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Development of Crosslinked Cationic Starches and Evaluation of Their Performance in the Microparticle Retention System

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ABSTRACT

Crosslinked corn starches were prepared to increase their molecular weights and their performance as a component of Compozil system was evaluated and compared with that of potato starches. It was shown that greater improvements in retention and strength properties could be achieved when crosslinked cationic corn starches rather than conventional cationic potato starches were used especially at high conductivity because of their molecular rigidity.

1. Introduction

Paper industry has made diverse efforts during last several decades to reduce manufacturing cost and to improve productivity and quality. Web forming is one of the most critical processes in achieving these objectives since retention, dewatering and fiber flocculation at the forming part of a paper machine are directly associated with the process economy, productivity and product quality.

Effectiveness of the microparticle retention systems in improving drainage, retention and formation has been recognized for many years,[1-5] and various microparticle retention systems including Compozil, Hydrocol and Compamzil systems have been used in many paper mills to obtain these advantages.[1,2,6]

Compozil system requires both cationic starch and anionic colloidal silica as components. Raw materials for cationic starches differ depending on the region. Potato is a predominant raw material for producing cationic starches in Europe, while corn is most widely employed in Asia and North America.[7] The types of raw materials affect the quality of cationic starch. Cationic starches made from potato are regarded to be superior to corn-based ones since they are high in molecular weights and amphoteric in nature.[5,7]

It is worthwhile, therefore, to examine the possibility of producing cationic starches with improved performance using the corn as a raw material. In this study, crosslinked corn starches were prepared to increase their molecular weight and the performance was evaluated and compared with that of potato starches.

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2. Materials and Methods

2. 1 Materials

Softwood and hardwood bleached kraft pulps and talc were used to prepare the stock. Two types of potato starches with the degrees of substitution (DS) of 0.055 and 0.074 and four different corn starches with the DS of 0.03, 0.05, 0.08 and 0.1 were kindly supplied by Samyang Genex Co. Crosslinking treatment was carried out to increase the molecular weights of corn starches with DS of 0.05 and 0.08. The granule size of starches determined with Malvern Mastersizer and Brookfield viscosity are shown in Table 1.

As seen in Table 1, the average granule size of the uncooked potato starches was about twice larger than those of corn starches. The granule size of corn starches decreased as crosslinking proceeded indicating the swellability of corn granules was decreased by this crosslinking treatment.[7) Brookfield viscosity of the potato starch was greater than that of the corn starch as seen in Table 1. This suggests that the molecular weight of potato starches are still higher than that of crosslinked corn starches. Brookfield viscosity of the crosslinked cationic corn starch ranged from 4.3-5.5 cPs and it increased as the level of crosslinking increased.

The cationic starches at a concentration of 1% were cooked in a water bath at a temperature of 95° C for 25 min and diluted to 0.5%. Fresh cooked starch solutions were prepared every day for the experiments.

2. 2 Experimental Methods

2. 2. 1 Stock preparation

Softwood and hardwood bleached kraft pulps were beaten separately to 450±10 mL CSF and mixed at a ratio of 8:2. Part of the mixed stock were dried in a drying oven at 105° C for 12 hours to simulate the dry broke, and blended with the virgin pulp stock. The blending ratio of the dried pulp was kept constant at 10%. After blending the dried pulp the whole stock was beaten again to 450±10 mL CSF and diluted to 0.5%. Fines content and water retention value of the stock were 23% and 1.91 g/g, respectively. Twenty percent of talc was added as filler. Calcium hardness and conductivity of the stock prepared in this way

Table 1. Raw materials

Raw materials	DS	Crosslinking	Notation in Figs.	Granule size (μm)	Viscosity* (cPs, 28℃)
Potato	0.055	No	Potato 0.06	51.51	80
	0.074	No	Potato 0.07	63.62	153
Corn	0.05	No	Corn 0.05	27.10	5.5
		Yes	Corn 490	22.19	11.5
		Yes	Corn 620	21.01	20
	0.08	No	Corn 0.08	26.42	5
		Yes	Corn 600	25.02	22.5
		Yes	Corn 1380	21.31	41
	0.1	No	Corn 0.10	---	4.3

* Brookfield viscosity

with tap water were 56 ppm and 460 μS/cm, respectively.

When investigating the influence of stock conductivity, the hardness level was adjusted to 100 ppm with calcium chloride, and then stock conductivity was adjusted to either 2000 or 4000 μS/cm with sodium chloride. When evaluating the performance of the cationic starch in Compozil System, 0.2% of an anionic colloidal silica(BMA 780) was added.

