily (Zhu et al. 2000). The bursting strength of linerboard sizing with starch was higher in comparison to sizing with water glass-starch and water glass, respectively. This is because the extensibility and modulus of elasticity of the organic membrane were higher than those of the inorganic membrane. Nevertheless, the requirements of use could be met by the water glass-starch compound system due to its good ring-crush strength and bursting strength.

Mechanism Analysis on Enhancement

Fiber strength, fiber bonding strength, the area of component fiber (Qing et al. 2004; Hubbe 2004), and the stiffness of the film forming on the paper surface relate to the ring-crush strength of paper. With help of improved these factors, the ring-crush strength of paper could be increased. From Fig. 4 it can be observed that the water glass fully wrapped the fiber surface at 6 g/m^2 coating weight, which was similar to internal sizing. Consequently, due to the fact that the strength of fiber was improved by the hardened water glass, the ring-crush strength of linerboard was increased. Due to the hardened water glass film (the strength reached 41.0 Mpa), there seemed to be a thin steel sheet present at the binding sites. Thus the fiber bonding strength was enhanced, and so the ring-crush strength of linerboard was also. Starch could improve the film-forming ability of water glass. Therefore, the surface of paper was more completely filled with surface sizing agents at low coating weight, and the base paper was trapped between two rigid solid membranes (Fig. 5). The effect was the same as sizing with water glass at high coating weight (Fig. 6). The ring-crush strength mainly depended on the strength of rigid solid membrane. Owing to the strength of water glass-starch film, ranging from 23.5 Mpa to 41 Mpa (Wang et al. 1994; Jansson et al. 2004; Tong et al. 2004), the ring-crush strength of linerboard was improved obviously.

Bursting strength is a measurement that shows how much force a paper or board can take before it ruptures. It depends largely on the tensile strength and extensibility of paper. When surface sizing with water-glass alone, it was impossible to form a continuous membrane on the paper surface at low coating weight. As a result, when applying an external force on the paper, the fiber still is able to undergo elastic deformation to absorb the energy of the external force (Zhang 2004). The deformation was higher, the energy absorbed more, the extensibility and modulus of elasticity of paper was higher, and the bursting strength of linerboard was higher. At high coating weight, water glass formed a continuous membrane on the paper surface (Fig. 6). The deformation degree mainly depends on the extensibility of water glass film. As with other inorganic membranes, the water glass film was too brittle and easy to crack. Therefore, the bursting strength was poor when sizing with just water glass at high coating weight. Starch improved not only film-forming, but also decreased brittleness of water glass. Consequently, the bursting strength of linerboard surface sizing with water glass-starch was greater than that of sizing with only water glass. Similarly, the bursting strength was increased with increasing coating weight to reach a peak value firstly, and then it was decreased. This was because the brittleness of water glass was not decreased by starch very effectively.

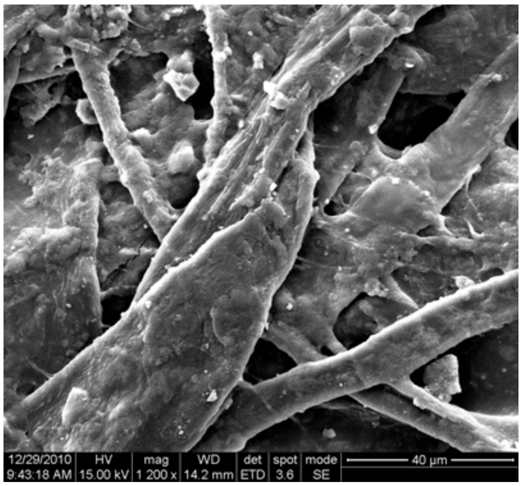

Fig. 4. Surface sizing with water glass at 6 g/m^2.

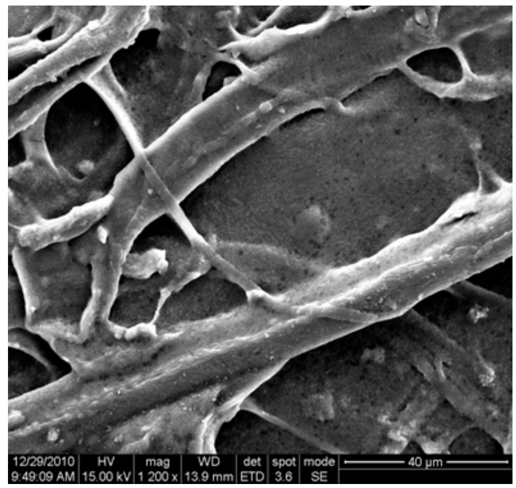

Fig. 5. Surface sizing with water glass-starch at 6 g/m^2.

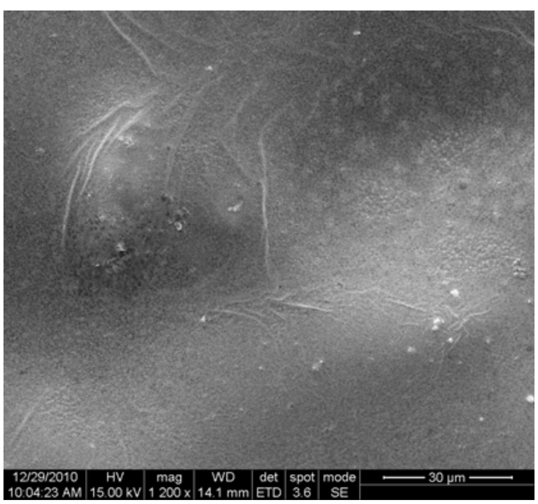

Fig. 6. Surface sizing with water glass at 16 g/m^2.