2. 2. 2 Measurement of fines retention and freeness

Fines retention and freeness were measured as depicted in Fig. 1. In this experiment a structured colloidal silica, BMA 780, was used. FTU turbidity of the filtrate was measured using DR/2000.

2. 2. 3 Handsheet forming and measurement of physical properties

While stirring the stock contained in a DDJ at 800 rpm, the cationic starch solution was

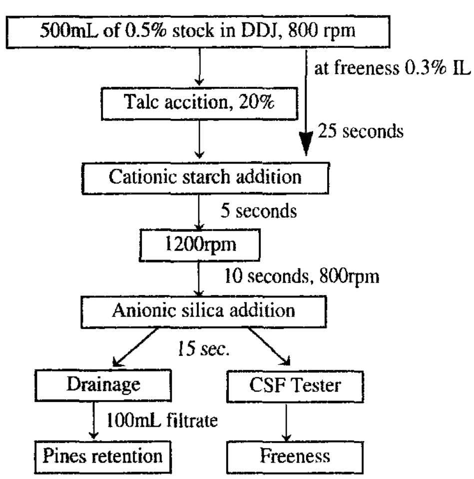


Fig. 1. Flow chart for measuring of fines retention and freeness.

added. Immediately after starch addition the stirring speed was increased to 1000 rpm, and agitated for 15 sec. After reducing the stirring speed to 800 rpm 0.2% of colloidal silica was added and stirred again for 15 sec.

Handsheets with basis weight of 80±1 g/m^2 were formed on a handsheet former, pressed and dried. Measurement of tensile strength and internal bonding strength was performed according to TAPPI Standard test methods. Formation was measured using a formation tester and expressed in NUI.

3. Results and Discussion

3. 1 Effect of crosslinking on fines retention

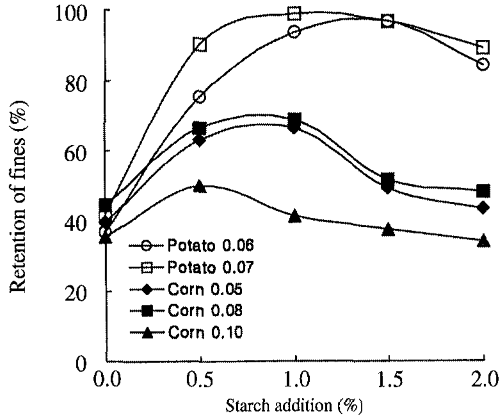
Influence of crosslinking treatment of cationic corn starches on fines retention and paper properties were investigated and compared with those obtained with cationic potato starches.

Fines retention obtained using cationic corn or potato starches as a component of Compozil system are shown in Fig. 2. In this experiment regular cationic corn starches, which were not crosslinked, were used. As seen here potato starches showed better retention performance than corn starches. And corn starch with the degree of substitution of 0.1 showed fines retention significantly lower than that obtained with lower DS starches when tap water was used. It indicates that the charge density of starches does not have a significant impact on fines retention. In other words, not the degree of substitution but the molecular weight of the cationic starch plays more vital role in fines retention. As shown in Fig. 2 (a), fines retention increased, reached maximum then decreased with the increase of starch addition. The fact that fines retention decreased when the amount of cationic starch was high suggested that nonadsorbed starch molecules reacted with anionic silica, which decreased the efficiency of microfloc formation of the colloidal silica.

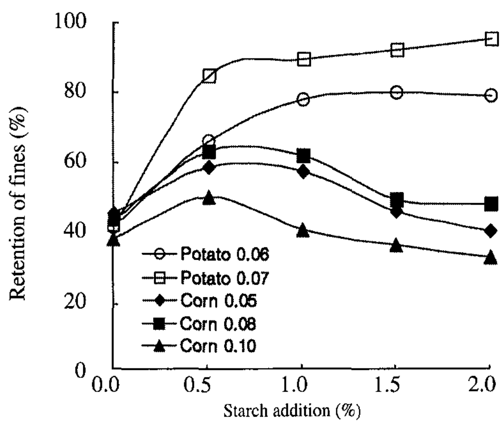
Fines retention obtained with the stocks at higher conductivity, i.e. 2000 μS/cm and 4000 μS/cm, are shown in Fig. 2 (b) and (c). As seen here the fines retention decreased as the conductivity increased. This indicates starch molecules contract due to charge neutralization at high conductivity and show low retention efficiency.[9] It is evident from Fig. 2 that the reduction of fines retention accompanying the increase of stock conductivity is minimal when a cationic corn starch with a high degree of substitution is used.

When the concentration of simple electrolytes increases counter ions concentrate around the charged group to reduce the repulsive force. This means that the conformation of charged starch molecules changes to more compact one at high conductivity.[1] This conformational change reduces the viscosity of starch solution as shown in Fig. 3.

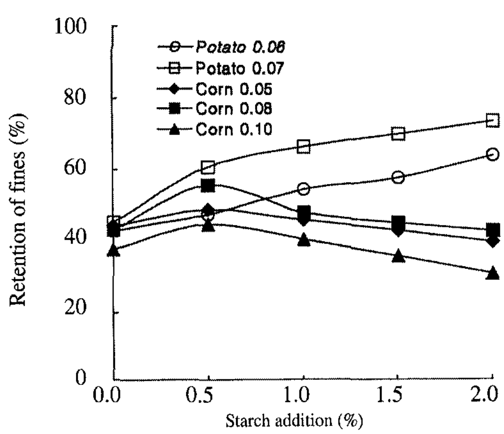
The fact that high retention efficiency was obtained when high molecular weight potato starches was used as shown in Fig. 2 suggested it might be possible to increase the reten-



(a) Tap Water



(b) 2000 μS/cm



(c) 4000 μS/cm

Fig. 2. Effects of cationic starch addition on fines retention.

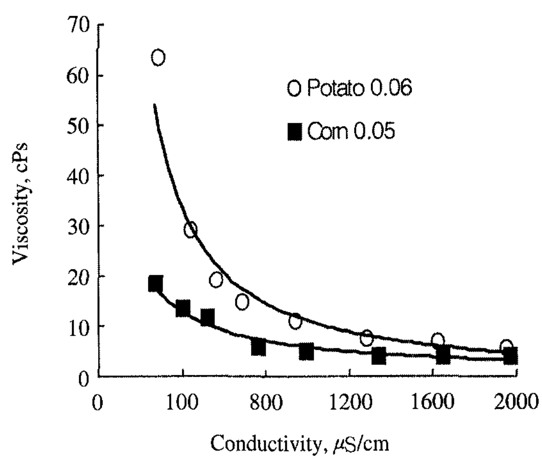


Fig. 3. Effects of conductivity on starch solution viscosity.