Based on the analysis above, the compound system yielded advantageous properties including high solids content, low viscosity, and good film-forming ability. It could not only produce high-strength linerboard from light weight base paper, saving plant fiber raw materials, but also reduce the load on the drying equipment and improve the machine speed in order to achieve more energy-savings, higher production efficiency, and lower-carbon production operations.

CONCLUSIONS

1. The water glass-starch compound system had higher solids content, lower viscosity, and better film-forming ability compared to water glass alone.
2. Although the stiffness of linerboard can be greatly enhanced sizing with water glass, the waterproof property of linerboard was very poor. Adding a certain amount of starch and silicone oil into water glass, the waterproof property was significantly improved.
3. The ring-crush strength and bursting strength of linerboard sizing with water glass-starch both ranged between those of sizing with water glass and starch, respectively. Thus the current requirements of usage could be met.

REFERENCES CITED

Byoug, C., and Gil, G. (2000). "Effect of the paper structure and composition on the surface sizing pick-up," *Tappi Journal peer reviewed paper*.

Exner, R. (2002). "Synthesis and application of polymer sizing agents," *J. Paper Technology* 43(6), 45-51.

Hubbe, M. A. (2004). *Chemical Additives and Paper Strength,* Short-Course Notes, presented at Nanjing Forestry University, Nanjing, China.

Iler, R. K. (1952). "Between polysilicic acid and polar organic compounds," *The Journal of Physical Chemistry* 56, 673-677.

Jansson, A., and Thuvander, F. (2004). "Influence of thickness on the mechanical properties for starch films" *Carbohydrate Polymers* 56, 4599-503.

Kang, Y. F., and Shen, Y. D. (2008). "Advances in research of stiffness agent for paper and paperboard," *J. China Pulp and Paper Industry* 9, 58-61.

Lee, H.-L., and Shin, J. Y. (2002). "Surface sizing with cationic starch: Its effect on paper quality and papermaking process," *J. TAPPI Journal* 1(1), 34-40.

Lehtinen, E. (2005). *Pigment Coating and Surface Sizing of Paper*, The Finnish Paper Engineers' Association, Finland, and TAPPI, USA.

Qing, P. Y., and Zhao, C. S. (2004). "Improve the ring-crush strength of corrugated paper by reinforcing agent," *South West Pulp and Paper* 33(2), 39-47.

Qiu, Z. C. (2005). "Through new surface size option maintains performance, less internal sizing," *J. World Pulp and Paper* 24(2), 57-58.

Tong, Q. Y., and Zhu, G. L. (2004). "Study on improve the intensity of edible starch films by denatured starch," *Food Science and Technology* 1, 53-56.

Wang, P., Yang, Y. X., Zhu, C. X., and Chen, R. S. (1992). "A Study on aging of water glass and its chemical modification," *Bulletin of the Chinese Ceramic Society* 6, 4-9.

Wang, W. Q., Huang, N. Y., Xun, J., and He, Z. F. (1994). "On the improvement of the bonding strength of sodium-silicate-bonded," *J. Huazhong Univ. of Sci. and Tech* 22(9), 23-28.

Wang, X. Q., and Zhou, X. F. (2011). "Novel starch solution prepared from the starch in NaOH/thiourea/urea aqueous solution and its application as surface sizing agent," *BioResources* 6(2), 1926-1938.

Xia, A. J., and Han, Q. (2008). "Application potential analysis of sodium silicate in papermaking industry," *Heilongjiang Paper Making* 1, 23-26.

Xu, H. Z., Zhao, C. S., and Qin, P. Y. (2004). "Several enhancing agents to improve the stiffness of linerboard," Proceedings of China Paper Chemicals R&D International Conference.

Xu, J. (2008). "The formation changes of silicate particles morphology cured by different methods and its reasons," *China Foundry Machinery & Technology* 4, 49-52.

Yao, G. F., Zhao, Q. M., Liu, J. M., and Jia, L. X. (2003). "The modified mechanism of the starch denaturant and the development of the research," *Shanghai Textile Science & Technology* 31(5), 20-21.

Zhang, J. D. (2004). "The brittleness of paper," *Hubei Paper Making* 4, 10-11.

Zhang, X. Z. (1994). "Improve the ring-crush strength of linerboard by adding water-glass," *Paper and Papermaking* 1, 25.

Zhou, Y. Y. (1985). *Physics and Chemistry of Sizing Agents,* Textile industry Press, Beijing, China.

Zhu, C. X., and Lu, C. (2001). "The progress to recognize the hardening mechanism of water glass,"*J. Inorganic Chemicals Industry* 33(1), 22-25.

Zhu, C. X., Lu, C., and Ji, D. S. (2000). *The Basic Theories of Water-glass Sand*, Shanghai Jiao Tong University Press, Shanghai, China.

Article submitted: May 8, 2011; Peer review completed: July 22, 2011; Revised version received: August 24, 2011; Accepted: August 28, 2011; Published: August 31, 2011.