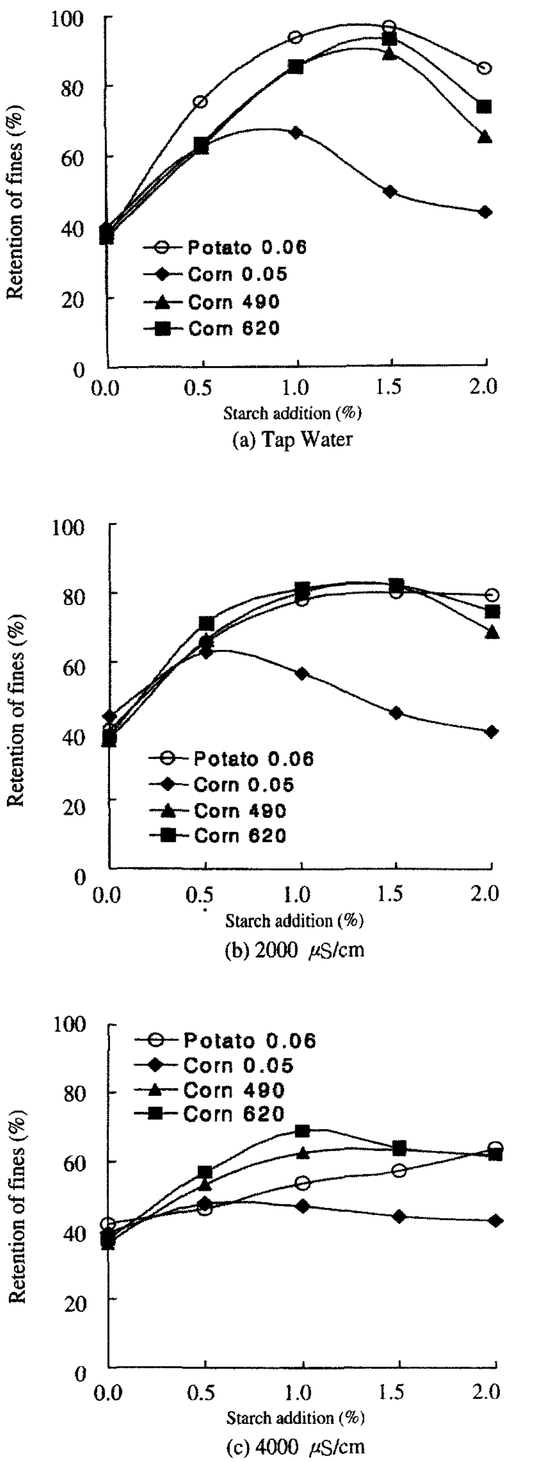


Fig. 4. Effects of cationic starch addition on fines retention (DS 0.05).

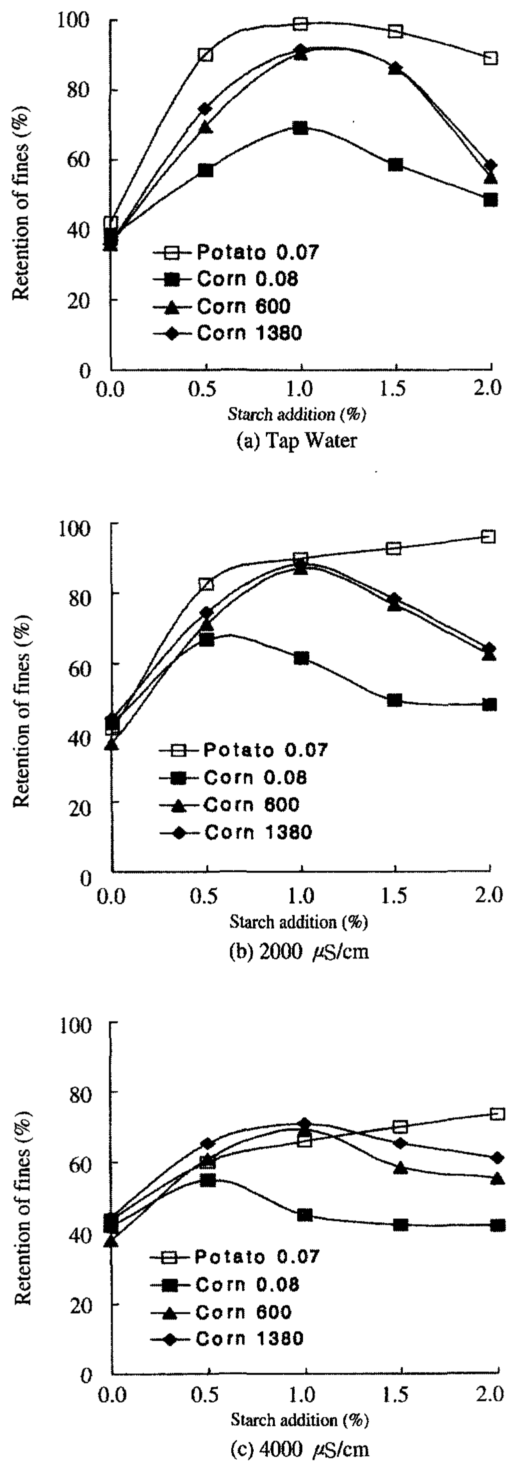


Fig. 5. Effects of cationic starch addition on fines retention (DS 0.08).

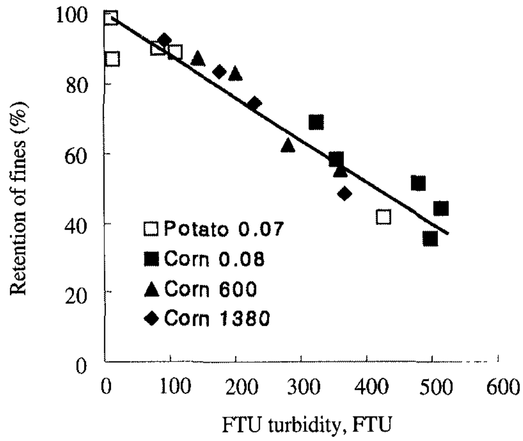


Fig. 6. Relationship between fines retention and FTU turbidity (Tap water).

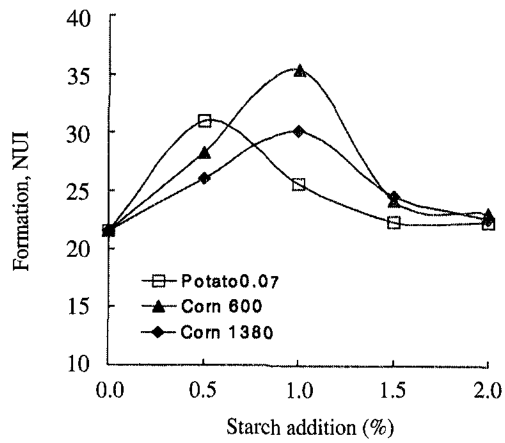


Fig. 7. Effects of cationic starch addition on formation (Tap water).

tion efficiency of the corn starches if their molecular weights are increased by crosslinking.[8] Crosslinked corn starches were prepared to examine this hypothesis, and their retention performance was examined using corn starches with DS 0.05 (Fig. 4).

As seen here fines retention increased with crosslinking treatment of corn starches. When tap water was used, potato starch still showed the highest retention (Fig. 4 (a)). The same results were obtained for crosslinked cationic starches with DS of 0.08 (Fig. 5).

The effects of crosslinked starches on fines retention in highly conductive systems are illustrated in Fig. 4 (b) and (c). Fines retention decreased as conductivity increased, however, the retention performance of crosslinked corn starches was affected less by conductivity increase than potato starch probably due to the rigidity of starch molecules provided by the crosslinking treatment. At a conductivity of 4000 μS/cm crosslinked corn starches showed greater fines retention than potato starch. It appeared, however, excessive crosslinking impaired the retention improvement since the flocculation ability of highly crosslinked starch molecules decreased.

Turbidity of the DDJ filtrate is closely associated with fines retention (Fig. 6). Thus it would be possible to evaluate the retention performance by measuring the filtrate turbidity.

Fig. 7 shows formation indices of handsheets formed using corn starches with DS of 0.08 and a potato starch with a DS of 0.074 as a component of the Compozil system. NUI formation deteriorated as the addition of cationic starches was increased at low addition rates. When the addition rate of starches was increased further, the formation of handsheets improved again. Deterioration of the sheet formation was most evident at the addition rate of 0.5% for a potato starch and at 1.0% for corn starches. This indicates a potato starch shows greater flocculation ability because of its higher molecular weight.

3. 2 Tensile and internal bond strength

Cationic starches function not only as a retention aid but also as a strength agent.[10] The

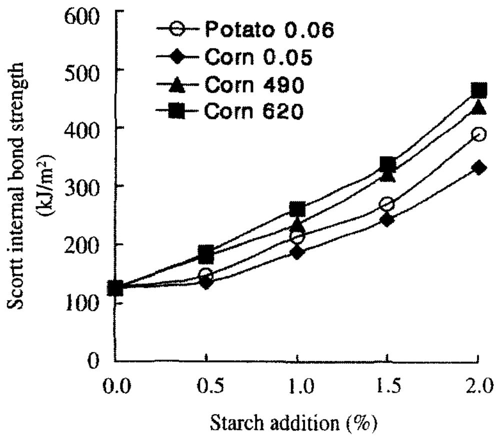


Fig. 8. Effects of starch addition on Scott internal bond strength.

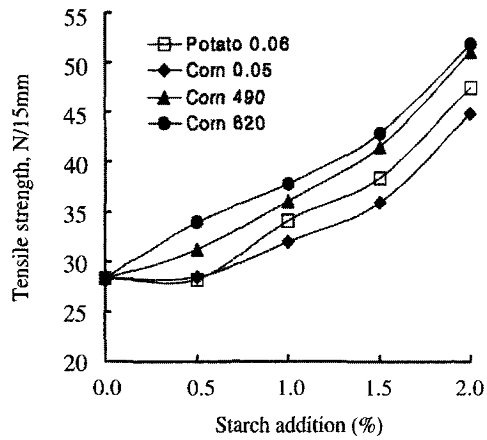


Fig. 9. Effects of starch addition on tensile strength.

internal bond strengths and tensile strength increased as the starch addition increased (Figs. 8-9). As the crosslinking level of corn starches increased, higher internal bond strength and tensile strength were obtained. Greater internal bond strength and tensile strength were obtained with crosslinked corn starches than with potato starch in most cases.

4. Conclusions

In this study cationic corn starches were prepared to evaluate the effectiveness of crosslinking of starches as a component of Compozil system. It has been shown that improvements both in retention and strength could be achieved by employing crosslinked cationic corn starches. Crosslinked cationic corn starches showed better retention properties when they were used especially in highly conductive systems because of their molecular rigidity.

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